Measurements of relative photoemission time delays in noble gas atoms

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Abstract
We determine relative photoemission time delays between valence electrons in different noble gas atoms (Ar, Ne and He) in an energy range between 31 and 37 eV. The atoms are ionized by an attosecond pulse train synchronized with an infrared laser field and the delays are measured using an interferometric technique. We compare our results with calculations using the random phase approximation with exchange and multi-configurational Hartree–Fock. We also investigate the influence of the different ionization angular channels.

Keywords: photoemission time delay, attosecond, RABITT, MCHF, RPAE

(Some figures may appear in colour only in the online journal)

1. Introduction
The photoionization of atoms and molecules has been extensively studied during the last decades using various light sources, such as lasers and synchrotron radiation, toward increasing precision and completeness (see e.g. [1] and references therein). One of the goals has been in particular to perform ‘complete’ experiments, which means that the partial amplitudes and the relative phases between the ionization channels are determined [2–4]. The dynamics between different channels of the photoionization process is then captured. Such experiments often require alignment of the atoms or molecules prior to photoionization, as well as angular resolution and/or light polarization control. An important application of attosecond pulses [5, 6] that has arisen during the last few years is the measurement of the photoemission time delay, equal to the derivative of the phase of the ionization transition matrix element with respect to the energy [7–9]. This phase is not the same as the relative phase between the different channels. It is a new experimental quantity which can be (and should be) compared with predictions from theoretical models. The photoionization time delay can be interpreted as the group delay of the outgoing ionized electronic wave packet created by the absorption of an attosecond pulse, as it propagates in the atomic potential [10, 11]. In the case of a single outgoing angular momentum channel, the phase of the photoemission amplitude is identical...
to the scattering phase \[12, 13\], while in a more general case, where two or more angular channels are present, it carries information on the different channels involved in the photo-emission. Measurements of the photoionization time delays allow us to get insight and understanding about the temporal dynamics of photoionization from any subshell and should ultimately be combined with other types of measurements to provide a complete picture.

One of the first time-resolved photoemission measurements was that of the difference in photoemission delays from the 2s and 2p shells in neon \[8\]. Using the streaking technique and single attosecond pulses centered around 80 eV, the difference was found to be \(21 \pm 5\) as. The interpretation of this result triggered an intense theoretical activity \[8, 14–19\] (see also earlier theoretical work \[20, 21\]). Other experiments, based on interferometry with attosecond pulse trains (APT) centered at \(\approx 30\) eV, studied resonance effects in \(\text{N}_2\) \[22, 23\] and \(\text{He}\) \[24\] or compared photoemission time delays between the 3s and 3p shells in \(\text{Ar}\) \[9, 25\]. The latter results also stimulated several theoretical studies which aimed at understanding the effect of the probe laser field on the measurement \[11, 26\] as well as accurately describing the time delays in an energy region where strong 3s–3p intershell correlation effects take place \[26–30\]. Recently, this approach has been extended to the case of double photoemission in xenon \[31\], using coincidence measurements.

In this work, we present measurements of the differences in photoionization time delays between outer shell electrons in helium, neon and argon. The time delays are extracted with an interferometric technique, using a frequency comb of high-order harmonics (with photon energies from 29 to 39 eV) and an infrared (IR) laser pulse. We make use of an actively stabilized interferometer, which allows us to precisely control the length difference between its two arms, and thus the delay between the IR and extreme ultraviolet (XUV) pulses. The experimental results are compared with calculations using random phase approximation with exchange (RPAE) and multi-configurational Hartree–Fock (MCHF) approaches and including contributions from several possible angular channels. In section 2, we present the experimental setup and the results. In section 3, we describe our calculations and compare the results with the experiment in section 4.

