1. What is the major advance reported in the paper?

In this experiment, applying a twin-seeded scheme of the free electron laser FERMI, the authors launched vibronic wave packets, which were extending over several vibrational and select electronic states, of the very dilute HeNe dimer target. Exploiting XUV wave packet interferometry (XUV-WPI), the authors then investigated the vibronic beat spectrum of HeNe, which is subject to decoherence due to interatomic Coulombic decay (ICD). Interference signals are presented that in principle could reveal the ultrafast time dependence of the ICD rate. However, the respective contributions of the different vibrational and electronic states needed to disentangle the dynamics are elusive at this point in time. Moreover, the current signal-to-noise ratio and the spectrally broad XUV excitation further prevent a real-time tracking at the moment. On the other hand, the authors were able to present the Fourier analysis of the interference fringes, which revealed the excitation spectrum of the dimer with a ~7 times better resolution than the energy bandwidth of the FEL pulses and showed a sensitivity of <1‰ to the FEL center wavelength. However, the latter may be compromised by the twin-seeding scheme of the FEL, and, hence, it remains unclear if the detected differences in the population ratios of the dimer excitation spectrum are meaningful. So in essence the presented spectra of these challenging experiments on the ICD dynamics of HeNe are rather ambiguous at the moment.

2. What is the immediate significance of this advance?

The XUV-WPI method seeks to provide high spectral and temporal resolution of ultrafast dynamical processes at the same time, something conventional XUV-pump NIR-probe spectroscopy usually struggles with. However, this deficiency has been recently overcome in the work of A. Plunkett et al., Phys. Rev. Lett. 128, 083001(2022), which separated the temporal probing and energy measurements steps via a precisely delayed Raman interference “detour”, which redistributed the wavepacket for high energy resolution detection in the final step (either proceeding via an autoionization process or another narrow bandwidth laser pulse); femtosecond time and micro-eV energy resolution is achievable.

Like previous work of the group (refs. [10, 11] in the draft), the results show, in principle, that time and energy resolutions better than the temporal and spectral bandwidths of the FEL can be achieved with
XUV-WPI. However, the complex experimental interferometric scheme is demanding and restricted to seeded FELs only, as high phase stability is a prerequisite. The here presented work reflects a step from atomic to (dilute) dimer targets, showcasing that investigations of chemical dynamics are in reach. However, given the emphasis on technique and the rather equivocal scientific results, this work appears to be an incremental advancement, which is more interesting for the specialized reader. Unless I am overlooking an important aspect, I can’t identify new insights and/or conceptual breakthroughs that would be of broad appeal to the general readership of Phys. Chem. Letters. As such I would think this draft is more suitable for journals like New J. of Phys., J. Phys. B At. Mol. Opt., Phys. Rev. A, or Phys. Rev. R.

3. Technical suggestions

The draft is very well written; the clear, honest, and modest style putting the measured results in perspective is much appreciated. I recommend to reference the work of A. Plunkett et al., Phys. Rev. Lett. 128, 083001(2022) in order to acknowledge the recent advancement in XUV-pump NIR-probe spectroscopy and compare the XUV-WPI method to it.

Reviewer: 2

Comments to the Author

The authors present an advancement in wavepacket interferometry by extending this technique into the XUV regime to study resonant ICD in the HeNe dimer in the time domain. They achieve the high phase stability necessary at shorter wavelengths by implementing a shot-to-shot cycling scheme with heterodyne lock-in detection. In addition to femtosecond temporal resolution, the authors show that a high resolution frequency domain spectrum can be retrieved from Fourier analysis of the interference fringes. The chosen system studied is an example in which conventional pump-probe measurements are unable to track the dynamics in real time, thus demonstrating the need for XUV-WPI.

Current limitations to the technique arise from the FEL light source, which can introduce a shift in energy between the two XUV pulses. While the resultant data leads to high resolution spectra in the frequency domain, theoretical modeling of the system is required to analyze the decay behavior in the time domain.

This manuscript outlines the experimental challenges and how they were overcome, where applicable. It would be interesting to see the ICD decay extracted from the time domain data for a full proof of concept, however the full theoretical modeling of the system seems beyond the scope of this letter.

Reviewer: 3
Comments to the Author

Uhl et al. carried out phase-locked double-pulse excitation experiments of the HeNe dimer in the XUV region using XFEL. They successfully observed interferences of the two XUV pulses by monitoring HeNe+ ion generated by inter-atomic Coulombic decay (ICD) of the He*Ne excited state that is directly photoexcited.

