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Attosecond Resolved Electron Release in Two-Color Near-Threshold Photoionization of N₂

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We have simulated two-color photoionization of N₂ by solving the time-dependent Schrödinger equation with a simple model accounting for the correlated vibronic dynamics of the molecule and of the ion N₂⁺. Our results, in very good agreement with recent experiments [Haessler et al., Phys. Rev. A 80, 011404 (2009)], show how a resonance embedded in the molecular continuum dramatically affects the phases of the two-photon transition amplitudes. In addition, we introduce a formal relation between these measurable phases and the photoelectron release time, opening the way to attosecond time-resolved measurements, equivalent to double-slit experiments in the time domain.

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Measurements and analysis of the cross sections for inelastic processes in the vicinity of a resonant frequency are invaluable tools to explore the structure and dynamics of reactive states in microscopic systems. An imposing corpus of references devoted to the analysis of resonance spectra [1] starting from the decay of unstable nuclei [2], covers Feshbach resonances observed in ultracold gases [3] and atomic and molecular phenomena involving autoionizing states [4]. The widths of the lines in the dispersion curves obtained in the energy domain give access to the lifetimes of the probed excited states. In the last ten years, the advent of harmonic sources delivering uv and extreme ultraviolet (xuv) pulses with attosecond durations (1 as) [5] and their odd harmonics with known phases were used to measure the phases of the oscillations resulting from the two paths' interferences, when the ir-xuv delay is varied. In its conventional implementations, a reference atom, with a smooth continuum, is used as a target: measuring the relative phases of the oscillations gives access to the relative phases of the harmonics and, by extension, to their emission time, with attosecond resolution [10,12].

With objective to probe in the time domain the photoelectron emission from a molecule, the method was recently implemented in an unusual manner [14]: an ir pulse and its odd harmonics with known phases were used to ionize N₂, which possesses a rich and structured continuum. Depending on the vibronic photoionization channel, the measured RABBIT phases presented a nontrivial behavior. This was attributed to the presence of a resonance embedded in the continuum, yet the relation between the RABBIT phases and the timing of the electron emission remained to be established.

Here, we present the results of simulations performed with a model system accounting for the relevant vibronic
dynamics of N$_2$ and N$_2^+$ in the Rydberg series converging to the X channel. The Hamiltonian reads, in atomic units (a.u.),

$$H_0 = -\frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} + V_e(\rho) - \frac{1}{2} \frac{\partial^2}{\partial x^2} + V_e(x, \rho).$$  (1)

The ion core potential $V_e(\rho)$ is associated with the Born-Oppenheimer (BO) energy of the ion in the considered channel. The electron-core potentials $V_e(x, \rho)$ were adjusted to reproduce the $\rho$-dependent BO energies [19] of the neutral, i.e., the G electronic energy when considering the A channel, and the G and R energies when considering the X channel. Within this single-active electron model, the autoionizing state is represented by a shape adjusted on the data of [17], which mostly couples to the X ionization channel. In the following, each of the considered vibronic state is designated by its corresponding electronic and vibrational labels, i.e., $\{G, v\}, \{R, v'\}, \{X, v\}$, and $\{A, v'\}$. Our model, similar to the one used in [18], consists in an active electron with coordinate $x$ and an ionic core with internuclear separation $\rho$ and reduced mass $\mu = 7$ amu. For a given electronic channel, the Hamiltonian reads, in atomic units (a.u.),

FIG. 1 (color online). (a) Electron-nuclei potential $V_e(x, \rho)$ for the X channel, cut at $\rho = 2$ a.u. (black full curve). Horizontal lines indicate the ground (G) and resonant (R) electronic energies as well as the ionization threshold (X). (b) Relevant molecular energies of the model treated in the BO approximation, for the X and A ionization channels. Horizontal lines indicate the first few vibrational energies of each curve. Vertical arrows indicate the photon energies corresponding to harmonics 11 and 13 of $\omega_L = 1.56$ eV.

between the maxima of the xv and ir envelopes. We used cos$^2$ envelopes with FWHM durations of approximately 25 and 40 fs for the xv and ir pulses, respectively, both with intensities within the linear regime.