2. Experiment

2.1. Experimental setup

A scheme of the experimental setup is shown in figure 1(a). We use a Ti:sapphire femtosecond laser system delivering 20 fs, 5 mJ pulses centered at 800 nm, with 1 kHz repetition rate. The laser is sent in two arms of a Mach–Zehnder interferometer. In one arm, the beam is focused in a gas cell where an XUV APT is created via high-order harmonic generation. A 200 nm Al filter is used to remove the fundamental radiation. In the second arm the pulse is delayed relative to the APT by a piezoelectric-controlled delay stage, and then is recombined with the APT by a reflection on a convex holey mirror. The APT and IR pulses are focused with a toroidal mirror into a magnetic bottle electron spectrometer where photo-electrons are collected in a solid angle of \(\pi / 2\) steradians. Both XUV and IR light fields are polarized vertically, i.e. perpendicularly to the electron detection axis which is horizontal. Although this choice can lead to a collection anisotropy whose effect is angular channel-dependent, the resulting change in the measured delays is within our error bars.

2.2. Interferometric measurements

Following ionization with an APT, electrons are created at discrete energies corresponding to absorption of odd harmonics, separated by \(2\hbar\omega\), where \(\omega\) is the IR frequency and \(\hbar\) the reduced Planck constant. The addition of a weak IR field allows further absorption or emission of one IR photon leading to sideband (SB) peaks in the electron spectra (see figure 2(a)). Each SB can be created through two different pathways so that the electron signal varies as \[33, 34\]

\[
S = A + B \cos \left(2\omega r - \Delta \phi_{\text{atto}} - \Delta \phi_{\text{ion}}\right),
\]

where \(r\) is the delay between the IR and the APT, \(\Delta \phi_{\text{atto}}\) is the phase difference between consecutive harmonics, and \(\Delta \phi_{\text{ion}}\) is
the difference in phase of the two-photon ionization matrix elements involved in the creation of a SB. As explained in section 3, \( \Delta \phi_{\text{ion}} \) is related to the photoemission time delay. Since \( \tau \) and \( \Delta \phi_{\text{ion}} \) are generally unknown, we cannot extract \( \Delta \phi_{\text{ion}} \) directly from the measured oscillation. Previously, we have been able to extract the difference in \( \Delta \phi_{\text{ion}} \) corresponding to ionization from different subshells [9, 25] by using different energy regions of the same photo-electron spectrogram. Here, the active stabilization of our spectrometer allows us to record several spectrograms, in different gases, while keeping control of the optical delay of the interferometer. Since \( \tau \) and \( \Delta \phi_{\text{ion}} \) are kept constant, we are able to determine the change in \( \Delta \phi_{\text{ion}} \) between two gases (labeled 1 and 2) at the same excitation energy and thus the difference in two photon emission time delay (\( \tau^{(2)} \)):

\[
\tau^{(2)}_1 - \tau^{(2)}_2 = \frac{\Delta \phi_{\text{ion},1} - \Delta \phi_{\text{ion},2}}{2 \omega}.
\]

Figure 2(b)–(d) schematically shows the involved (uncorrelated) ionization paths from the ground state to the different final states of the ion and an outgoing electron, which are coupled to the total angular momentum \( ^1S_e \) or \( ^1D_e \). The final states are np\(^2\)P, where \( n = 3 \) in Ar, and \( n = 2 \) in Ne, (b)–(c) or 2s\(^2\)S in He (d). At large distances from the ion the different angular momentum channels for the photoelectron can be unambiguously defined since the coupling between them goes to zero when \( r \to \infty \). For shorter distances the channels do couple, which is properly accounted for with the many-body methods discussed below (see [35], equations (5)–(7) for more details).

Some of the pathways interfere, [p \( \to \) d \( \to \) p and p \( \to \) s \( \to \) p (m = 0)] since two angular momentum paths reach the same final state. In contrast, final \( f \) states can only be reached by a single angular momentum path [p \( \to \) d \( \to \) f (m = 0, \( \pm 1 \))] and consequently no interference is expected. The different final states are added incoherently in an angle-integrated experiment, which is the case in the present work.

The influence of the different channels on the SB oscillation will be analyzed in section 3. In all the measurements presented in this work, (see figure 1(b)), the SB oscillations exhibit a good contrast, of the order of 90%, allowing us to easily extract the phase by Fourier transform.