It is impressive that they realized phase-locked double-pulse excitation in the XUV region, which requires special techniques that are not necessary for the optical regions. In this sense, this paper reports a nice demonstrative experiment, and I think it is publishable in JPC Letter in principle. However, the authors need to make proper revisions for the following several points before the publication:

1. I found several overstatements in this manuscript. First, The phase-locked double-pulse excitation is now a standard technique in the optical region, and it has been established that the double-pulse excitation is essentially equivalent to the single narrow-band excitation with frequency scanning. In other words, the experiments they report in this paper are action (absorption) spectra monitoring HeNe+ ion. The authors should make this point clear. Second, the authors discuss their experiments in relation to the classic experiment on the NaI photodissociation. However, these two experiments are essentially different. In the NaI experiment, the excited-state wavepacket is initiated by a single ultrashort pulse, and the wavepacket motion disappears as the bound excited-state NaI molecule is dissociated at the crossing point between the bound and dissociative potentials. In contrast, the authors’ experiments, they observe the interference of the two wavepackets that are launched with the first and second excitations. The connection to the ICD process is not clear in this case.

2. The importance of this paper, in my opinion, is the impressive technical demonstration in the XUV region. Therefore, I think that author should provide more descriptions of the experimental techniques and apparatus by adding sufficient descriptions (probably also a figure) in the main text and/or Supporting Information.

Author’s Response to Peer Review Comments:
Response to reviewer comments

Journal: The Journal of Physical Chemistry Letters
Manuscript ID: jz-2022-016196
Title: "Extreme Ultraviolet Wave Packet Interferometry of the Autoionizing HeNe Dimer"
Authors: Uhl et al.

We thank all reviewers for their time and efforts in critically evaluating our manuscript and their helpful advice for improvements.

The response to the reviewer comments are given below. Changes in the manuscript are marked in blue in the supplied manuscript file.

Reviewer #1 (Remarks to the Author):
Recommendation: While the work is good and publishable, a more appropriate journal is recommended such as New J. of Phys., J. Phys. B, Phys. Rev. A, Phys. Rev. R

Comments:
1. What is the major advance reported in the paper?

In this experiment, applying a twin-seeded scheme of the free electron laser FERMI, the authors launched vibronic wave packets, which were extending over several vibrational and select electronic states, of the very dilute HeNe dimer target. Exploiting XUV wave packet interferometry (XUV-WPI), the authors then investigated the vibronic beat spectrum of HeNe, which is subject to decoherence due to interatomic Coulombic decay (ICD). Interference signals are presented that in principle could reveal the ultrafast time dependence of the ICD rate. However, the respective contributions of the different vibrational and electronic states needed to disentangle the dynamics are elusive at this point in time. Moreover, the current signal-to-noise ratio and the spectrally broad XUV excitation further prevent a real-time tracking at the moment. On the other hand, the authors were able to present the Fourier analysis of the interference fringes, which revealed the excitation spectrum of the dimer with a ~7 times better resolution than the energy bandwidth of the FEL pulses and showed a sensitivity of <1‰ to the FEL center wavelength. However, the latter may be compromised by the twin-seeding scheme of the FEL, and, hence, it remains unclear if the detected differences in the population ratios of the dimer excitation spectrum are meaningful. So in essence the presented spectra of these challenging experiments on the ICD dynamics of HeNe are rather ambiguous at the moment.

We appreciate the acknowledgement of the experimental achievements in our work. For further discussion please see our response to comment #2.

2. What is the immediate significance of this advance?

The XUV-WPI method seeks to provide high spectral and temporal resolution of ultrafast dynamical processes at the same time, something conventional XUV-pump NIR-probe spectroscopy usually struggles with. However, this deficiency has been recently overcome in the work of A. Plunkett et al., Phys. Rev. Lett. 128, 083001(2022), which separated the temporal probing and energy measurements steps via a precisely delayed Raman interference “detour”, which redistributed the wavepacket for high energy resolution detection in the final step (either proceeding via an autoionization process or another narrow bandwidth laser pulse); femtosecond time and micro-eV energy resolution is achievable.
Like previous work of the group (refs. [10, 11] in the draft), the results show, in principle, that time and energy resolutions better than the temporal and spectral bandwidths of the FEL can be achieved with XUV-WPI. However, the complex experimental interferometric scheme is demanding and restricted to seeded FELs only, as high phase stability is a prerequisite. The here presented work reflects a step from atomic to (dilute) dimer targets, showcasing that investigations of chemical dynamics are in reach. However, given the emphasis on technique and the rather equivocal scientific results, this work appears to be an incremental advancement, which is more interesting for the specialized reader. Unless I am overlooking an important aspect, I can’t identify new insights and/or conceptual breakthroughs that would be of broad appeal to the general readership of Phys. Chem. Letters. As such I would think this draft is more suitable for journals like New J. of Phys., J. Phys. B At. Mol. Opt., Phys. Rev. A, or Phys. Rev. R.

