

## Coherent control of the multiple wavelength lasing of $N_2^+$ : coherence transfer and beyond: supplement

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# Coherent control of the multiple wavelength lasing of $N_2^+$ : coherence transfer and beyond: supplement

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**Abstract:** This document provides supplementary information to "Coherent control of the multiple wavelength lasing of  $N_2^+$ : coherence transfer and beyond".

In what follows, we present more details of our theoretical model and the corresponding calculated results. The content is organized in two parts: I. Model system and II. Time-domain pump-probe signal.

## I. Model system.

Our experiments showed the ultrafast dynamics of electronic excitations of nitrogen cations, where the two-color seeding pulses are interacting with the molecules as successive process following the strong pumping by an infrared pulse. We adopt the three-level description as a simplified model for the molecules of interest [1]. The molecule-field interaction then reads  $V(t) = V_b(t) + V_c(t)$  and

$$V_b(t) = -\Omega(t - T_1)|e\rangle\langle b|e^{i\omega_{eb}t} - \text{h. c.}, \quad V_c(t) = -\Omega(t - T_2)|e\rangle\langle c|e^{i\omega_{ec}t} - \text{h. c.} \quad (1)$$

where  $b, c$  denote the two vibrational levels ( $v = 0, v = 1$ ) in the ground state  $X^2\Sigma_g^+$  and  $e$  denotes the level  $v' = 0$  in the electronic excited state  $B^2\Sigma_u^+$ .  $\Omega(t - T_n)$  describes the pulse shape in time domain such that

$$\Omega(t - T_n) = \Omega_n e^{-(t-T_n)^2/2\sigma_n^2} e^{-i\omega_n(t-T_n)} \quad (2)$$

and  $\omega_n$  represents the pulse central frequency and  $\sigma_n$  is the temporal width of the pulse.  $T_1$  and  $T_2$  correspond to the delays  $\tau_{p-s1}$  and  $\tau_{p-s2}$  varied in experiments, by assuming the infrared pump pulse arrives at  $t = 0$ . Notice that we have neglected the  $b \leftrightarrow e$  transition induced by pulse 2 and  $c \leftrightarrow e$  transition induced by pulse 1. This is due to the fact that the pulse bandwidth in the experiments cannot cover the vibrational splitting, namely,  $2\pi\sigma_n^{-1} < \omega_{bc}$ . We adopt the density matrix formalism to describe the dynamics of the molecules, and it obeys the quantum Liouville-von Neumann equation

$$\dot{\rho} = i[\rho, V(t)] \quad (3)$$

in the interaction picture and we set  $\hbar = 1$ . The infrared pulse creates the populations on the three levels and the vibrational coherence  $\rho_{bc}$ , i.e.,  $\rho_0 = \sum_{i=b,c,e} \rho_{ii}|i\rangle\langle i| + \rho_{bc}|b\rangle\langle c| + \rho_{bc}^*|c\rangle\langle b|$  with  $\sum_{i=b,c,e} \rho_{ii} = 1$ . This takes the rational when noting the fact of the incoherent nature of the strong-field ionization [2, 3]. The electronic coherence in  $N_2^+$  therefore dies out. The solution to Eq.(3) in Schrödinger picture is given by

$$\rho(t) = \hat{G}(t)\hat{\mathcal{T}}e^{-i\int_{-\infty}^t \hat{V}_-(\tau)d\tau}\rho_0, \quad (4)$$

where the superoperators are defined as  $\hat{V}_-(\tau) \equiv [V(\tau), *]$  and  $\hat{G}(t) = e^{-(iH_{0,-} - L)t}$  is the free propagator of the molecule in the absence of pulses.  $H_{0,-} \equiv [H_0, *]$  yields to the unitary part of the evolution and  $L$  stands for the relaxation superoperator dictated by the Redfield master equation or quantum stochastic Liouville equation, resulting in the non-unitary dynamics [4, 5].