2.3. Interferometer stabilization and measurement procedure

In order to stabilize the Mach-Zehnder interferometer (see figure 1(a)), we split off a small fraction of the beam in each arm. Part of the pump beam is picked off after the generation cell. The fraction of the probe beam used for stabilization is transmitted through the recombination mirror. The two beams are overlapped on a camera chip at a small angle leading to an interference fringe pattern. The fringe position, which depends on the relative delay between the pump and probe pulses, is used as the error signal for the stabilization and is fed back to the controller of the piezolectric delay stage in the probe arm. The active stabilization allows us to keep the delay fluctuations to below 50 as over 5 min. A slow, thermally-induced drift of approximately 1 fs per hour, remains. It can be minimized by keeping both pump and probe pulse energies constant during long periods of time, and by stabilizing the pressure in the generating gas cell [36]. Stabilization schemes, which do not show this thermal drift have been used by other groups [37–39]. These techniques, however, require the use of an additional, co-propagating laser beam.

Figure 3 shows consecutive measurements of the phase of SB22 in argon and in neon. Rather than plotting phases along the vertical axis, we show delays, i.e. phase (or phase difference) divided by the period of the process, \( \pi / \omega = 1.3 \text{ fs} \). Each scan, resulting in a point on the graph, takes about five minutes, so that the total measurement time is about 1 h. The statistical error on the delay determination for each scan is estimated to be approximately 25 as. The drift can be measured by repeating the scans, alternating between the two gases. It is found to be approximately linear with time, which allows us to determine the difference in delay by taking the difference between the experimental measurement in one gas (Ar) with the line fitted to the measurements in the other gas at the same time, as shown in the inset. The error bars were estimated by taking the standard deviation of the statistical series (with a 68% confidence interval). They include Poisson
3. Theory

3.1. Background

In the single active electron approximation, the matrix element describing ionization by absorption of two photons is

\[
M^{(2,0)}(k) = -iE_\omega E_{\Omega} \lim_{\epsilon \to 0} \sum_\nu \int \frac{k|d\psi|\psi(dl)}{\epsilon + \epsilon_\nu + i\epsilon}.
\]  

(3)

Atomic units are used throughout. We use, for simplicity, notations corresponding to a single active electron approximation, though our approach, as explained in more details below, includes channel coupling and correlation effects [35]. We choose the quantization axis to be the (common) polarization vector of the two fields. The complex amplitudes of the laser and the harmonic fields are denoted by \(E_\omega\) and \(E_{\Omega}\), with photon energies \(\omega\) and \(\Omega\), respectively (in the case of two-photon ionization, we assume absorption of one IR photon). The dipole operator is represented by \(d\) (\(= z\) for laser polarization along the z-axis). The initial state is denoted \((i, l_i, m_i)\) and the final state \((k, L, M)\). The energies of the initial and intermediate states are \(\epsilon_i\) and \(\epsilon_{\nu}\), respectively. The sum in the expression for \(M^{(2)}\) is performed over all possible intermediate states \((\nu, \lambda, \mu)\), both discrete and continuum. We refer the reader to [26] for detailed manipulations of the two-photon matrix element.

The next step consists in separating the angular and radial parts of the wavefunctions. We obtain

\[
M^{(2,0)}_{L\ell}(k) = -iE_\omega E_{\Omega} \sum_{L=\ell=1}^{\infty} \sum_{\mu=\pm1} e^{i\eta_L(k)\ell} Y_{LM}(\hat{k})
\]

\[
\times \left( L \begin{array}{cc} 1 & \lambda \\ -M & 0 \end{array} \right) \left( \begin{array}{cc} \lambda & 1 \\ 0 & \mu \end{array} \right) \left( \begin{array}{cc} -\mu & m_i \end{array} \right) T_{\ell L}^{(2,0)}(k),
\]  

(4)

where \(\eta_L(k)\) is the scattering phase and \(Y_{LM}\) a spherical harmonic. The reduced matrix element, \(T_{\ell L}^{(2,0)}(k)\) can be written as

\[
T_{\ell L}^{(2,0)}(k) = \hat{L} \hat{\ell} Y_{LM}(\hat{k}) \left( \begin{array}{cc} 1 & \lambda \\ 0 & 0 \end{array} \right) \left( \begin{array}{cc} \lambda & 1 \\ 0 & 0 \end{array} \right) \left( R_{\ell L} | \rho_{\omega} \rangle \right),
\]  