We solved Eq. (2) by expanding $\Psi(x, \rho, t)$ as

$$\Psi(x, \rho, t) = \sum_{\nu' = 0}^{N-1} f_{\nu'}(x, t) \chi_{\nu'}(\rho).$$  (3)

Here, the functions $\chi_{\nu'}(\rho)$ are associated with the $N$ first vibrational states of the ionic core, i.e., eigenfunctions of the first two terms of $H_0$ in Eq. (1), while $f_{\nu'}(x, t)$ are $\nu'$-dependent electronic wave packets. This representation of $\Psi(x, \rho, t)$ provides a compact way of dealing with its $\rho$ dependence, as only a few vibrational states of the ion are populated (typically $N < 10$), and gives access directly to $\nu'$-resolved observables for each electronic channel. Ionization probabilities and electron spectra were extracted from $f_{\nu'}(x, t)$ propagated after the end of the radiation pulses until the influence of the ionic core on the ejected electron becomes negligible. The RABBIT phases $\theta_{2q}$ were deduced by fitting the evolution of the sideband SB$_{2q}$ in the electron spectra against the delay $\tau$ with the generic function

$$g_{2q}(\tau) = a + b \cos(2 \omega_L \tau + \theta_{2q}),$$  (4)

where $\omega_L$ is the fundamental ir frequency [21].

The channel-dependent RABBIT phases obtained with $\omega_L = 1.56$ eV, close to the frequency used in [14], are displayed in Fig. 2 and compared with the experimental ones. For all the considered sidebands (SB$_{12-18}$), the phases in the A channel remain above $-0.3 \pi$ rad and go monotonically to zero with increasing harmonic order, with practically no dependence on the final vibrational state $\nu'$. These variations are representative of the ones.
obtained with a smooth continuum. The same is observed in the X channel for all sidebands but SB$_{12}$. Indeed, the latter presents important and unusual shifts, down to $-\pi$ rad, which strongly depend on $v'$. For that value of $\omega_L$, H$_{11}$ is expected to hit the continuum between the first two vibrational states of the resonance [see Fig. 1(b)], thus affecting the subsequent transition towards SB$_{12}$. The agreement between simulations and experiments is excellent in the A channel. It remains very satisfactory in the X channel, although the SB$_{12}$ phase dependency on $v'$ is different—which can be ascribed to the extreme sensitivity of the phase on the precise value of the laser frequency when scanning a resonance, as seen below.

To clarify the effect of the resonance on the RABBIT phase changes, we varied $\omega_L$ between 1.53 and 1.58 eV in our simulations, allowing H$_{11}$ to finely scan the vicinity of the resonance, now focusing exclusively on the X channel. Figure 3(a) displays the $v'$-resolved ionization probability with H$_{11}$ alone, as a function of $\omega_L$. For each $v'$, the curve exhibits two peaks approximately located at $11\omega_L = 17.0$ and 17.3 eV, corresponding to ionization through the resonant states $|R, v'' = 0\rangle$ and $|R, v'' = 1\rangle$, respectively. Note that the H$_{11}$ bandwidth, of about $\sim-0.15$ eV, is 1 order of magnitude larger than $\Gamma_R$ and governs the width of the photoelectron peaks. We verified that the ionization probability at each peak is proportional to the corresponding Frank-Condon (FC) product $|X(v', R, v'')(R, v'')(0, 0)|^2$. Because of much smaller FC overlap with the ground state, the resonant states $v'' > 1$ do not contribute. These results indicate that, when $\omega_L$ varies, H$_{11}$ probes two neighboring resonances, $|R, 0\rangle$ and $|R, 1\rangle$, respectively, with relative ionization efficiencies depending on the final state $|X, v'\rangle$ of the ion.

The SB$_{12}$ phases in the same frequency range are shown in Fig. 3(b). Their evolution are linked to the H$_{11}$ ionization probabilities: each $v'$-resolved phase displays a smooth $\sim -\pi$ jump as H$_{11}$ crosses the resonances, around $\omega_L = 1.546$ and 1.574 eV, respectively. Between them, the phase evolution depends strongly on $v'$: it remains almost flat for $v' = 1$ and 2, while it goes through a stiff $-\pi$ jump at $\omega_L = 1.565$ eV for $v' = 0$ [22].

