nature portfolio

Peer Review File

Super-resolution femtosecond electron diffraction reveals electronic and nuclear dynamics at conical intersections

Corresponding Author: Professor Dao Xiang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript presents a study that applies mega-electron-volt ultrafast electron diffraction (MeV-UED) to resolve femtosecond-scale nuclear and electronic dynamics in the prototypical photochemical system, 1,3-cyclohexadiene (CHD). By achieving an instrument response functon(IRF) of approximately 80 femtoseconds, the authors successfully visualize nuclear motions associated with conical intersection (CI) traversal with real-space resolution. To date, this level of temporal resolution represents the highest reported for time-resolved MeV-UED experiments on gas-phase molecular systems, showcasing state-of-the-art instrumentation and beamline engineering.
It is important to note that this manuscript appears to be based on a prior version submitted to Nature under the title "Femtosecond atomic-scale visualization of molecular quantum dynamics." Although the current submission carries a new title and includes some textual refinements, the core experimental data, figures, and interpretive framework—particularly regarding Δs-PDF analysis—remain substantially unchanged.
While the manuscript is generally well-structured and persuasive in demonstrating methodological innovation, several issues remain unresolved or require clarification before the manuscript can be considered for publication. These are outlined below:

1. On full structural modeling and kinetic interpretation:
The current analysis focuses on the time evolution of Δs-PDF intensities at selected r-values. While this approach minimizes model dependence, the manuscript would benefit from further structural modeling or kinetic fitting that reconstructs the transient molecular geometry. Even a qualitative model consistent with both the ΔPDF and Δs-PDF data would provide more comprehensive insight into the molecular evolution during the reaction.

2. On simulation–experiment mismatch in the 1–2 Å region:
Extended Data Fig. 7 shows pronounced oscillations in the 1–2 Å region based on trajectory surface hopping simulations. However, these features are not observable in the experimental ΔPDF data. The authors should address the origin of this discrepancy and clarify whether it stems from limited time resolution, insufficient excitation fraction, or noise. This issue is particularly important, as it affects the credibility of capturing rapid CI-passage dynamics using the reported setup.

3. On the unsupported claim of Δs-PDF resolving R2 and R3:
In Supplementary Note 7, the authors write:
"In addition, the Δs-PDF successfully resolves the peak for the diagonal C–C atom pair distance (R3) at ~2.8 Å, which was indistinguishable from the second-nearest C–C atom pair distance (R2) at ~2.4 Å."
Similarly, the caption of Supplementary Fig. S8 states that the Δs-PDF clearly resolves the R3 peak and distinguishes it from R2, unlike the conventional ΔPDF.
However, this claim is not substantiated by the data presented in the manuscript. In the main-text Fig. 3a (experimental Δs-PDF), the expected positions of R1, R2, and R3 are explicitly annotated, yet there is no discernible peak or dip at the position of R3 (~2.8 Å). Instead, the signal at this location exhibits only a smooth zero-crossing. Moreover, even in the simulated Δs-PDF results shown in Fig. 3b–c, the R3 feature is not clearly resolved either—the signal near ~2.8 Å lacks the structure needed to support the claimed separation.
Therefore, both the experimental and simulated data contradict the assertion that Δs-PDF clearly resolves R2 and R3. The

statements in Supplementary Note 7 and the caption of Fig. S8 overstate the method's spatial resolution and interpretive power in this range. These inaccuracies should be explicitly corrected, and any such claims should be reformulated to accurately reflect the limitations shown in the data.
We recommend that the authors:
- Revise the relevant portions of Supplementary Note 7 and Fig. S8's caption to remove or qualify the claim that R3 is clearly resolved by Δs-PDF.
- Clarify that no direct evidence of peak resolution at ~2.8 Å is present in either experimental or simulated Δs-PDF results.
- Temper the interpretive language regarding spatial resolution enhancement, ensuring that claims are grounded in what is visually and quantitatively observable.
Overall, this point is critical because the claimed benefits of the super-resolution algorithm hinge on its ability to resolve closely spaced pair distances—yet such a case is not convincingly demonstrated.

4. On visual consistency and data representation in Fig. S8:
Unlike other figures where the gray level in the colormap corresponds to zero signal, Fig. S8 appears to use a shifted colormap where gray does not represent zero. If this adjustment was intentional, it must be clearly stated and justified. Otherwise, this inconsistency could lead to misinterpretation of the figure or raise concerns about presentation bias. For clarity and fairness, the colormap should be harmonized with the rest of the figures, particularly when ΔPDF and Δs-PDF are being visually compared.

In summary, the manuscript showcases a significant advancement in MeV-UED instrumentation and demonstrates the potential of a model-free inversion algorithm in probing ultrafast structural dynamics. However, its central interpretive claims —particularly regarding spatial resolution beyond the diffraction limit—require stronger visual and analytical support. Addressing the above concerns will substantially enhance the clarity and rigor of the manuscript, thereby strengthening its contribution to the ultrafast science community.