(5)

with \(\hat{L} = \sqrt{2L + 1}\) and where \(| \rho_{\omega} \rangle\) is the so-called radial
perturbed wavefunction, defined as
\[ \rho_{\kappa\lambda}(r) = \lim_{\varepsilon \to 0^+} \sum_{\nu} |R_{\kappa\lambda}(r)|^2 \frac{1}{\varepsilon_i + \varepsilon_f - i\varepsilon}. \]  

The momentum \( \kappa \) is the on-shell momentum, which corresponds to a pole in the integrand in equation (6) and \( \lambda \) is the angular momentum of the perturbed wave function. To evaluate the phase of this quantity, as explained in more detail in [26], we approximate \( R_{\kappa\lambda}(r) \) and \( \rho_{\kappa\lambda}(r) \) by their asymptotic values and evaluate analytically the integral \( \langle R_{\kappa\lambda}|\rho_{\kappa\lambda} \rangle \) in equation (5). We obtain
\[ \text{arg}\left[T^{(c,c)}_{\kappa\lambda}(k)\right] \approx (L - \lambda) \frac{\pi}{2} + \eta_{\kappa}(\kappa) - \eta_{\lambda}(\lambda) + \phi_{cc}(k, \kappa). \]  

The matrix element in the case of the emission of the IR photon \( M^{(c,c)}(k) \) has a similar expression. The perturbed wave function now lies above the final state. The difference of phase which is measured in the experiment does not depend on \( \eta_{\lambda}(\lambda) \) which cancels out, and is given by
\[ \Delta \phi_{\text{ion}} = \eta_{\lambda}(\kappa_+ \lambda - \kappa_- \lambda) + \phi_{cc}(k, \kappa_+) - \phi_{cc}(k, \kappa_-). \]  

Figure 5. (a) Cross section (blue) and phase (red) of different ionization channels in Ar, Ne, He; (a), (b) 3p \( \rightarrow \) e\( ^d \) (cross section: solid line, phase: dashed–dotted, line); 3p \( \rightarrow \) e\( ^s \) (cross section: dashed line, phase: dotted line); (a) RPAE; (b) MCHF; (c) Ne, RPAE, 2p \( \rightarrow \) e\( ^d \) (cross section: solid line, phase: dashed–dotted line); 2p \( \rightarrow \) e\( ^s \) (cross section: dashed line, phase: dotted line); (d) He, RPAE: 1s \( \rightarrow \) e\( ^p \) (cross section: solid line, phase: dashed line).
\[ \tau^{(2)}(k) = \frac{\Delta \theta_{\text{fin}}}{2\omega} = \varepsilon^{(1)}(k) + \tau_{cc}(k), \quad (9) \]

where

\[ \varepsilon^{(1)}(k) = \frac{\eta_\omega(k, \omega) - \eta_\omega(k, \omega^*)}{2\omega} = \frac{\Delta \eta_\omega(k, \omega)}{2\omega}, \quad (10) \]

is a finite difference approximation to the Wigner time delay \( d\eta_\omega/df \) \[13\] and thus reflects the properties of the electronic wave packet ionized by one-photon absorption into the angular channel \( \lambda \). \( \tau^{(2)} \) also includes a contribution from the IR field which is independent of the angular momentum

\[ \tau_{cc}(k) = \frac{\phi_{cc}(k, \omega) - \phi_{cc}(k, \omega^*)}{2\omega}. \quad (11) \]

### 3.2. One-photon ionization phases and cross sections

The phase and amplitude of the photoionization transition matrix element can be determined using the RPAE (for details of the theory, see \[30\]). The dipole matrices in equation (3) are replaced by screened dipole interactions which include the dynamical correlations among all electrons in the two outermost occupied atomic orbitals. The atomic orbitals are calculated using the Hartree–Fock method. Figure 5 shows the calculated phases and cross sections for all the channels involved in the photoionization of argon (a), neon (c) and helium (d) between 20 and 40 eV (25 and 40 for Ne and He) \[30\]. An important feature is that, the channels going from the ground state to excited d states in Ne and Ar are the dominant channels in the region investigated experimentally as predicted by the Fano propensity rule \[40\]. This is not the case in argon at high energy (48 eV) due to the presence of a Cooper minimum \[41\].

