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Photoionization of NaI: inward-outward asymmetry in the wave packet detection

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Abstract. The nuclear wave packet in the A state of NaI has been monitored in a pump-probe femtosecond experiment using a resonant two-photon ionization detection scheme. A strong asymmetry depending on the direction of propagation of the wave packet is observed in the Na^+ ion signal. This phenomenon, well reproduced by a full quantum wave packet calculation, has been assigned to the combination of two effects: i) the motion of the wave packet in the intermediate state of the two-photon probe process, ii) the R-dependence of the photoionization efficiency of this intermediate state.

PACS. 33.80.-b Photon interactions with molecules – 33.80.Rv Multiphoton ionization and excitation to highly excited states (e.g., Rydberg states)

1 Introduction

In the last ten years a significant amount of research has been aimed at the understanding of real time dynamics of molecular systems subsequent to excitation by ultra- fast laser pulses [1]. This understanding is required if one intends to control photochemical reactions with adequately tailored laser pulses [2].

In a recent experiment [3] we have shown that the wave packet evolution of NaI in its first excited state (the A state) can be monitored through direct femtosecond photoionization to the dissociative continuum of the ion. Classical [3] and quantum dynamics simulations [4] have clearly demonstrated that it is possible to map the sodium iodide molecular dynamics along the internuclear coordinate by recording time- and energy-resolved photoion and photoelectron spectra [5,6]. In this paper we present experimental and theoretical results obtained when ionization occurs *via* a resonant two-photon path.

The work of Zewail [7–15] has thoroughly illustrated the R-dependent nature of the probe process. When the wave packet is probed at a turning point of the motion, a single series of peaks is observed, with a period corresponding to one oscillation in the potential. When the wave packet is probed elsewhere, a splitting of the signal occurs, according to the fact that the wave packet experiences the probe twice in a period. This has been observed experimentally by Cong *et al.* in the probe of NaI by laser induced-fluorescence [13]. In addition a very small peak asymmetry is reported between inward and outward motions. This has been related by the authors to the different shapes of the wave packet after and before reflection at the outer turning point and is well reproduced by the quantum dynamics predictions [13].

A similar study, using a two-photon probe process to detect the B state dynamics of I_2, has also provided evidence for the splitting of signal peak series [16]. In this case, however, the asymmetry observed is not only much larger than that predicted by Metiu and Engel [17], but is also inverted, *i.e.* the first peak series is less intense than the second one. This surprising effect is unfortunately neither discussed nor explained by the authors [16].

In this paper, we present evidence for the occurrence of a significant inward outward asymmetry effect in the resonant two-photon ionization probe process of the NaI (A state) wave packet. A qualitative model able to account for this effect is proposed and has been confirmed by quantum dynamics calculations.

2 Experimental setup

The experimental setup is the same as previously described [3]. It consists in a supersonic beam coupled with a dual photoion photoelectron time-of-flight spectrometer and a femtosecond pump-probe laser. Briefly, the pump wavelength λ_1 (309−313 nm) is obtained by doubling the red light issued from a femtosecond dye laser with a 1mm

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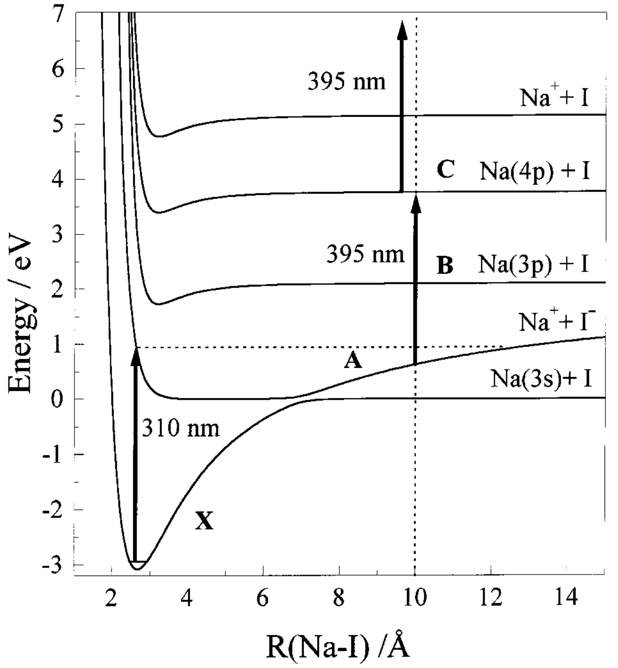