Reviewer #2

(Remarks to the Author)
This work presents an advance in the application of UED by combining a high temporal resolution with a super-resolution algorithm. The authors studied the ring-opening reaction of cyclohexadiene (CHD) and retrieved details on the dynamics that were not captured in a previous UED study [Wolf et al, Nature Chemistry 11, 504–509 (2019), REF 23 in this manuscript]. The authors observe an inelastic scattering signal at early times at low scattering angle, and, in combination with numerical simulations, retrieve the time delay for the wavepacket to travel from a first to a second conical intersection. The main advance of this manuscript is technical in the combination of high temporal resolution with spatial super-resolution. The authors chose a well studied system as an example, and their results confirm what is already known but do not add anything new to the story.
In terms of technical advances, the authors present results from a very impressive instrument which has the highest time resolution for gas phase UED at 80 fs (almost a factor two better than the SLAC MeV-UED instrument at 150 fs which is the competing instrument). They combined this with an algorithm capable of improving the spatial resolution of the data by approximately a factor of two from 0.6 A to 0.3 A. This combination produces very nice results as it elucidates additional information about the dynamics not captured in a previous UED study. All of these advances have been previously demonstrated and published. The double-achromat device used to produce short electron pulses was demonstrated in REF 34 [Qi et al, PRL 124, 134803 (2020).] Additionally, the same instrument was used by some of the same authors, in a previous gas phase UED study that already showed the same time resolution as this experiment, 80 fs. This is in Ma et al, PNAS 119 (15) e2122793119 (2022), REF 36. The algorithm used for super resolution was demonstrated in a previous publication and applied to UED data on CHD, the same molecule studied here REF 43 [Natan, PRA 107, 023105 (2023)]. Thus, the main advance is the combination of these two methods and highlighting the performance of the instrument.
Technical comments:
1. The super-resolution algorithm relies on a sparcity constraint, and while it has been shown to work for CHD, it may not work for larger molecules as the PDF becomes more dense with distances. Since the algorithm is an important part of this work, the authors should describe the advantages and limitations of this algorithm compared to other retrieval methods.
2. A relative yield of 32% for ring opened products was reported. The authors should provide an uncertainty for this value, and it should be compared with the results reported in previous works, and also with the results from the trajectories reported in this manuscript.
3. Figure 3 provides the delta PDF, which relies on the FT of the delta-sM. At early times, there is a signal at low s that the authors attribute to changes in the electronic structure. The transform from sM to PDF assumes that only nuclear motions contribute to the signal, thus this electronic signal will introduce artifacts. Was this signal removed before the transform? How? More details are needed about how the authors generated the delta-PDF.
4. Figure 3 should show also the delta-PDF retrieved using the super-resolution algorithm. The lineouts in Fig. 4 are not sufficient to judge whether the delta-s-PDF is really reliable. This is important because super-resolution algorithms are known to introduce artifacts, and directly comparing the two delta-PDFs, in the form shown in Figure 3a, would be helpful to notice the quality of the retrieval.
5. The presence of the positive signal at early times also brings into question the interpretation of the s-PDF at early times. For the super resolution delta-s-PDFs, the lower limit is taken as s = 1.3 A^-1. However, it seems that a significant part of the positive low s signal might extent beyond 1.3 A-1, possibly affecting the conversion to delta-PDF. I recommend the authors redo the PDF transforms starting at 2.0 A^-1 to make sure that the early dynamics are not influenced by this signal. Or better check that the results are robust to using different ranges in s.
6. The authors assign a signal in the delta-s-PDF to a specific interatomic distance (C1-C6). It is not clear why this is the only

atom-pair that could produce this signal. This interpretation could be strengthened if the authors showed that this is indeed the case in calculations by analyzing the trajectory simulations. One could imagine distortions of the ring structure that produce positive and negative signals in this region of the delta-PDF which is not necessarily a direct evidence of the ring-opening.

Reviewer #3

(Remarks to the Author)
This manuscript describes a cutting-edge ultrafast experiment, using UED to observe the ring opening of cyclohexadiene (CHD) following absorption. This is a “fruit-fly” type photochemical reaction, in that it is very well studied and understood. It is known that relaxation occurs via passage through two conical intersections. Yet passage through the conical intersections has never been directly observed. In this work, it is argued that the authors observe such passage for the first time using a combination of experimental (DBA) and data analysis (super-resolution) methods. This is a very exciting result. The experimental data appears to be of extremely high quality, with high information content and low signal to noise. The theory is done with cutting edge methods (surface hopping, CASPT2). The theory agrees very well with experiment, as presented in figure 4, making a very compelling case that the observed dynamics are precisely what is predicted by theory.

I encourage publication of this work in Nat Comm, but I do suggest that the authors clarify a few points regarding the comparison of theory to experiment before the manuscript is finalized.

1) It is a little difficult for me to understand the claim that the conical intersections themselves are directly observed. The theory agrees well with experiment, and theory suggests that the reaction occurs through conical intersections. But it is not obvious to me that one can see a clear signature of a conical intersections here (such as geometric phase). IAM does not contain any information about changes in the electronic wave functions. Would the dynamics look different, for example, if they were totally adiabatic?

2) Was the super-resolution inversion performed using Natan’s software or the author’s own implementation? Is there software widely available for this technique? For reproducibility’s sake and for comparison to future theory, it would be useful if the software were made available one way or another.

Reviewer #4

(Remarks to the Author)
The work "Super-resolution femtosecond electron diffraction reveals electronic and nuclear dynamics at conical intersections"
by Xiang et. al. describes a new way to study the photodynamics at conical intersection using femtosecond electron diffraction techniques.
Both experimental measurements and computational simulation were used to investigate the ring-opening reaction of 1,3-cyclohexadiene.
The combination of both experiment and theory makes this approach an interesting tool for the study of photodynamic processes. The manuscript is well written, still I have a few open questions/comments that should be addressed before publication.

The authors use the standard 6 electrons in 6 orbitals (6e, 6o) active space combined with a triple zeta basis set.
One issue of CAS-Methods is the issue of intruder states, which increases with basis set size and with the use of diffuse basis sets.
Did the authors encounter this issue or was the real shift of 0.5 Hartree enough to prevent this for the used triple zeta basis set?

In equation 5 the formula is given with which the diffraction signals of the simulated nuclear structures are computed.
However it is not clear to me, how the f_i(s) are computed from the simulation data.
Could the authors explain these in more detail?

The authors write that the location of the first CI is an issue, due to the absence of wave packet bifurcation. From a theoretical point of view, the wave packet should always bifurcate at a conical intersection. Could the authors elaborate how they mean this?

To estimate the quantum yield, the author compute ΔsM with the simulated results obtained at varying quantum yields.
However it is not clear to me, how the simulated results at varying quantum yields were obtained?
Could the authors describe this in more detail?