In figure 5(b), we present a different calculation in Ar using a MCHF approach \[28\] convoluted in energy by the width of the XUV field (0.1 eV). The average behavior of both phases and amplitudes is quite similar to those obtained with RPAE. MCHF also accounts for the influence of doubly excited states, which leads to multiple resonance structures, superposed on a smooth background.

### 3.3. Influence of multiple channels

The photoionization phases and cross sections presented in figure 5 strongly depend on the final angular momentum. In this subsection, we examine how different angular momenta both in the intermediate and final steps of the two-photon ionization process (figure 2) contribute to the SB oscillation and how it is possible to deduce experimental photoionization time delays from the measurements. Including both quantum paths (with absorption and emission of the IR photon), the total signal is equal to

\[ I = \sum_{LM} M_{LM}^2 + M_{LM}^{2\pi}. \quad (12) \]

We consider first the case of two channels with the same intermediate step like in He (see figure 2(d)). The total signal is:

\[ I \approx \left| M_{20}^{\omega} + M_{20}^{\omega*} \right|^2 + \left| M_{00}^{\omega} + M_{00}^{\omega*} \right|^2. \quad (13) \]

The interferometric traces corresponding to different final states oscillate in phase, since the phase of these oscillations does not depend on the final state. They can be added incoherently without any blurring of the SB oscillations and the measured phase difference corrected by the influence of the IR field can be interpreted unambiguously as the \( s \rightarrow p \) ionization delay.

In the case of Ar and Ne, however, the situation is more complex. The total signal is

\[ I = 2 \left| M_{20}^{\omega} + M_{20}^{\omega*} \right|^2 + 2 \left| M_{11}^{\omega} + M_{11}^{\omega*} \right|^2 + \left| M_{00}^{\omega} + M_{00}^{\omega*} \right|^2. \quad (14) \]

The first three terms oscillate in phase, because the intermediate state is uniquely a d-wave. The fourth term contains contributions from both intermediate s and d-waves and requires extra attention. The channels \( p \rightarrow s \rightarrow p \) and \( p \rightarrow d \rightarrow p \ (m = 0) \) interfere coherently. The measurement of the ionization delay corresponding to the channel \( p \rightarrow d \) requires that the \( p \rightarrow s \) channel is weak, or alternatively that its phase variation remains close to that of the \( p \rightarrow d \) channel.

To estimate the influence of multiple channels, we calculate the phase corresponding to the interfering \( p \rightarrow d \) and \( p \rightarrow s \) channels in Ar. The coherent addition of two interfering channels with amplitudes \( A_{pdp} \) and \( A_{pdp} \) can be written as

\[ e^{i\eta_{\text{fin}} A_{\text{int}}} = e^{i\eta_{pdp}} + e^{i\eta_{pdp}}. \quad (15) \]

Assuming that IR absorption (or emission) contributes with the same amplitude, and accounting for the angular coefficients for the different steps, we have \( A_{pdp}/A_{pdp} \approx -\sqrt{8\eta_{s2}/25\eta_0} \) where \( \eta_{s2} \) and \( \eta_0 \) are the differential photo-absorption cross sections with final angular momentum 0, 2 respectively. The resulting phase is given by the following equation

\[ \eta_{\text{int}} \approx \eta_2 + \arctan \frac{\sin(\eta_0 - \eta_2)}{\cos(\eta_0 - \eta_2) - \sqrt{8\eta_0/25\eta_0}}. \quad (16) \]

Figure 6(a) compares the derivatives of \( \eta_2, \eta_0 \) and \( \eta_{\text{int}} \). To mimic the experiment, we represent finite approximations to these derivatives, \( \eta^{(1)} \). The ‘interference’ delay, \( \tau^{(1)}_{\text{int}} \), deviates slightly from that of the \( p \rightarrow d \) channel especially toward high photon energy, due to the increasing \( p \rightarrow s \) cross section.