The simplified model above is inadequate to describe the diatomic molecules in the sense of nonradiative transitions. Such transitions play a significant role in a variety of polyatomic molecules where the vibronic interaction results in the excited-state relaxation. These processes have been extensively measured in various time-resolved spectroscopic experiments, including the time-gated fluorescence and two-dimensional pump-probe spectroscopy [6-10]. We therefore include the excited-state relaxation processes, in order to model the experimental data with better accuracy. According to the recent experiment, laser pulses are inducing the vertical transitions from the ground-state vibrational levels  $v = 0, 1$ . The  $N_2^+$ , in fact, has the electronic excited energy surface (ES) showing a small shift of the minimum from the electronic ground state energy surface, depicted in Fig. 5(a) in the main text. This indicates that the lowest electronically excited level must have a lower energy than that induced by vertical transition from the level  $v = 0$ . To elaborate this, we start off with the Hamiltonian for diatomic molecules interacting with the field [11-13]

$$H_M = H_g(p, q)|g\rangle\langle g| + H_e(p, q)|e\rangle\langle e| - [\Omega(q)|e\rangle\langle g| + \Omega^*(q)|g\rangle\langle e|] \\ H_g(p, q) = \frac{\omega_0}{2}(p^2 + q^2), \quad H_e(p, q) = \omega_{eg}^0 + \frac{\omega_1}{2}(p^2 + (q - d)^2) \quad (5)$$

using Born-Oppenheimer and harmonic approximations, where  $d$  denotes the offset between the ground and electronic excited ESs and  $\omega_{eg}^0$  gives the energy difference between the minimums of the two ESs.  $p$  and  $q$  are the dimensionless momentum and coordinate of the nuclear vibrations, respectively.  $\Omega(q) = \mu(q)E(t)$  and  $\mu(q) =$

$-e \int \psi_e^*(x, q) x \psi_g(x, q) dx$  provides the electronic transition dipole. The eigenfunctions of the molecular Hamiltonian in Eq. (5) are of the two-component form

$$\Psi_n^{(g)}(x, q) = \psi_g(x, q) \chi_n^{(g)}(q), \quad \Psi_m^{(e)}(x, q) = \psi_e(x, q) \chi_m^{(e)}(q - d) \quad (6)$$

where  $\psi_g(x, q)$  and  $\psi_e(x, q)$  are the eigenfunctions of electrons at electronic ground and the first excited states, respectively.  $\chi_n^{(g)}(q)$  and  $\chi_m^{(e)}(q - d)$  represent the nuclear vibrational wave functions. The transition dipole moment is quantified by the matrix elements

$$\mu_{e_m, g_n} = \int \mu(q) \chi_m^{(e)}(q - d) \chi_n^{(g)}(q) dq \quad (7)$$

in the basis of Franck-Condon principle. Obviously, the lowest electronically excited state has the energy  $E_{v'=0} = \omega_{eg}^0$  associated with the wave function  $\Psi_0^{(e)}(x, q) = \psi_e(x, q) \chi_0^{(e)}(q - d)$  when neglecting the zero-point energy  $\omega_i/2$ ;  $i = 0, 1$  of the nuclear vibrations. For  $N_2^+$ ,  $E_{v'=0} = 25461.4 \text{ cm}^{-1}$ , whereas the vertical transition resonant with 391 nm pulse has the frequency  $\nu_{00} = 25566.04 \text{ cm}^{-1} > E_{v'=0}$  [14]. The detuning  $\delta = E_{v'=0} - \nu_{00} \approx -105 \text{ cm}^{-1}$ , which is much lower than the vibrational frequency of  $N_2^+$ . Thus the ground-state vibrational wavefunction  $\chi_n^{(g)}(q)$  has a substantial overlap with the excited-state vibrational wave function  $\chi_0^{(e)}(q - d)$ , leading to nonvanishing transition dipole moments  $\mu_{e_0, g_n}$  defined in Eq. (7). The two pulses thereby pump the system into a superposition of several vibrational levels in the electronic excited manifold, namely,

$$\Psi_e(x, q) = \psi_e(x, q) \left[ C_0 \chi_0^{(e)}(q - d) + C_1 \chi_1^{(e)}(q - d) + \dots \right] \quad (8)$$

with  $|C_0|^2 \gg |C_i|^2$ ;  $i = 1, 2, \dots$ . Thus, the mode  $v' = 0$  dominates while the modes  $v' \geq 1$  have fairly low probability to be populated. We can then neglect the incoherent population transfer towards the minimum of the ESs, as denoted by the blue wavy arrows in Fig. 5(a) in the main text. The  $N_2^+$  undergoes a near-resonant Raman process associated with the three-level scheme involving an effective detuning  $\Delta \approx 105 \text{ cm}^{-1}$ , as illustrated in Fig. 5(b) in the main text. In the three-level model, the levels  $v = 0$ ,  $v = 1$  and  $v' = 0$  are labelled by  $b$ ,  $c$ , and  $e$ , respectively.