The authors write, that they use a narrow excitation energy window with a ~2 nm FWHM.
In my opinion it would help the reader if the excitation energy window would be also given in eV, as this makes it easier to estimate the energy window.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
We appreciate the authors' comprehensive response to the original review, and we acknowledge that most of the concerns raised, particularly those regarding structural modeling (Point 1), simulation–experiment mismatch (Point 2), and colorbar consistency (Point 4), have been addressed effectively and with clarity. However, regarding Point 3, we find the response concerning the claim that Δs-PDF "clearly resolves" the diagonal C–C atomic pair distance R3 (~2.8 Å) from R2 (~2.4 Å) remains only partially convincing. The authors assert that the Δs-PDF resolves these pair distances due to its sparse reconstruction capabilities and provide Fig. R1 to support this claim.
Yet, even in Fig. R1, the ΔPDF exhibits a broadened and asymmetric negative feature near ~2.5 Å. This signal alone suggests overlapping contributions that could be analyzed using signal decomposition techniques such as Gaussian fitting, as potentially arising from multiple nearby pair distances, including R3. That is, the ΔPDF appears to contain enough information to infer such structures, even without invoking sparsity-based inversion. If so, the advantage of Δs-PDF lies not in its exclusive ability to resolve these distances, but rather in offering an alternative reconstruction formalism that emphasizes automation and sparsity-based regularization.
Most importantly, we would like to emphasize the interpretive caution that must accompany any sparsity-based representation. In cases such as wavepacket delocalization or vibrationally hot molecular states, where the pair distribution is physically broadened, the Δs-PDF may approximate this spread-out distribution using multiple discrete peaks. These discrete peaks, while mathematically well-defined, do not necessarily imply the presence of multiple distinct physical structures. This may lead to an "illusion of resolution," in which the sparse reconstruction yields artificially fine structural features that may not correspond to real, distinguishable atomic arrangements.
To prevent overinterpretation, we strongly encourage the authors to clarify in the manuscript that:
1. The resolution of R3 in Δs-PDF arises from a sparsity-constrained mathematical inversion, and does not in itself prove the existence of a well-separated structural signal at that distance.
2. In situations involving broadened or delocalized wavefunctions, such as those arising from vibrational excitation or wavepacket spreading, the Δs-PDF may represent a continuous distribution using multiple discrete points, which should not be over-interpreted as indicating distinct structural populations.
3. The Δs-PDF formalism offers clear practical advantages in regularization and visualization, but its physical interpretability depends critically on the sparsity and localization of the underlying pair distributions.
We emphasize that the Δs-PDF remains a valuable approach, particularly in sparse conditions, but its advantage over standard ΔPDF-based analysis should be framed in terms of algorithmic benefits and practical implementation, rather than being interpreted as inherently offering superior spatial resolution.

Reviewer #2

(Remarks to the Author)
The authors have addressed all of my concerns, and I can now recommend the manuscript for publication.

Reviewer #3

(Remarks to the Author)
I am satisfied with the authors' response, and therefore recommend publication.

Reviewer #4

(Remarks to the Author)
The authors have addressed all comments satisfactorily and I think this manuscript can be published.

This manuscript presents a study that applies mega-electron-volt ultrafast electron diffraction (MeV-UED) to resolve femtosecond-scale nuclear and electronic dynamics in the prototypical photochemical system, 1,3-cyclohexadiene (CHD). By achieving an instrument response function (IRF) of approximately 80 femtoseconds, the authors successfully visualize nuclear motions associated with conical intersection (CI) traversal with real-space resolution. To date, this level of temporal resolution represents the highest reported for time-resolved MeV-UED experiments on gas-phase molecular systems, showcasing state-of-the-art instrumentation and beamline engineering.

It is important to note that this manuscript appears to be based on a prior version submitted to *Nature* under the title "Femtosecond atomic-scale visualization of molecular quantum dynamics." Although the current submission carries a new title and includes some textual refinements, the core experimental data, figures, and interpretive framework—particularly regarding Δs-PDF analysis—remain substantially unchanged.

While the manuscript is generally well-structured and persuasive in demonstrating methodological innovation, several issues remain unresolved or require clarification before the manuscript can be considered for publication. These are outlined below:

1. On full structural modeling and kinetic interpretation:

The current analysis focuses on the time evolution of Δs-PDF intensities at selected *r*-values. While this approach minimizes model dependence, the manuscript would benefit from further structural modeling or kinetic fitting that reconstructs the transient molecular geometry. Even a qualitative model consistent with both the ΔPDF and Δs-PDF data would provide more comprehensive insight into the molecular evolution during the reaction.

2. On simulation–experiment mismatch in the 1–2 Å region:

Extended Data Fig. 7 shows pronounced oscillations in the 1–2 Å region based on trajectory surface hopping simulations. However, these features are not observable in the experimental ΔPDF data. The authors should address the origin of this discrepancy and clarify whether it stems from limited time resolution, insufficient excitation fraction, or noise. This issue is particularly important, as it affects the credibility of capturing rapid CI-passage dynamics using the reported setup.

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In Supplementary Note 7, the authors write:

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However, this claim is not substantiated by the data presented in the manuscript. In the main-text Fig. 3a (experimental Δs-PDF), the expected positions of R_1, R_2, and R_3 are explicitly annotated, yet there is no discernible peak or dip at the position of R_3 (~2.8 Å). Instead, the signal at this location exhibits only a smooth zero-crossing. Moreover, even in the simulated

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We recommend that the authors:

- Revise the relevant portions of Supplementary Note 7 and Fig. S8's caption to remove or qualify the claim that R_3 is clearly resolved by Δs-PDF.
- Clarify that no direct evidence of peak resolution at ~2.8 Å is present in either experimental or simulated Δs-PDF results.
- Temper the interpretive language regarding spatial resolution enhancement, ensuring that claims are grounded in what is visually and quantitatively observable.