We also examine the influence of the incoherent channels on our interferometric measurement. The total interferometric
signal (equation 14) can be expressed as

\[
I = I_0 + I_2 \cos \left[ 2\omega (\tau - \tau_{1(1)} - \tau_{cc}) \right] + I_{\text{int}} \cos \left[ 2\omega (\tau - \tau_{\text{int}} - \tau_{cc}) \right] = I_0 + I_{\text{tot}} \cos \left[ 2\omega (\tau - \tau_{\text{tot}} - \tau_{cc}) \right],
\]

where \(I_0\), \(I_2\), \(I_{\text{int}}\) and \(I_{\text{tot}}\) are intensities and where the total signal oscillates with a phase equal to \(2\omega (\tau_{\text{tot}} + \tau_{cc})\), where \(\tau_{\text{tot}} = \tau_{2(1)}\),

\[
= \frac{1}{2\omega} \arctan \frac{I_{\text{int}} \sin \left[ 2\omega (\tau_{2(1)} - \tau_{\text{int}}) \right]}{I_2 + I_{\text{int}} \cos \left[ 2\omega (\tau_{2(1)} - \tau_{\text{int}}) \right]}. \tag{18}
\]

The results presented in figure 6(a) show that \(\tau_{\text{tot}}(1)\) is very close to \(\tau_{2(1)}\) so that, in these conditions, the p \(\rightarrow\) d channel has little influence on the measured delay. Vice versa, the delay that we measure in our experiment (corrected for the influence of the IR field) can be interpreted as the group delay of the p \(\rightarrow\) d ionizing wave packet, with a small offset of the order of 10 as [26]. This conclusion might change in other situations where two interfering channels have comparable amplitudes.

3.4. Influence of the atomic structure

In figure 6(b), we present a different calculation in Ar using a MCHF approach [28], including, as above, all of the channels. This approach accounts for the influence of doubly excited states as well as 3s-excitation channels, which lead to multiple resonance structures. The MCHF photoionization delay looks quite noisy. This is due to the influence of the resonances on the phase (see figure 5(b)) in combination with the finite approximation of the phase derivative. The energy of the structures can be calculated only within an accuracy of \(\approx 0.5\) eV. This affects the determination of the time delays, leading to a possible error when comparing to the experiment, of the order of the observed structures (at most \(\pm 20\) as).
Finally, we present in figure 6 one-photon delays in Ne (c) and He (d) calculated using RPAE. These delays are quite similar, since in this region, correlation effects are weak. The calculated delay mostly reflects the variation of the Coulomb phase in this energy region [26], as also shown by comparing to the one-photon delays for a Coulomb potential (red). In contrast, the difference obtained in Ar emphasizes the sensitivity of the delay to the atomic structure in general.

3.5. Two-photon ionization delays

The two-photon ionization delay can be approximated by adding the one photon delay and the continuum–continuum delay according to equation (8). Figure 7(a) shows the $\tau_{cc}$ delay for the three gases investigated (Ar, Ne, He) as a function of the harmonic order. The difference between atoms is simply due to the difference in kinetic energy of the outgoing electron.

4. Comparison with experiment

In figure 8, we compare theoretical (RPAE + CC, two-photon RPAE) and experimental results for the delay differences. We also present calculations where $\tau_{Ar}$ is calculated with the MCHF approach (+CC) and $\tau_{Ne}$ or $\tau_{He}$ with RPAE + CC. The agreement is excellent for the differences in delay between Ne and He, which can be accurately calculated, since the influence of correlation is small. There is a larger difference between theory and experiment in the case of Ar.

The imprecision in determination of the energy of each resonance in the MCHF method implies that a better representation of the MCHF results would be a smooth curve averaging over the resonances combined with a ‘theoretical’ error bar of ±20 as. This average curve (which the reader can visualize by eye) increases from 31 to 35.5 eV and then decreases until 37 eV. It fits the experimental observation better for both SBS 22 and 24 than RPAE (figures 8(a) and (b)). This might indicate that the theoretical description of the Ar delays requires the inclusion of double excitations in this energy range.