Fig. 1. Schematic representation of the pump and probe scheme with the X, A, B and C potential curves of the ground and first excited states of NaI. The upper potential corresponds to the ion ground state. Note that the probe photon energy matches the energy difference between the C and the A states at an internuclear distance of 10 Å. The accurate X and A potentials have been taken from reference [24,13], while the B, C and the ion potentials are just schematic.

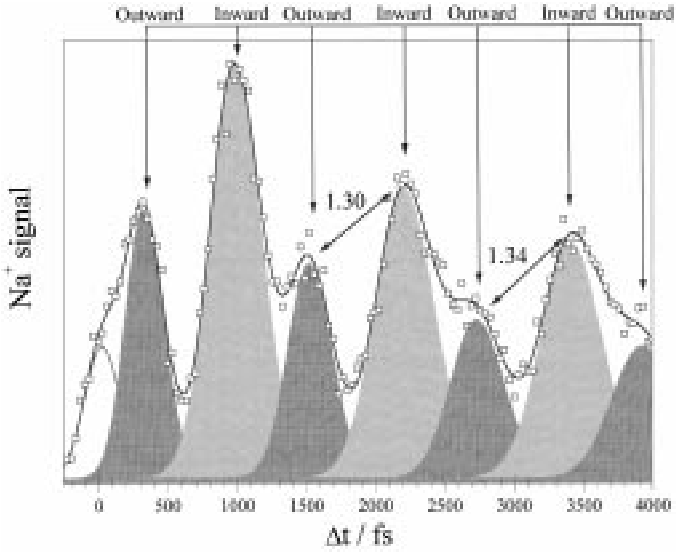

Fig. 2. Observed Na^+ ion signal as a function of the delay between the pump (310 nm) and the probe (395 nm) laser pulses. The signal has been fitted by a sum of Gaussian peaks. For a delay time $\Delta t = 0$, a small (white) peak due to the direct three-photon process is bearly visible. The average integral ratio between corresponding inward (light gray) and outward (dark gray) peaks is found to be 1.32 ± 0.05. The ratio between the first inward and outward peaks is not indicated since at a delay time $\Delta t = 300$ fs the pump and probe pulses still overlap and the ionization mechanism is more complicated than the one discussed here with well separated pulses.

thick BBO crystal. The pulse energy is typically in the order of 5 μJ, the spectral bandwidth is about 1 nm and the temporal width is in the 200–300 fs range.

The probe wavelength $\lambda_2(395 \pm 1$ nm) is obtained by frequency doubling the light of the Ti-Sapphire regenerative amplifier. The probe pulse is typically 150–200 fs broad and the pulse energy is in the order of 50 μJ. The lasers are delayed in time by scanning a delay line by 33 fs steps. Both lasers are mildly focused in the beam in between the grids of the spectrometer by 1m lenses. A typical spectrum is obtained by averaging 10 to 20 scans with 25 laser shots per scan step.

3 Experimental results

Previous works [3,4,7–10] have shown that the A-state wave packet, prepared in the inner repulsive wall with a 310 nm photon, moves back and forth between this point ($\sim$ 3 Å) and the outer turning point ($\sim$ 12 Å). In particular, we have shown in references [3,4] that the wave packet dynamics can be monitored by a one-photon ionization probe scheme at 263 nm. This probe process was found to be very selective with the internuclear distance, with a maximum efficiency on the ionic part of the A state potential: the signal shows a period of 1.2 ps, with the first maximum at the outer turning point of the motion, *i.e.* after a pump-probe delay of 600 fs.

In the present experiment the wave packet is prepared with a 310 nm pump pulse (duration 200–300 fs) and its evolution is monitored by ionization using a 395 nm probe pulse (duration 150–200 fs). At this wavelength two probe photons are necessary to ionize the NaI molecule (see Fig. 1). Only Na^+ ions were observed, indicating the ionic fragmentation of the NaI^+ ions initially formed.