Overall, this point is critical because the claimed benefits of the super-resolution algorithm hinge on its ability to resolve closely spaced pair distances—yet such a case is not convincingly demonstrated.

4. On visual consistency and data representation in Fig. S8:

Unlike other figures where the gray level in the colormap corresponds to zero signal, Fig. S8 appears to use a shifted colormap where gray does not represent zero. If this adjustment was intentional, it must be clearly stated and justified. Otherwise, this inconsistency could lead to misinterpretation of the figure or raise concerns about presentation bias. For clarity and fairness, the colormap should be harmonized with the rest of the figures, particularly when ΔPDF and Δs-PDF are being visually compared.

In summary, the manuscript showcases a significant advancement in MeV-UED instrumentation and demonstrates the potential of a model-free inversion algorithm in probing ultrafast structural dynamics. However, its central interpretive claims—particularly regarding spatial resolution beyond the diffraction limit—require stronger visual and analytical support. Addressing the above concerns will substantially enhance the clarity and rigor of the manuscript, thereby strengthening its contribution to the ultrafast science community.

Response to Reviews for
"Super-resolution femtosecond electron diffraction reveals electronic and nuclear dynamics at conical intersections"

May 25, 2025

Report of the First Referee

This manuscript presents a study that applies mega-electron-volt ultrafast electron diffraction (MeV-UED) to resolve femtosecond-scale nuclear and electronic dynamics in the prototypical photochemical system, 1,3-cyclohexadiene (CHD). By achieving an instrument response function (IRF) of approximately 80 femtoseconds, the authors successfully visualize nuclear motions associated with conical intersection (CI) traversal with real-space resolution. To date, this level of temporal resolution represents the highest reported for time-resolved MeV-UED experiments on gas-phase molecular systems, showcasing state-of-the-art instrumentation and beamline engineering.

It is important to note that this manuscript appears to be based on a prior version submitted to Nature under the title "Femtosecond atomic-scale visualization of molecular quantum dynamics." Although the current submission carries a new title and includes some textual refinements, the core experimental data, figures, and interpretive framework—particularly regarding Δs-PDF analysis—remain substantially unchanged.

While the manuscript is generally well-structured and persuasive in demonstrating methodological innovation, several issues remain unresolved or require clarification before the manuscript can be considered for publication.

Our reply:

We thank the Referee for the thorough review and insightful comments. We are grateful for the positive assessment on the methodological advance and new findings of our work. This manuscript is indeed a revised version transferred from a prior submission to Nature following editorial office's recommendation. Given that the objective of this manuscript is to demonstrate the capability of super-resolution UED in elucidating the complex dynamics at CI utilizing a well-studied molecule, the title was revised to its current form to appeal to a specific readership. We have made changes based on the referee's suggestions to address the issues raised below.

1-On full structural modeling and kinetic interpretation:

The current analysis focuses on the time evolution of Δs-PDF intensities at selected r-values. While this approach minimizes model dependence, the manuscript would benefit from further structural modeling or kinetic fitting that reconstructs the transient molecular geometry. Even a qualitative model consistent with both the ΔPDF and Δs-PDF data would provide more comprehensive insight into the molecular evolution during the reaction.

Our reply:

We thank the Referee for the suggestion. Our motivation for using Δs-PDF is indeed to minimize model dependence in our data interpretation, as atomic pair distances are ultimately the direct observables in our gas-phase MeV-UED experiments. We are aware of structural modeling methods such as generic fitting algorithm [Yang et al., Science 368, 885-889 (2020)] or structural determination method [Yong et al., Faraday Discuss. 228, 104-122 (2021)]. These approaches are very effective for coherent nuclear motions, where the nuclear wave packet remains narrow and does not bifurcate. In such cases, a single structure corresponding to the center of the wave packet at any given time can be used to reconstruct a "molecular movie". Unfortunately, these methods do not work for the CHD case here, as the wave packet broadens within 100 fs - even before bifurcation occurs, as evidenced by the relatively broad distribution shown in Fig. 3b, c. We agree that further structural analysis could help provide a more intuitive picture. To facilitate our understanding of the structural changes at conical intersections, we have revised Fig. 3 to include the Δs-PDF of all determined *r*-values alongside the conventional ΔPDF, offering a more comprehensive view of structural evolution in real time. Also, in conjunction with the revised Extended Data Fig. 7 and the newly added Fig. S8, the evolution of the C_1-C_6 pair distance emerges as a key structural feature of the reaction (see Supplementary Note 7). The super-resolved observation of the pair distance change at conical intersections—ranging from approximately 1.95 Å (CI_1) to 2.3 Å (CI_2) near CI_2—offers direct qualitative insight into the structural dynamics of the molecule.

When it comes to kinetic interpretation, theoretical structures and simulated trajectories are used to model and fit the full dynamical evolution of the system. In this work, 193 trajectories are computed in our theoretical analysis. To minimize artificial influences, we reduce the number of fitting parameters as much as possible. Ultimately, we find that only a slight adjustment of the theoretical branching ratio was sufficient to achieve a good agreement with the experimental results, as shown in Fig. 2e, f in the main text. Thus, the set of theoretical trajectories with an adjusted branching ratio can thus be regarded as a tool for kinetic interpretation. This also reflects the high level of consistency between the experimental data and the independently performed theoretical calculations.

To better clarify these points, we revise the description in the Methods section Quantum yield and excitation ratio estimation) by adding: "The simulated results with the adjusted branching ratio can thus be regarded as a kinetic fit based on selected trajectories, providing a useful framework for analyzing the ring-opening dynamics."