We disagree with the reviewer’s assessment of our work. Our work is based on all-XUV interferometry of which so far only very few experimental demonstrations exist. The reviewer compares our work to XUV-IR interferometry, which is experimentally much easier to implement due to the orders of magnitude lower demand on phase stability and the circumvention of optical XUV interferometers. As such, indeed many XUV-IR interferometry examples are reported in the literature, e.g. RABBITT and the recent XUV-IR Raman interferometry pointed out by the reviewer (A. Plunkett et al., Phys. Rev. Lett. 128, 083001(2022)). These schemes exploit the interference between phase-related XUV and IR pulses to increase the attainable resolution. However, as a major disadvantage XUV-IR interferometry provides only relative frequency information among the excited states, which leads to ambiguities. The ambiguity can be lifted by correlation to the electron kinetic energy (eKE) spectrum, as nicely demonstrated by Plunkett et al.. While this was demonstrated for atoms, the scheme will be much more challenging for molecular systems due to the large number of cationic states leading to congested eKE distributions even if narrowband probe lasers are used. This is a general, well-known issue in molecular photoelectron spectroscopy. Similar problems arise in the study of solid state systems. In contrast, our all-XUV interferometry approach determines the absolute frequency spectrum directly referenced to the cold molecular ground state, which hence solves an important problem in the study of complex systems such as molecules. This key feature of our method is not available in XUV-IR interferometry methods.

In this view, it is important to demonstrate the transfer of all-XUV interferometry from simple atomic systems to more complex target systems and target processes. Like in XUV-IR interferometry, this transfer is neither trivial in all-XUV interferometry as many more degrees of freedom become involved. As such, our work, extending for the first time XUV-WPI to molecular beam samples, which are for the studied system orders of magnitude less dense when compared to atomic beams, and extending to ultrafast ICD processes, represents a significant and important extension. Even though at the current state further experimental improvements are necessary to fully exploit the potential of the method, the demonstrated extension clearly shows a significant step forward and opens up many new perspectives in ultrafast XUV experiments. Therefore, our work requires immediate communication among the broad AMO and physical chemistry community, which is also suggested by reviewer #2 and #3.

To make these points clearer to the reader, we have modified para 2 of the introduction (p.2):

“In contrast, molecular systems are much more complex, in particular when high-lying states in the XUV absorption region are studied, featuring typically a high density of electronic, vibrational and rotational neutral and intermixing cationic states. In these systems, all-XUV interferometry could so far only access the beat spectra between different excited states 21,22 which provides only relative
spectral information and thus can lead to ambiguities in the spectral assignments. The same issue applies to XUV-NIR interferometry, which is more frequently performed due to the lower demands on phase stability and the circumvention of XUV beamline interferometers. In a recent demonstration, XUV-IR Raman interferometry was combined with photoelectron spectroscopy (PES) which lifted the degeneracy in the beat spectra with high resolution. A related coherent multidimensional PES scheme has been demonstrated in the visible spectral domain. Yet, so far these schemes were only demonstrated for atomic targets. They will be much more difficult to implement for more advanced systems, e.g. molecules, where the large number of cationic states usually causes a congestion of the photoelectron spectra. In contrast, all-XUV interferometry with sufficient phase stability and sensitivity to directly track the beatings between the system’s excited and the initial ground state solves these issues. Here, absolute frequency information correlated to the ground state is gained without the need of advanced electron detectors or knowledge of the system’s cationic states.”

We would like to add, that against the reviewer’s opinion our method is not restricted to seeded FELs. We have recently demonstrated the method’s feasibility also for tabletop high harmonic generation which opens a great perspective for many more applications and addresses a much larger community. This further broadens the impact of our work.

We have added the following statement to the conclusions section of our manuscript (p. 14) to make this clearer:

“The experimental scheme is not restricted to seeded FELs and can also be applied in tabletop high-order harmonic generation (HHG), where spectral bandwidths are much larger and interferometric schemes will be even more beneficial. The current study extending XUV-WPI to molecular targets and ultrafast dynamics demonstrates thus a promising step in several directions of all-XUV interferometry.”

3. Technical suggestions

The draft is very well written; the clear, honest, and modest style putting the measured results in perspective is much appreciated. I recommend to reference the work of A. Plunkett et al., Phys. Rev. Lett. 128, 083001(2022) in order to acknowledge the recent advancement in XUV-pump NIR-probe spectroscopy and compare the XUV-WPI method to it.

We thank the reviewer for this appreciation and thank her/him for pointing out the recent XUV-IR Raman interferometry experiment. We have added the reference according to the reviewer’s suggestion (p. 4, para. 2):

“In a recent demonstration, XUV-IR Raman interferometry was combined with photoelectron spectroscopy (PES) which lifted the degeneracy in the beat spectra with high resolution.”