The evolution of the Na^+ signal as a function of the time delay between the pump and the probe laser pulses is presented in Figure 2. The Na^+ signal is essentially composed of two series of recurrences, having the same 1.2 ps periodicity; the second one being shifted by a time delay of 700 fs.

Although not presented here, the time delay $\Delta t = 0$ has been determined by studying the ionization efficiency of diethylaniline as a function of the delay between the pump laser ($\lambda_1 = 310$ nm induces the $S_1 \leftarrow S_0$ transition) and the probe laser ($\lambda_2 = 395$ nm ionizes the excited molecule). With this experiment the temporal delay between the pump and the probe pulses can be determined with a precision better than 100 fs.

Whereas in the one-photon ionization the Na^+ signal maxima, located every 1.2 ps from the first peak at 600 ± 50 fs, corresponds to the probe of the wave packet at the outer turning point of the motion [3,4], these same delays now correspond to signal minima in the present two-photon probe experiment. The maxima of Na^+ signal exhibit now two, symetrically localized (+350 and −350 fs) with respect to the above mentioned minima. One should thus conclude that these maxima correspond now to the probe of the wave packet at a well-localized intermediate internuclear distance, which is thus experienced twice in a period.

The observed signal has been fitted by a superposition of Gaussian peaks whose height, width and center have been allowed to vary freely: the result of this fit is superimposed to the data in Figure 2. The decay through the avoided crossing between the ionic Na^+-I^- state and the covalent dissociative Na-I state is clearly observed and has been already well studied by Zewail's group [13]. One can also clearly see that the recurrences (in dark gray in Fig. 2), having a maximum at 300 fs, 1500 fs and 2700 fs are less intense than the ones having their maximum at 1000 fs, 2200 fs and 3400 fs respectively (in light gray). As an example the area ratio of the light gray peak at 2200 fs to the dark gray peak at 1500 fs is 1.30. The first peak at $\Delta t = 0$ is due to a direct three-photon process that will not be discussed hereafter. Since the first peak at 300 fs occurs before the time necessary for the wave packet to reach the outer turning point ($R = 12$ Å) and the second one (1000 fs) is obtained when the wave packet is going towards the inner turning point, it is clear that the ionization efficiency strongly depends upon the propagation direction. This observation is quite unexpected since quantum dynamics simulations have already shown that the wave packet in the A state, produced by a 320 nm pump laser, exhibits almost the same shape at a given position, whatever its direction of propagation [4,13].

This unexpected behavior can be crudely explained with simple arguments if we assume that the nuclear wave packet dynamics follows roughly the classical equations of motion. Exact quantum mechanical calculations are also presented to ascertain the validity of this model.

4 Qualitative interpretation

Let us assume that the ionization is due to a two-photon *resonant* process through the intermediate C state (see Fig. 1) and that within the same ionizing (probe) laser pulse two photons are *sequentially* absorbed.

After the first laser pulse (310 nm) is fired, we consider a wave packet moving in the A state potential. From the energy conservation principle, this wave packet can be promoted onto the excited C state correlating to the asymptotic fragments $\text{Na}(4\text{p}\ ^2\text{P}) + \text{I}(5\text{p}\ ^2\text{S})$ if its kinetic energy is conserved during the photon absorption (Franck-Condon principle). This criterion is only satisfied at the particular internuclear distance where the photon energy matches the energy difference between the A and C potentials. This distance corresponds to the point $R \cong 10$ Å indicated in Figure 1. Actually, the first experimental peak of Figure 2 appears after a delay of 300 fs which roughly corresponds to the same NaI internuclear distance of 10 Å (this can be estimated using either classical [3] or quantum time propagation [4]).

This simple Franck-Condon behavior allows us to account for the absence of NaI^+ ions in our mass spectrum. Indeed, since the wave packet is promoted on the ion ground state potential curve around $R \cong 10$ Å, its relative nuclear kinetic energy is of the order of 0.3 eV (see Fig. 1). This amount of energy largely exceeds the binding energy of NaI^+ at this large distance, thus implying a complete dissociation of the ions formed in the ionization process.