2. On simulation–experiment mismatch in the 1–2 Å region:

Extended Data Fig. 7 shows pronounced oscillations in the 1–2 Å region based on trajectory surface hopping simulations. However, these features are not observable in the experimental ΔPDF data. The authors should address the origin of this discrepancy and clarify whether it stems from limited time resolution, insufficient excitation fraction, or noise. This issue is particularly important, as it affects the credibility of capturing rapid CI-passage dynamics using the reported setup.

Our reply:

We thank the Referee for pointing out this. The absence of these oscillations in the experimental data can be attributed to the limited time resolution of the measurement. It should be noted that the evolutions of the C_1-C_6 distance in original Extended Data Fig. 7 were obtained in simulation without convolving with the instrument response function of the measurement. To clearly show the expected evolution at the experimental resolution, we updated the figure to include the results after applying temporal convolution. After considering the 80 fs temporal resolution, it is clear that these oscillations are no longer visible. However, the characteristic changes in pair density near the conical intersection remain visible at the 80 fs temporal resolution (see the discussion in Supplementary Materials on the effect of temporal resolution).

We clarified this by updating Extended Data Fig. 7 and adding sentences to the Methods section (Simulated population and nuclear dynamics): "When the temporal resolution is taken into account in Extended Data Fig. 7d-f (i.e., by convolving the trajectories with the instrument response function), the oscillations in the ring-closing trajectories are no longer visible. This underscores the pivotal role of temporal resolution in shaping experimental observations. Therefore, extracting CI-passage dynamics requires careful consideration of temporal resolution (see Supplementary Note 8)."

3. On the unsupported claim of Δs-PDF resolving R_2 and R_3:

In Supplementary Note 7, the authors write: "In addition, the Δs-PDF successfully resolves the peak for the diagonal C–C atom pair distance (R_3) at ~2.8 Å, which was indistinguishable from the second-nearest C–C atom pair distance (R_2) at ~2.4 Å." Similarly, the caption of Supplementary Fig. S8 states that the Δs-PDF clearly resolves the R_3 peak and distinguishes it from R_2, unlike the conventional ΔPDF. However, this claim is not substantiated by the data presented in the manuscript. In the main-text Fig. 3a (experimental Δs-PDF), the expected positions of R_1, R_2, and R_3 are explicitly annotated, yet there is no discernible peak or dip at the position of R_3 (~2.8 Å). Instead, the signal at this location exhibits only a smooth zero-crossing. Moreover, even in the simulated Δs-PDF results shown in Fig. 3b–c, the R_3 feature is not clearly resolved either—the signal near ~2.8 Å lacks the structure needed to support the claimed separation. Therefore, both the experimental and simulated data contradict the assertion that Δs-PDF clearly resolves R_2 and R_3. The statements in Supplementary Note 7 and the caption of Fig. S8 overstate the method's spatial resolution and interpretive power in this range. These inaccuracies should be explicitly corrected, and any such claims should be reformulated to accurately reflect the limitations shown in the data. We recommend that the authors: - Revise the relevant portions of Supplementary Note 7 and Fig. S8's caption to remove or qualify the claim that R_3 is clearly resolved by Δs-PDF. - Clarify that no direct evidence of peak resolution at ~2.8 Å is present in either experimental or simulated Δs-PDF results. - Temper the interpretive language regarding spatial resolution enhancement, ensuring that claims are grounded in what is visually and quantitatively observable. Overall, this point is critical because the claimed benefits of the super-resolution

algorithm hinge on its ability to resolve closely spaced pair distances—yet such a case is not convincingly demonstrated.

Our reply:

We fully understand the referee's concern regarding the spatial resolution of the super-resolution methodology. We take this opportunity to clarify this and the claimed benefits of the super-resolution algorithm remain valid.

In this work, we use the super-resolution technique to reconstruct sparse atomic pair distributions. The reconstructed pair distribution is represented as a set of δ-functions, each assigned a corresponding weight. The sparse pair distribution is the so called s-PDF, encoding both the pair distance and the pair density information, as illustrated by the static s-PDF shown in Fig. 1g. For such sparse distributions at different time delays, conventional visualization methods—such as 2D density maps used for ΔPDF(t)—are not well-suited. A better way to highlight the improved resolution of the super-resolved Δs-PDF may be to show the reconstructed positions of these sparse pair distributions at each time point as scatter points overlaid on the conventional ΔPDF plots. For example, in the original Fig. S8, the scatter points near 2.8 Å indicate that the super-resolution method has reconstructed an atomic pair distribution corresponding to a specific pair distance (R_3). Therefore, the Δs-PDF successfully resolves the peak corresponding to the diagonal C–C atomic pair distance (R_3) at approximately 2.8 Å.

In the original manuscript (Fig. 3 in the main text), only the conventional ΔPDFs (both the experimental and simulated results) were shown, while the corresponding Δs-PDF date set was placed in the Supplementary Materials. We find that this separation could lead to potential misunderstandings. To avoid confusion, we have now included the Δs-PDF data set in the main text, enabling a direct comparison between the ΔPDF and Δs-PDF.

In the revised Fig. 3, the Δs-PDF not only shows clearer identification of coherent oscillations in atomic pair distributions arising from the rotation of the terminal ethylene groups, but also reveals a distinct peak near 2.8 Å corresponding to R_3, marked by the sparsely reconstructed peak positions (scatter points). In the early stages of the reaction, atomic pairs shorter than R_3 extend through the R_3 distance during the ring-opening process. This elongation masks the depletion of the diagonal C-C interatomic distance, resulting in positive features around R_3. Consequently, the negative peak at R_3, which arises from the depletion, becomes apparent only after the system has undergone ring opening (beyond ~100 fs). Moreover, Δs-PDF can help us observe the bifurcation of atomic pair distributions near pericyclic minimum. In Fig. 3, we primarily leverage the interatomic distance information provided by the super-resolved reconstruction, while in Fig. 4, we further utilize the reconstructed pair density evolution to analyze the CI structural dynamics.