## II. Time-domain pump-probe signal

The frequency-resolved emission measured in the experiment is given by  $S(\omega) = 2\text{Im}[E^*(\omega)P(\omega)]$ . Here  $E(\omega) = E_1(\omega) + E_2(\omega)$  is the Fourier component of the positive-frequency part of the seeds where

$$E_i(\omega) = \tilde{E}_i(\omega - \omega_i) e^{i\omega T_i} \quad (9)$$

and  $\tilde{E}_i(\omega - \omega_i) = \int E_i(t) e^{i(\omega - \omega_i)t} dt$  is the pulse envelop in frequency domain. The spectral measurement in the experiments requires the Fourier transform of emitted photons  $P(\omega) = \int P(t) e^{i\omega t} dt$ , where  $P(t)$  gives the far-field dipolar radiation. Quantum mechanically, the far-field dipolar radiation is the mean value of the dipole operator, namely,  $P(t) = \text{Tr}[\mu \rho(t)]$ , given  $\mu = \mu_{eb} |e\rangle \langle b| + \mu_{ec} |e\rangle \langle c| + \text{h.c.}$ . Molecular density matrix can be found by the 3<sup>rd</sup>-order perturbative expansion with respect to molecule-field coupling, which yields

$$P(t) = (-i)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \text{Tr}(\mu(t_3 + t_2 + t_1)[V(t_2 + t_1), [V(t_1), [V(0), \rho_0]]]) \quad (10)$$

using Hilbert space description. One has to recast Eq. (10) into Liouville space in order to describe the excited-state relaxation.

### 428nm seed acts prior to 391nm seed

Inserting Eq. (1) into Eq. (10) and invoking the impulsive approximation  $\Omega(t - T_n) \propto \delta(t - T_n)e^{-i\omega_n(t-T_n)}$  which is valid since the two-color pulses are temporally well separated, we obtain

$$P_1(\omega) = -\frac{2\mu_{be}}{\omega - \omega_{eb} + i\gamma} \left[ |\Omega_1|^2 |\Omega_2|^2 (\rho_{cc} - \rho_{ee}) e^{i\omega_{eb}T_1} + \Omega_1^2 \Omega_2^* \rho_{bc} e^{i(2\omega_{eb}T_1 - \omega_{ec}T_2)} + |\Omega_1|^2 \Omega_2 \rho_{cb} e^{i\omega_{ec}T_2} \right]$$

$$P_2(\omega) = -\frac{2\mu_{ce}}{\omega - \omega_{ec} + i\gamma} \left[ |\Omega_1|^2 \Omega_2 (\rho_{cc} - \rho_{ee}) e^{i\omega_{ec}T_2} + \Omega_1 |\Omega_2|^2 \rho_{bc} e^{i\omega_{eb}T_1} \right] \quad (11)$$

where  $T_1 > T_2$  is imposed and  $\rho_{cc}, \rho_{ee}$  and  $\rho_{bc}$  are the populations and vibrational coherence created by the infrared pulse, respectively. The full polarization reads  $P(\omega) = P_1(\omega) + P_2(\omega)$ . Along the line of the experiment, we essentially calculate the time-resolved transmission at the pulse central frequency  $\omega_i$  given by  $2\text{Im}[E_i^*(\omega_i)P_i(\omega_i)]$ , and subsequently find

$$S_1(\omega_1; T_1) \approx \frac{4|\Omega_1|^2 |\Omega_2|}{\gamma} \left[ |\Omega_2| (\rho_{ee} - \rho_{cc}) - 2|\Omega_1| |\rho_{bc}| \cos(\Delta T_1) \cos(\tilde{\omega}_1 T_1 - \omega_2 T_2 + \Delta T_2 + \vartheta) \right]$$

$$S_2(\omega_2; T_1) \approx \frac{2|\Omega_1| |\Omega_2|^2}{\gamma} \left[ |\Omega_1| (\rho_{ee} - \rho_{cc}) \cos(\Delta T_2) - |\Omega_2| |\rho_{bc}| \cos(\tilde{\omega}_1 T_1 - \omega_2 T_2 + \vartheta) \right] \quad (12)$$

by dropping the slowly-oscillating factor, where  $\tilde{\omega}_1 = \omega_1 - \Delta$  and  $\omega_1 - \omega_{eb} = \omega_2 - \omega_{ec} = \Delta$ . The phases of pulses and coherence  $\rho_{bc}$  have been absorbed into the phase  $\vartheta$ . Hence Eq. (1) in the main text is obtained. The signal given by Eq. (12) is plotted in Fig. S3, elaborating more details on the phase modulation between the oscillations of the two frequency components.