But where does the asymmetry between the inward or outward motion come from? When promoted on the C state, the nuclear wave packet keeps its kinetic energy as well as its direction of propagation, and the nuclei move at a relative speed which can be evaluated around 0.017 Å/fs. After the absorption of the first probe photon, the nuclei will either move away if the delay between the pump and the probe laser is for instance 300 fs, or get closer for a delay time of 1000 fs. If the probe pulse duration is long enough to allow the nuclear wave packet to leave the $R \cong 10$ Å region before a second photon is absorbed, a difference may be observed between the inward and outward directions of propagation if the two following conditions are verified: first, the ionization efficiency must show an important variation with the internuclear distance, and second, the depopulation of the C state by photoionization must be small during the probe pulse. This latter condition is required to avoid a total ionization of the C state wave packet as soon as it is created.

The ionization efficiency of a molecule generally depends upon the spatial position of the nuclei, and as clearly demonstrated in [3,4] the ionization efficiency of the NaI diatom is exceptionally sensitive to the internuclear distance. This behavior is due to the R-dependence of the ionic character of any electronic state of NaI. For instance, let us first consider the propensity for ionization of the A state of NaI. Roughly speaking, the probability for ionizing an A-state wave packet located at $R > 7$ Å where the potential is almost completely ionic ($\text{Na}^+ \ldots \text{I}^-$) is two orders of magnitude larger than the ionization probability of the same wave packet located in the covalent part of the potential ($R < 7$ Å) due to the fact that the photodetachment cross section of I^- is ~ 200 times larger than the ionization cross section of the ground state sodium atom [3,4].

We will now use here a similar argument for the C state ionization process: the ionic character of this state varies with R. We only consider that the first pulse prepares the C state in a Σ symmetry, while an additional state of Π symmetry correlates to the asymptotic limit $\text{Na}(4\text{p}) + \text{I}(5\text{p})$. This assumption is quite realistic since at large internuclear distances the C ← A transition consists in a simple electron transfer from I^- to Na^+, which is more likely a Σ−Σ transition since the overlap between the 5p_σ and 4p_σ atomic orbitals of I and Na is larger than the overlap between the 5p_π and 4p_π orbitals at large distances.

To derive the internuclear distance dependence of the C state ionization transition dipole, we use a two-electron valence bond model that is valid at large internuclear distances: $R > 4$ Å. The NaI C state, although almost completely covalent in nature Na($4p_\sigma$)... I($5p_\sigma$), is slightly mixed with the ionic configuration Na^+... I^-, due to the ionic-covalent interaction term in the electronic Hamiltonian. We may therefore write the C state electronic wavefunction ϕ_{Cstate} as the following linear combination of ionic and covalent wavefunctions

$$\phi_{\mathrm{Cstate}} = \alpha(R)\phi_{\mathrm{ionic}} + \beta(R)\phi_{\mathrm{covalent}}, \tag{1}$$

where ϕ_{ionic} and ϕ_{covalent} denote the following charge localized two electron valence bond normalized Slater determinants [21,22]

$$\phi_{\mathrm{ionic}} = |5\bar{\mathrm{p}}_\sigma 5\mathrm{p}_\sigma| \tag{2a}$$

$$\phi_{\mathrm{covalent}} = \{|4\bar{\mathrm{p}}_\sigma 5\mathrm{p}_\sigma| - |4\mathrm{p}_\sigma 5\bar{\mathrm{p}}_\sigma|\}/N. \tag{2b}$$

The norm N may be calculated with the overlap integral $S_{\mathrm{NaI}}(R)$ between the sodium $4p_\sigma$ and the iodine $5p_\sigma$ Slater atomic orbitals separated by a distance R:

$$N = \{2(1 + S^2_{\mathrm{NaI}}(R))\}^{1/2}. \tag{3}$$

The ionic and covalent coefficients $\alpha(R)$ and $\beta(R)$ are then easily expressed as

$$\alpha(R) = \frac{(1 - S_{\mathrm{ic}}(R))^{1/2} - (1 + S_{\mathrm{ic}}(R))^{1/2}}{2(1 - S^2_{\mathrm{ic}}(R))^{1/2}} \tag{4a}$$

$$\beta(R) = \frac{(1 - S_{\mathrm{ic}}(R))^{1/2} + (1 + S_{\mathrm{ic}}(R))^{1/2}}{2(1 - S^2_{\mathrm{ic}}(R))^{1/2}}, \tag{4b}$$

where $S_{\mathrm{ic}}(R)$ represents the overlap integral between the ionic and covalent wavefunctions ϕ_{ionic} and ϕ_{covalent}, *i.e.*

$$S_{\mathrm{ic}}(R) = \frac{2S_{\mathrm{NaI}}(R)}{\{2(1 + S^2_{\mathrm{NaI}}(R))\}^{1/2}}. \tag{5}$$