To better clarify the advantage of super-resolution, Fig. R1 presents a comparison between the Δs-PDF and the conventional ΔPDF at a selected time point (1 ps). The super-resolved reconstruction not only resolves the peak near the R_3 atomic pair, demonstrating that the spatial resolution of the super-resolution method can approach 0.3 Å, but also more effectively separates atomic pair densities at different distances.

This enables more accurate extraction of pair density information at specific interatomic positions.

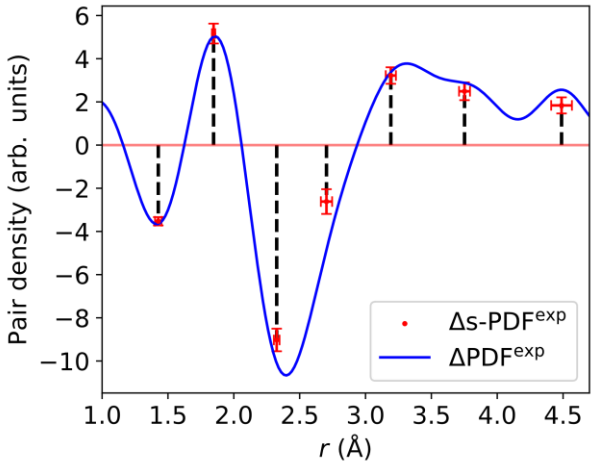

Fig. R1: Comparison between Δs-PDF and ΔPDF at 1 ps.

4. On visual consistency and data representation in Fig. S8:
Unlike other figures where the gray level in the colormap corresponds to zero signal, Fig. S8 appears to use a shifted colormap where gray does not represent zero. If this adjustment was intentional, it must be clearly stated and justified. Otherwise, this inconsistency could lead to misinterpretation of the figure or raise concerns about presentation bias. For clarity and fairness, the colormap should be harmonized with the rest of the figures, particularly when ΔPDF and Δs-PDF are being visually compared.

Our reply:

We thank the Referee for the suggestion. To facilitate a clearer comparison between the ΔPDF and Δs-PDF, we have moved Fig. S8 into the main text and harmonized the color bar.

In summary, the manuscript showcases a significant advancement in MeV-UED instrumentation and demonstrates the potential of a model-free inversion algorithm in probing ultrafast structural dynamics. However, its central interpretive claims—particularly regarding spatial resolution beyond the diffraction limit—require stronger visual and analytical support. Addressing the above concerns will substantially enhance the clarity and rigor of the manuscript, thereby strengthening its contribution to the ultrafast science community.

Our reply:

We thank the Referee for their precise summary of our work. We have revised the manuscript following the referee's suggestions that have greatly improved the clarity of our manuscript. The updated Fig. 3 in the main text, along with Fig. R1, demonstrate the superior resolution beyond the diffraction limit achieved by the super-resolution approach as well as its advantage in extracting changes in atomic pair density. We believe the provided evidence is convincing.

Report of the Second Referee

This work presents an advance in the application of UED by combining a high temporal resolution with a super-resolution algorithm. The authors studied the ring-opening reaction of cyclohexadiene (CHD) and retrieved details on the dynamics that were not captured in a previous UED study [Wolf et al, Nature Chemistry 11, 504–509 (2019), REF 23 in this manuscript]. The authors observe an inelastic scattering signal at early times at low scattering angle, and, in combination with numerical simulations, retrieve the time delay for the wavepacket to travel from a first to a second conical intersection. The main advance of this manuscript is technical in the combination of high temporal resolution with spatial super-resolution. The authors chose a well studied system as an example, and their results confirm what is already known but do not add anything new to the story. In terms of technical advances, the authors present results from a very impressive instrument which has the highest time resolution for gas phase UED at 80 fs (almost a factor two better than the SLAC MeV-UED instrument at 150 fs which is the competing instrument). They combined this with an algorithm capable of improving the spatial resolution of the data by approximately a factor of two from 0.6 A to 0.3 A. This combination produces very nice results as it elucidates additional information about the dynamics not captured in a previous UED study. All of these advances have been previously demonstrated and published. The double-achromat device used to produce short electron pulses was demonstrated in REF 34 [Qi et al, PRL 124, 134803 (2020).] Additionally, the same instrument was used by some of the same authors, in a previous gas phase UED study that already showed the same time resolution as this experiment, 80 fs. This is in Ma et al, PNAS 119 (15) e2122793119 (2022), REF 36. The algorithm used for super resolution was demonstrated in a previous publication and applied to UED data on CHD, the same molecule studied here REF 43 [Natan, PRA 107, 023105 (2023)]. Thus, the main advance is the combination of these two methods and highlighting the performance of the instrument.

Our reply:

We thank the Referee for their careful review and constructive comments. We are grateful for the positive assessment on the significance of our work. We appreciate the referee's recognition that our work has successfully retrieved details on the CHD dynamics that were not captured in previous studies, benefiting from improved temporal resolution and spatial resolution. In this work, we aim to demonstrate the potential of UED with high temporal and spatial resolution for probing complex ultrafast dynamics involving conical intersections. The ring-opening nonadiabatic dynamics of CHD, a textbook example of electrocyclic reactions, provides an ideal benchmark for this purpose. By combining experimental measurements with reliable nonadiabatic molecular dynamics simulations, we extract the CI-passage dynamics associated with the CHD ring-opening reaction. Our results show that UED with high spatiotemporal resolution is capable of capturing structural dynamics during CI passage with high fidelity. This methodology can be applied to a wide range of

nonadiabatic CI dynamics studies. We hope our work can stimulate more efforts in this field.

1. The super-resolution algorithm relies on a sparcity constraint, and while it has been shown to work for CHD, it may not work for larger molecules as the PDF becomes more dense with distances. Since the algorithm is an important part of this work, the authors should describe the advantages and limitations of this algorithm compared to other retrieval methods.