### 391nm seed acts prior to 428nm seed

For the scenario where the 427.8 nm pulse follows the 391.4 nm pulse, the polarization is given by

$$P_1(\omega) = -\frac{\mu_{be}}{\omega - \omega_{eb} + i\gamma} \left[ |\Omega_2|^2 \Omega_1 (\rho_{bb} - \rho_{ee}) e^{i\omega_{eb}T_1} + \Omega_2 |\Omega_1|^2 \rho_{bc} e^{i\omega_{ec}T_2} \right]$$

$$P_2(\omega) = -\frac{2\mu_{ce}}{\omega - \omega_{ec} + i\gamma} \left[ \Omega_2 |\Omega_1|^2 (\rho_{bb} - \rho_{ee}) e^{i\omega_{ec}T_2} + \Omega_2^2 \Omega_1^* \rho_{bc} e^{i(2\omega_{ec}T_2 - \omega_{eb}T_1)} + |\Omega_2|^2 \Omega_1 \rho_{cb} e^{i\omega_{eb}T_1} \right] \quad (13)$$

where  $T_1 < T_2$ . Along the line of the experiment scanning  $T_2$ , we calculate the time-resolved transmission at the pulse central frequency  $\omega_i$  given by  $2\text{Im}[E_i^*(\omega_i)P_i(\omega_i)]$ , and subsequently find

$$S_1(\omega_1; T_2) \approx \frac{2|\Omega_2| |\Omega_1|^2}{\gamma} \left[ |\Omega_2| (\rho_{ee} - \rho_{bb}) \cos(\Delta T_1) - |\Omega_1| |\rho_{bc}| \cos(\tilde{\omega}_2 T_2 - \omega_1 T_1 + \vartheta) \right]$$

$$S_2(\omega_2; T_2) \approx \frac{4|\Omega_2|^2 |\Omega_1|}{\gamma} \left[ |\Omega_1| (\rho_{ee} - \rho_{bb}) - 2|\Omega_2| |\rho_{bc}| \cos(\Delta T_2) \cos(\tilde{\omega}_2 T_2 - \omega_1 T_1 - \Delta T_1 + \vartheta) \right] \quad (14)$$

by dropping the slowly-oscillating factor, where  $\tilde{\omega}_2 = \omega_2 - \Delta$ .  $\vartheta$  is of the same definition as in Eq. (12).

## References:

1. Y. Liu, P. J. Ding, G. Lambert, A. Houard, V. Tikhonchuk and A. Mysyrowicz, *Phys. Rev. Lett.* **115**, 133203-133207 (2015)
2. X. M. Tong, Z. X. Zhao and C. D. Lin, *Phys. Rev. A* **66**, 033402-033412 (2002)
3. Q. Zhang, *et al.*, *Commun. Phys.* **3**, 50-55 (2020)
4. H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2007)
5. Y. Tanimura, *J. Phys. Soc. Jp.* **75**, 082001-082039 (2006)
6. C. H. Kim and T. Joo, *Phys. Chem. Chem. Phys.* **11**, 10266-10269 (2009)
7. K. Ramasesha, L. De Marco, A. Mandal and A. Tokmakoff, *Nat. Chem.* **5**, 935-940 (2013)
8. S. Ruhman, A. G. Joly and K. A. Nelson, *J. Chem. Phys.* **86**, 6563-6565 (1987)
9. F. Kelkensberg, *et al.*, *Phys. Rev. Lett.* **103**, 123005 (2009)
10. G. Haran, E. A. Morlino, J. Matthes, R. H. Callender and R. M. Hochstrasser, *J. Phys. Chem. A* **103**, 2202-2207 (1999)
11. Y. J. Yan and S. Mukamel, *Phys. Rev. A* **41**, 6485-6504 (1990)
12. Y. J. Yan, M. Sparpagione and S. Mukamel, *J. Phys. Chem.* **92**, 4842-4853 (1988)
13. S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, Oxford, 1995)
14. G. Herzberg, *Molecular Spectra and Molecular Structure – Vol. I* (Reitell Press, Paris, 2007)