One may notice that at large internuclear distances the overlap integrals $S_{\mathrm{NaI}}(R)$ and $S_{\mathrm{ic}}(R)$ become small compared to 1, and the ionic character of the C state $\alpha(R)$ becomes simply proportional to $S_{\mathrm{NaI}}(R)$ while its covalent character $\beta(R)$ approaches unity.

We can now extract from the expansion (1) a simple analytical expression for the R-dependence of the transition dipole between the C state of NaI and the ground state of the NaI^+ ion

$$\mu_{\mathrm{ion}\leftarrow\mathrm{C\,state}}(R) = \alpha(R)\mu_{\mathrm{ionic}} + \beta(R)\mu_{\mathrm{covalent}}. \tag{6}$$

The ratio between the μ_{ionic} and μ_{covalent} transition moments (assumed to be constants) may be deduced from the ratio between the I^- and Na atomic photodetachment and ionization cross-sections σ_{I^-} and σ_{Na} respectively

$$\frac{\mu_{\mathrm{ionic}}}{\mu_{\mathrm{covalent}}} = \left(\frac{\sigma_{I^-}}{\sigma_{\mathrm{Na}}}\right)^{1/2} \approx \sqrt{200}. \tag{7}$$

Equation (7) relies on the approximation that the ionization cross section of the covalent state (at large internuclear distances) is similar to ionization cross section of the sodium atom (of the order of $\sigma_{\mathrm{Na}} \approx 0.1$ Mb [18,19]) and that the one of the ionic state (again at large internuclear distances) is close to the photodetachment cross section of I^- (of the order of $\sigma_{I^-} \approx 20$ Mb [20]). In addition, the energy dependence of the transition dipole has also been neglected. Numerically, the only ingredients necessary to calculate this approximate ionization transition dipole (6) are the Slater exponents $\xi_{4p}(\mathrm{Na}) = 0.319$ and $\xi_{5p}(\mathrm{I}) = 1.90$ [21] of the $4p_\sigma$ and $5p_\sigma$ orbitals of the sodium and iodine atoms, respectively.

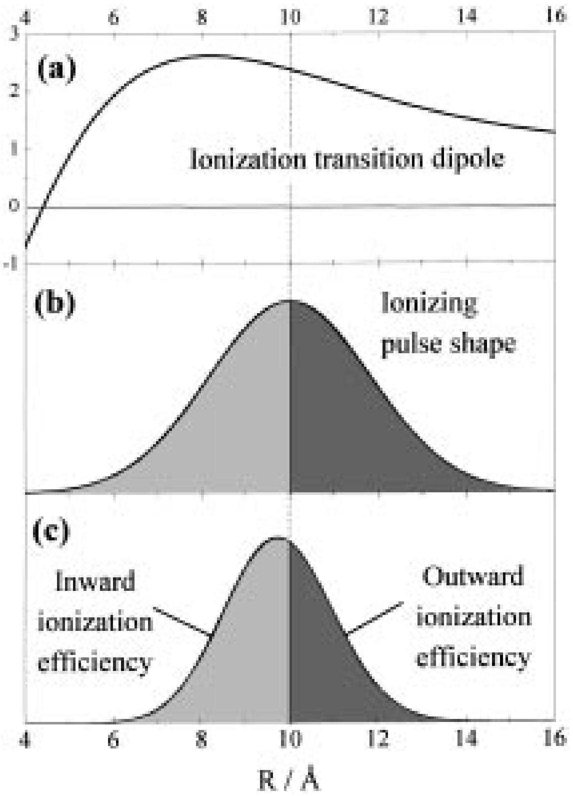

Fig. 3. (a) Variation of the ionization transition dipole (arbitrary unit) of the NaI C state as a function of the internuclear distance. (b) Projection of the temporal width of the ionizing probe laser on the internuclear axis, assuming that the C state wave packet evolves at a speed of 0.017 Å/fs. (c) Square of the product of the ionizing laser shape of the inset (b) by the ionization transition dipole of the inset (a). The asymmetry of this ionization efficiency curve indicates clearly that the wave packet has a higher ionization probability when moving toward short internuclear distances than in the opposite direction. The ratio of the inward (light gray) to outward (dark gray) integrals is evaluated to be 1.4.