Additional Questions:

Urgency: Moderate
Significance: Moderate
Novelty: Moderate
Scholarly Presentation: High

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors’ area of research?: No
Reviewer: 2

Recommendation: This paper represents a significant new contribution and should be published as is.

Comments:

The authors present an advancement in wavepacket interferometry by extending this technique into the XUV regime to study resonant ICD in the HeNe dimer in the time domain. They achieve the high phase stability necessary at shorter wavelengths by implementing a shot-to-shot cycling scheme with heterodyne lock-in detection. In addition to femtosecond temporal resolution, the authors show that a high resolution frequency domain spectrum can be retrieved from Fourier analysis of the interference fringes. The chosen system studied is an example in which conventional pump-probe measurements are unable to track the dynamics in real time, thus demonstrating the need for XUV-WPI.

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This manuscript outlines the experimental challenges and how they were overcome, where applicable. It would be interesting to see the ICD decay extracted from the time domain data for a full proof of concept, however the full theoretical modeling of the system seems beyond the scope of this letter.

We thank the reviewer for the positive evaluation of our manuscript and recommendation for publication.

Additional Questions:

Urgency: Moderate
Significance: High
Novelty: High
Scholarly Presentation: High

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors' area of research?: Yes

Reviewer: 3

Recommendation: This paper is probably publishable, but major revision is needed; I do not need to see future revisions.

Comments:

Uhl et al. carried out phase-locked double-pulse excitation experiments of the HeNe dimer in the XUV region using XFEL. They successfully observed interferences of the two XUV pulses by monitoring HeNe+ ion generated by inter-atomic Coulombic decay (IDC) of the He*Ne excited state that is directly photoexcited.

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reports a nice demonstrative experiment, and I think it is publishable in JPC Letter in principle. However, the authors need to make proper revisions for the following several points before the publication:

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In general, we agree with the reviewer, that a two-pulse WPI experiment provides the same information as an action-detected narrow-band excitation experiment. An additional probe pulse would be needed in the WPI experiment to clock the relaxation dynamics in the system. However, in the current study, the ICD process serves as the probing step to clock the relaxation dynamics. Hence, real-time information about relaxation dynamics are encoded in the data as well. To make this clearer, we have added the following statements to the manuscript:

P. 6-7: “We note, that this information can be also gained with a frequency-domain absorption experiment 29. Yet, the time-domain WPI approach allows adding a separated probe process to clock the system’s dynamics correlated to the spectrally-resolved excitations, thus offering high spectro-temporal resolution. The deferred probe process is usually performed with a third laser pulse photoionizing the system. In the current study, the ICD process instead serves as the probe step, leading to the ionization of the system.”

P. 11, para. 2: „Distinguishing different decay mechanisms based on the absorption line profiles is often difficult and direct time-domain approaches are favorable in this case. Yet, so far, only few time-resolved experiments have been dedicated to the non-exponential decay behavior of ICD, where the dynamics were indirectly deduced in frequency-domain coincidence experiments 40,41, however, not directly with femtosecond spectroscopy in the time domain.”

We agree with the reviewer, that the comparison with the NaI dissociation measurement may lead to confusion. We have therefore removed this statement from the manuscript.

2.

The importance of this paper, in my opinion, is the impressive technical demonstration in the XUV region. Therefore, I think that author should provide more descriptions of the experimental techniques and apparatus by adding sufficient descriptions (probably also a figure) in the main text and/or Supporting Information.

We have added the following details about the experimental technique in the manuscript and we have extended Fig. 3 with more details about the experimental method.

P.8, para. 2: “This approach enabled the generation of two XUV pulses with the phase properties controlled by those of the seed. Special attention was given to the preparation of the electron beam
phase space driving the FEL amplification process. The energy-phase modulations in the beam were minimized, obtaining a region of few hundred of fs to accommodate the double pulses modulating the electron density and driving the amplification.“

P. 9, figure caption: “Phase-cycled seed laser pulses are generated in a Mach-Zehnder interferometer comprising an acousto-optical modulator (AOM1, AOM2) in each interferometer arm to control the relative phase between the pulses and a delay stage to control the inter-pulse delay $\tau$. The UV seed pulses drive the high-gain harmonic-generation (HGHG) in the FEL leading to phase-cycled XUV pulses. The iTOF signal is gated with a boxcar integrator and amplified with a lock-in amplifier.”

Additional Questions:

Urgency: High
Significance: High
Novelty: High
Scholarly Presentation: Moderate

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors’ area of research?: Yes

Other changes made in the manuscript:

- We removed the section headers, added a TOC graphic, changed the bibliography style.
- We have updated the funding information in the funding section