Our reply:

We thank the Referee for this suggestion. To clarify the advantages and limitations of the super-resolution technique, we add the following discussion in the Methods section (Super-resolved real-space inversion):

"The model-free super-resolution reconstruction algorithm is based on the theory of compressed sensing [Candes et al., IEEE Transactions on Information Theory, 52(2): 489-509 (2006)], where the reconstruction accuracy of the super-resolution approach is influenced by the degree of sparsity. In the event that the distribution is characterized by concise representations when expressed in a proper basis, it is possible to accurately recover the sparse distribution beyond the diffraction limit. In comparison to alternative methods that depend on global optimization and exhaustive structure refinement, the super-resolution method exhibits superior efficiency and reduced computational demands. However, for atomic pair distributions that are not sufficiently sparse, the reconstruction accuracy is known to decrease. This issue can be resolved through a transformation of the distribution into a different basis, thereby rendering it sparse. However, it should be noted that such transformations frequently depend to a significant extent on prior knowledge. Additionally, while super-resolution can facilitate the recovery of atomic pair distributions, it does not inherently yield detailed molecular structural information, such as angular configurations in three-dimensional space. In this work, the critical real-space information is found in the evolution of the C_1–C_6 atomic pair distance, which can be reconstructed using the super-resolution method."

2. A relative yield of 32% for ring opened products was reported. The authors should provide an uncertainty for this value, and it should be compared with the results reported in previous works, and also with the results from the trajectories reported in this manuscript.

Our reply:

We thank the Referee for this suggestion. Following the referee's suggestion, we have calculated the standard deviation of the branching ratio through bootstrap resampling and have updated the main text (32 ± 3%). In addition, we have included the following discussion to compare our results with those reported in previous studies:

"The best fit yielded a quantum yield of 32 ± 3% for the HT isomers (see Methods), which is comparable to the predicted value from the simulation (about 42%) and to

the measured value obtained through spectroscopic methods (about 30%) [Adachi et al., The Journal of Physical Chemistry Letters, 6(3): 343-346 (2015)]. It is noteworthy that the branching ratio derived from the fitting is lower than the value (about 50%) reported in a previous UED measurement [Wolf et al., Nature Chemistry, 11, 504–509 (2019)]. This discrepancy could be ascribed to the slightly different central wavelengths of the pump pulses (267 nm vs 273 nm) used in the two experiments."

3. Figure 3 provides the delta PDF, which relies on the FT of the delta-sM. At early times, there is a signal at low s that the authors attribute to changes in the electronic structure. The transform from sM to PDF assumes that only nuclear motions contribute to the signal, thus this electronic signal will introduce artifacts. Was this signal removed before the transform? How? More details are needed about how the authors generated the delta-PDF.

Our reply:

We thank the Referee for the question. In the original manuscript, we had a brief discussion in the Method section. When performing the conventional ΔPDF transformation, we removed the inelastic scattering contribution to retain only the elastic scattering signal. Figure 2a shows the raw experimental data in momentum space, where it is evident that the inelastic signal is concentrated in the low-s region. At its maximum, the inelastic signal will affect the region with $s<1.2$ Å^{-1}. To ensure that the inelastic scattering contribution was excluded, we excluded all signals with $s<1.3$ Å^{-1} during the ΔPDF transformation and filled the missing region via extrapolation (details in Supplementary Note 3). The actual ΔsM used for the Fourier transform is shown in Fig. S3. We also compare the ΔPDF obtained with and without extrapolation (Fig. S4), and find that the effect of extrapolation on the PDF features is minimal. It is worth noting that for the super-resolution reconstruction, it is not necessary to extrapolate the signal with $s<1.3$ Å^{-1}, and this minimizes artifacts.

To clarify these procedures, we have revised the descriptions in both the main text and the Methods section by adding the following sentences.

In the main text:

"Figure 3a-c show the measured and simulated difference PDFs (ΔPDFs) obtained from a Fourier-sine transform of ΔsM in Fig. 2a-c after removing the inelastic scattering contribution at small scattering angles (see Supplementary Note 3)"

In the Methods section:

"It should be noted that we need to remove the inelastic scattering contribution to retain only the elastic scattering signal when performing the conventional PDF transformation (more details in Supplementary Note 3)."

4. Figure 3 should show also the delta-PDF retrieved using the super-resolution algorithm. The lineouts in Fig. 4 are not sufficient to judge whether the delta-s-PDF is really reliable. This is important because super-resolution algorithms are known to introduce artifacts, and directly comparing the two delta-PDFs, in the form shown in Figure 3a, would be helpful to notice the quality of the retrieval.

Our reply:

We thank the Referee for the suggestion. Following the suggestions of both referee 1 and referee 2, we have marked the full set of the sparse atomic pair distributions reconstructed via super-resolution in updated Fig. 3a (information on atomic pair distances). These super-resolved traces not only provide a clearer view of the nuclear wavepacket evolution following ring-opening, but also allow us to resolve features—such as the peak near R_3—that are not distinguishable in the conventional PDF. Also, the quality of the retrieval can be visually assessed from Fig. R1.

5. The presence of the positive signal at early times also brings into question the interpretation of the s-PDF at early times. For the super resolution delta-s-PDFs, the lower limit is taken as s = 1.3 A^-1. However, it seems that a significant part of the positive low s signal might extent beyond 1.3 A^-1, possibly affecting the conversion to delta-PDF. I recommend the authors redo the PDF transforms starting at 2.0 A^-1 to make sure that the early dynamics are not influenced by this signal. Or better check that the results are robust to using different ranges in s.