Figure 3a represents the ionization transition dipole (6) of the C state as a function of the internuclear distance R. Since it decreases with the internuclear distance for $R > 8$ Å one can easily understand why the ionization of the NaI molecule is not equivalent when the wave packet moves in one direction compared to the other. When the wave packet moves outwards (*i.e.* $R > 10$ Å), it explores a region where the integrated ionization probability is less than when it moves in the opposite direction (*i.e.* $R <$ 10 Å).

But can this simple scenario give the right order of magnitude for the asymmetry between the inward and outward ionization? To answer this question let us consider two particular delay times between the pump and the probe pulses: 300 fs (the first time the wave packet exactly arrives at 10 Å) and 1000 fs (the first time the wave packet comes back at 10 Å). It is then possible to build a schematic representation of the envelope of the probe laser pulse seen by the wave packet as it moves on the C state. This representation, shown in Figure 3b, is simply obtained by projecting the temporal laser pulse envelope (assumed Gaussian) on the internuclear axis using the speed of the wave packet on the C state already mentioned above, *i.e.* 0.017 Å/fs, which is constant in the $R = 10$ Å region according to the flatness of the C state at these distances. This internuclear distance representation of the pulse shape has been centered at 10 Å corresponding to the time delays 300 fs and 1000 fs mentioned above. The excitation of the A state nuclear wave packet occurring in a very narrow region centered at 10 Å, the two half gaussian shapes shown in Figure 3b correspond to the laser amplitude seen by the C state wave packet for the inward and the outward motions. Assuming now a negligible depopulation of the C state by the laser field, the total ion signal is directly proportional to the integral of the square of these internuclear laser shapes (Fig. 3b) multiplied by the ionization transition dipole (Fig. 3a) from 10 to 0 Å if the wave packet is going inwards and from 10 Å to infinity if the wave packet is moving outwards (see Fig. 3c). The inward integral is found to be larger, the ratio of the two integrals being 1.4, which is very close to the mean observed value 1.32 ± 0.05 of the maximum intensity for two consecutive outward-inward peaks (see Fig. 2). Finally, at the end of the probe pulse the remaining C state population will simply undergo dissociation in the Na(4p) + I(5p) channel. Although the previous assumptions already give fair results, a more rigorous quantum calculation is necessary to test this simple interpretation.

5 Quantum dynamics simulations

If a non-vertical non-simultaneous absorption of two photons within a single pulse is responsible for the inward-outward asymmetry measured in the femtosecond probing of NaI nuclear dynamics, a quantitative simulation can be performed using an adequate time- dependent approach. We extend here the quantum dynamics formalism used recently to explore the possibilities of control over the two-body ($\mathrm{NaI^+ + e^-}$) *vs.* the three-body ($\mathrm{Na^+ + I + e^-}$) break-up of the molecule in femtosecond experiments [4]. We include now the two-photon ionization process of the A state wave packet *via* the resonant C state.

This approach uses the very stable and efficient time propagator developed by Feit *et al.* [23] for the spatial grid representation of time-dependent wavefunctions. The time-dependent electronuclear wavefunction of NaI is expressed as a simple Born-Oppenheimer product on the various X, A and C electronic states involved in the present experiment. The electronic continuum of NaI is accounted for by expanding the free part of the electronuclear wave packet on a discretized set of one-electron Coulomb continuum wavefunctions. A significant numerical simplification in our simulation is obtained by using the rotating wave approximation, thus implying that the propagation is performed in a simplified dressed state picture. The X, A and ion potentials and couplings are the same as those used in [4]. The C state potential is assumed to be parallel to the ion ground state potential since it already shows a strong Rydberg character. The predissociation of the NaI nuclear wave packet in the adiabatic A potential is included using a unitary diabatic to adiabatic transformation at each time step. Finally, the $\mathrm{Na^+}$ ion yield is calculated by projecting the final set of nuclear wave packets obtained at the end of the probe pulse on the field-free dissociated nuclear wavefunctions of the $\mathrm{NaI^+}$ ground state potential.