We summarize our experimental and theoretical results in table 2.

![Figure 7](image_url)

**Figure 7.** (a) $\tau_{cc}$ delay in Ar (solid line), Ne (dashed line), He (dotted line); (b) two-photon ionization delays: $\tau_{Ar}$ (RPAE + CC, blue, solid line; two-photon RPAE black squares; MCHF, magenta); $\tau_{Ne}$ (RPAE + CC, blue, dashed line; two-photon RPAE, empty circles) and $\tau_{He}$ (RPAE + CC, blue, dotted line; two-photon RPAE, full circles).

| Atom | Sideband | 20 | 22 | 24 |
|------|----------|----|----|----|
| Photon energy (eV) | 31 | 34.1 | 37.2 |
| Ar | $\tau_{cc}$ | -47 | -38 | -31.6 |
| | RPAE + CC | 8.9 | 12.6 | -0.2 |
| | RPAE 2 photons | 7.9 | 10.3 | 7.3 |
| | MCHF + CC | 8.9 | 7.5 | 11 |
| Ne | $\tau_{cc}$ | -82 | -59 | -45.5 |
| | RPAE + CC | -37.9 | -29.9 | -23.8 |
| | RPAE 2 photons | -51.7 | -40.7 | -33.2 |
| He | $\tau_{cc}$ | -120 | -77.1 | -56.3 |
| | RPAE + CC | -62.5 | -47.4 | -38 |
| | RPAE 2 photons | -64 | -49.1 | -37.8 |
5. Conclusion and outlook

In conclusion, the new experimental scheme presented here allows an accurate measurement of the photo-emission time delay between different atomic systems, providing more data to test the different theoretical approaches. The small discrepancy between experiment and theoretical calculations indicates that both more accurate measurements and calculations should be performed in particular in the case of argon. This technique can potentially allow the measurement of the delays in molecules, relative to those in a reference atom. Our results highlight the importance of including doubly excited states as well as all angular channels in the theoretical calculations. Using an angularly-resolved detection technique, such as a velocity map imaging spectrometer, would help disentangle the different channels.

Table 2. Time delay measurements and calculations. All delays given in as.

| Sideband        | 20   | 22   | 24   |
|-----------------|------|------|------|
| Photon energy (eV) | 31   | 34.1 | 37.2 |
| $\tau_{\text{Ar}} - \tau_{\text{Ne}}$ | $68 \pm 15$ | $70 \pm 12$ | $52 \pm 25$ |
| RPAE + CC       | 46   | 38   | 24   |
| RPAE 2 photons  | 59.6 | 51   | 40   |
| MCHF(Ar)-RPAE(Ne) + CC | 46   | 42   | 34   |
| $\tau_{\text{Ar}} - \tau_{\text{He}}$ | $82 \pm 15$ | $83 \pm 22$ | $71 \pm 21$ |
| RPAE + CC       | 71   | 55   | 38   |
| RPAE 2 photons  | 71.9 | 59.4 | 45.1 |
| MCHF(Ar)-RPAE(He) + CC | 71   | 60   | 49   |
| $\tau_{\text{Ne}} - \tau_{\text{He}}$ | $23 \pm 4$ | $12 \pm 4$ | $10 \pm 8$ |
| RPAE + CC       | 23   | 15   | 14   |
| RPAE 2 photons  | 12.3 | 8.4  | 4.6  |

Figure 8. Comparison between experiment and theory. (a) $\tau_{\text{Ar}} - \tau_{\text{Ne}}$ (b) $\tau_{\text{Ar}} - \tau_{\text{He}}$ and (c) $\tau_{\text{Ne}} - \tau_{\text{He}}$. The red crosses correspond to the experimental measurement, the blue curves to one photon RPAE + CC, the black symbols to two-photon RPAE. The magenta curve has been obtained by using MCHF + CC in Ar.
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