As explained in [14], the second-order perturbative treatment of two-photon ionization predicts that, when varying the frequency, a $\pi$ jump occurs in the RABBIT phase $\theta_{2q}$ when one of the adjacent harmonics crosses a resonance. An additional $\pi$ jump is expected between two resonances, at the frequency where their respective contributions compensate each other. Therefore, when changing the frequency and scanning two resonances, three phase jumps are expected: two are located at the resonant energies, the third one being in between. This latter jump may be seen or not, depending on the resonance parameters, namely, on their widths and magnitudes, and also on the intrinsic resolution of the pump pulse. This is well illustrated in our simulations, where the relative magnitudes of the two neighboring resonances vary significantly with $v'$. The ionization peak ratio, governed by the corresponding FC factors, is 15:1 for $v' = 0$ while it is 5:1 and 2:1 for $v' = 1$ and 2, respectively. This leads to the appearance of the intermediate phase jump for $v' = 0$ while it is absent for $v' = 1$ and 2.

To uncover the relation between the sideband phase behavior and the electron release timing, we have performed additional two-color simulations where the xuv pulse consists of a single harmonic, either H$_{11}$ or H$_{13}$. Then, we estimated the SB$_{12}$ formation times through the H$_{11}$ and H$_{13}$ paths, respectively $\tau_{11}$ and $\tau_{13}$. This was achieved in our simulations by determining the arrival
times of the corresponding electronic wave packets, at a distance where they no longer experience the influence of the core. The time difference between the two paths, $\Delta \tau_{12} = \tau_{11} - \tau_{13}$, is displayed for each final vibrational state $v'$ in Fig. 4(a). The formation time turns out to be strongly affected by the resonances: when $H_{11}$ hits either $|R, 0\rangle$ or $|R, 1\rangle$, we find that the $SB_{12}$ formation is delayed by several femtoseconds as compared to the nonresonant path involving $H_{13}$. Moreover, the variations of $\Delta \tau_{12}$ between the resonances clearly depends on $v'$: it remains large and positive for $v' = 0$, while it takes negative values around $\omega_L = 1.56$ eV for $v' = 1$ and 2.

A “time-of-flight” simulation with such an ultrashort time resolution corresponds to a gedanken experiment: its realizability is well beyond the capabilities of current detection methods. It can, however, be shown that $\Delta \tau_{2q}$ is related to the change of the RABBIT phase when varying the energy of the driving laser frequency (i.e., of the photoelectron kinetic energy $E_{2q}$) [23]:

$$\Delta \tau_{2q} = - \frac{\hbar}{E_{2q}} \frac{\partial E_{2q}}{\partial \Omega} = - \frac{\hbar}{2q} \frac{\partial \theta_{2q}}{\partial \omega_L}.$$  

We have thus taken the derivative of the phases displayed in Fig. 3(b). The resulting times, shown in Fig. 4(b), are in excellent agreement with the ones shown in Fig. 4(a), with comparable $v'$ dependences. The same delays of $\sim 8$ fs are obtained around the resonant frequencies ($\omega_L \approx 1.546$ and 1.574 eV), and the same crossings of the 0 delay line are obtained before the resonances ($\omega_L \leq 1.538$ eV) for all $v'$, and between the resonances ($\omega_L \approx 1.562$ eV) for $v' = 1$ and 2. Moreover, the steep $\pi$ jump observed between the resonances only for $v' = 0$ induces a delay exceeding 12 fs. The phase derivative at this frequency is much larger than the “measured” time, the latter being bounded by the durations of the ir and xuv pulses.

In summary, relying on a simple model designed to represent the vibronic dynamics of $N_2$, we have investigated how a near-threshold resonance affects vibrationally resolved two-color photoionization phases in a molecular RABBIT measurement. We have found that the photoemission dynamics is strongly modified by the presence of an intermediate resonance and shown how experimentally observable data, i.e., the RABBIT phases, can be exploited to retrieve the attosecond photoelectron release profile. We would like to emphasize that such time-resolved measurements are nowadays feasible, thanks to the development of tunable intense ir sources combined with accurate detection methods [15].

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[20] This approximation is here supported by the shape of the corresponding photoionization peak (at $\sim 723$ nm, see Fig. 3 of Ref. [17]), which presents a $q \sim 0$ Fano profile. Further investigations are required prior to extending it to any autoionizing state.
[21] We have removed the known harmonic phases from $\theta_{2q}$, as done in the analysis of the experimental data in [14].
[22] Note that there is a frequency, close to 1.573 eV, for which the phases computed for $v' = 0$, 1, and 2 coincide simultaneously with the experimental ones.
[23] J. Caillat et al. (to be published).