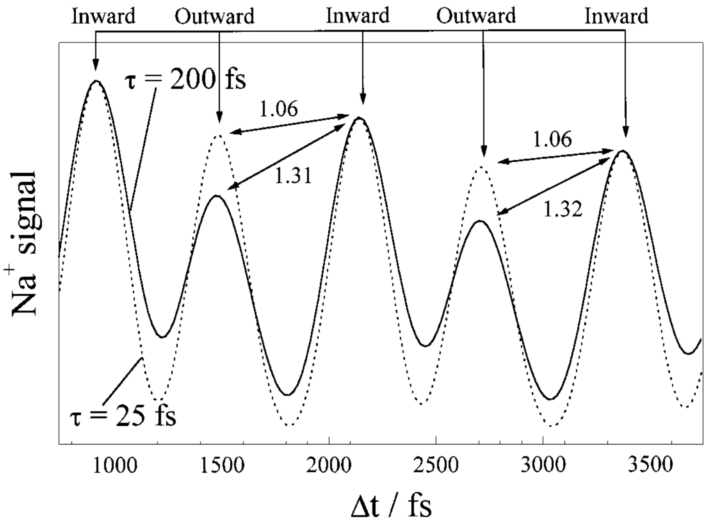

Fig. 4. Quantum dynamics simulation of the $\mathrm{Na^+}$ ion signal as a function of the pump-probe time delay for a probe pulse duration of 200 fs (solid line) and 25 fs (dotted line). The pump ($\lambda_1 = 310$ nm) and probe ($\lambda_2 = 395$ nm) pulses have Gaussian profiles and the pump pulse duration is 300 fs. The integral ratios between the successive inward and outward peaks are indicated in a similar way as in Figure 2.

Figure 4 shows the $\mathrm{Na^+}$ ion signal calculated (solid line) within this quantum model as a function of the pump-probe time delay. The asymmetry that has been observed experimentally and explained schematically in the previous section is clearly supported by this more rigorous quantum dynamics simulation. The ratio between the outward and inward ionization peaks is in very good agreement with the experimental values (see Figs. 2 and 4). This demonstrates that the two-photon ionization of the NaI wave packet in the A state is not a direct process with a direct vertical absorption of two photons, but is a resonant process which occurs *in two steps within the same ionizing pulse.*

In addition, if the probe pulse duration is shortened to 25 fs the asymmetry between the outward and inward ionization probabilities is significantly reduced (see Fig. 4, dotted line). This is in agreement with our interpretation of the asymmetry since in 25 fs the wave packet is frozen at the position $R = 10 \pm 0.4$ Å, and we then observe an almost vertical transition with about the same probability for the inward and outward motion, the ratio between the inward and outward peaks being reduced to 1.06.

6 Conclusion

We have presented in this paper the observation and the interpretation of a surprising inward-outward asymmetry in the femtosecond two-photon ionization of NaI nuclear wave packets. A quantum model has been developed to ascertain our interpretation. These results highlight the role of a resonant state in a two-photon probe process in real time experiments. Indeed, the inward-outward asymmetry measured with such a probe scheme does not reflect only the intrinsic dynamics of the wave packet, *i.e.*, the evolution of the wave packet shape alone, but is also greatly influenced by the dynamics of the wave packet in the intermediate state during the probe process itself. Such effects can be expected when using a resonant multiphoton ionization probe scheme, if the pumping up rate of the probe laser is not too large (the wave packet has time to evolve in the intermediate state before being ionized) and if the ionization step of the probe scheme, *i.e.*, the ionization of this intermediate state, is R-dependent. According to the fact that these conditions are currently fulfilled in two-photon probe experiments, one should conclude that this effect should be systematically taken into account for interpretating the time-resolved signal measured. As an example, the present model might be a key for understanding the asymmetry observed on the B state dynamics of the I_2 system [16].

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