Our reply:

We thank the Referee for the suggestion. To simultaneously minimize the influence of inelastic scattering and enhance spatial resolution, we chose a relatively small lower limit s = 1.3 $Å^{-1}$. To validate whether different choices of the s-range affect the observed CI structural dynamics, here we show the structural dynamics during passage through the two CIs calculated by two different s-ranges in Fig. R2. The lower limit of the momentum transfer used for the Δs-PDF transformation is set to 1.5 $Å^{-1}$ in Fig. R2a, c and 1.7 $Å^{-1}$ in Fig. R2b, d. By comparing with the results in Fig. 4a, c of the main text, we find that varying the lower limit of the s-range has no noticeable effect on the characteristic features observed in the Δs-PDF evolution (knee structure). These findings indicate that our results are robust against different s-ranges. Qualitatively, this robustness arises because the dynamics near the conical intersection involve relatively small structural changes, which primarily contribute to scattering signals at larger scattering angles.

To clarify this, we have included this part of the response in the Supplementary Information (Supplementary Note 9: Effect of *s*-range on imaging the CI dynamics).

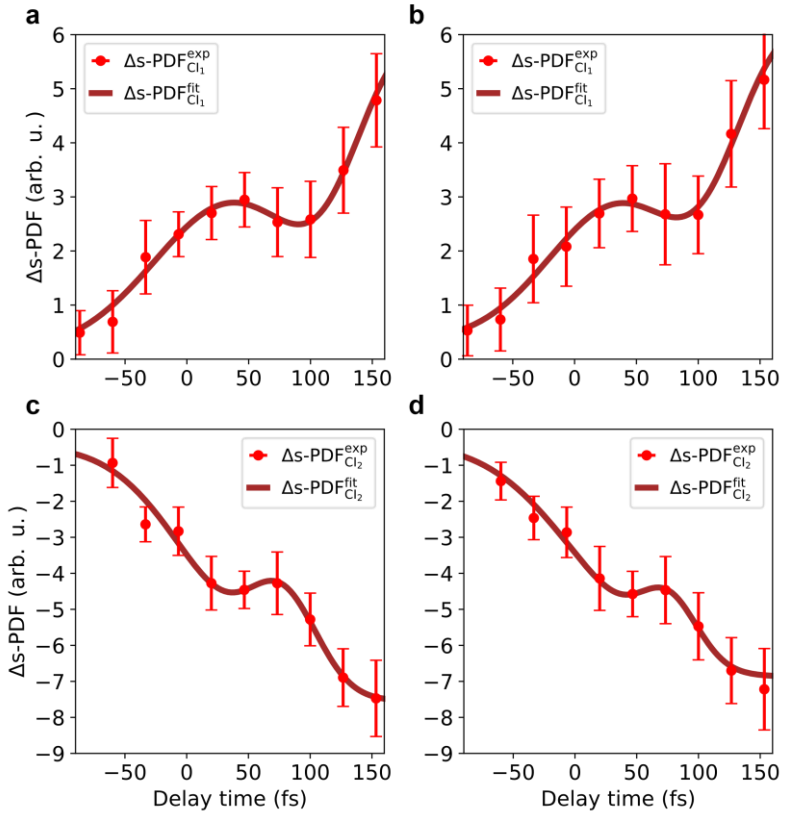

Fig. R2: Structural dynamics during passage through the two CIs calculated by two different s-ranges. a and **c**, Measured intensity of Δs-PDF at ~1.95 Å and ~2.30 Å, respectively. The lower limit is taken as 1.5 $Å^{-1}$. **b** and **d**, Measured intensity of Δs-PDF at ~1.95 Å and ~2.30 Å, respectively. The lower limit is taken as 1.7 $Å^{-1}$.

6. The authors assign a signal in the delta-s-PDF to a specific interatomic distance (C-C6). It is not clear why this is the only atom-pair that could produce this signal. This interpretation could be strengthened if the authors showed that this is indeed the case in calculations by analyzing the trajectory simulations. One could imagine distortions of the ring structure that produce positive and negative signals in this region of the delta-PDF which is not necessarily a direct evidence of the ring-opening.

Our reply:

We thank the Referee for the insightful thought. Since the scattering signals are dominated by carbon atoms, we focus on the influence of C-C pairs on structural dynamics. In addition to the analyzed C_1-C_6 pair, Figure R3 shows the evolution of C_1-C_2 (nearest) and C_1-C_3 (next-nearest) obtained using the simulated trajectories. The dynamics of these two interatomic distances can help us assess the impact of molecular distortions beyond the contributions from the C_1–C_6 pair and explain why the evolution of C_1-C_6 was used to qualitatively analyze the characteristic changes in atomic pair density near 1.95 Å and 2.3 Å within the first 100 fs, respectively.

We first consider the Δs-PDF near 1.95 Å. As shown in Fig. R3a, in the absence of C_1-C_6 pair, the nearest atomic pairs arising from molecular distortion or vibration typically contribute to signals below 1.75 Å, and thus have minimal impact at 1.95 Å.

Also, Figure R3b shows that next-nearest pairs (R_2) generally influence regions beyond 2.1 Å, indicating that their contribution to the 1.95 Å signal is also negligible. Therefore, the feature at 1.95 Å primarily originates from the early-stage opening of the C_1-C_6 pair, as it approaches and crosses the 1.95 Å region.

Since the excess kinetic energy of the molecule reaches its maximum after the electronic state decays to its ground state, structural distortions and vibrational motions are not pronounced during the early stage of the CI passage. As shown in Fig. R3b, d, the evolution of the next-nearest pair remains largely unchanged within the first 80 fs. Significant C_1–C_3 oscillations only appear after the wavepacket passes through the second CI, when the molecule gains substantial kinetic energy. Therefore, although the Δs-PDF feature near 2.3 Å lies within the typical range of R_2, during the initial 80 fs of CI dynamics, the signal arising from molecular distortions is relatively weak. The observed knee feature at ~2.3 Å in the Δs-PDF is primarily attributed to the progressive elongation of the C_1–C_6 pair distance approaching this distance.

To clarify this, we have included this part of the response in the Supplementary Note 7.

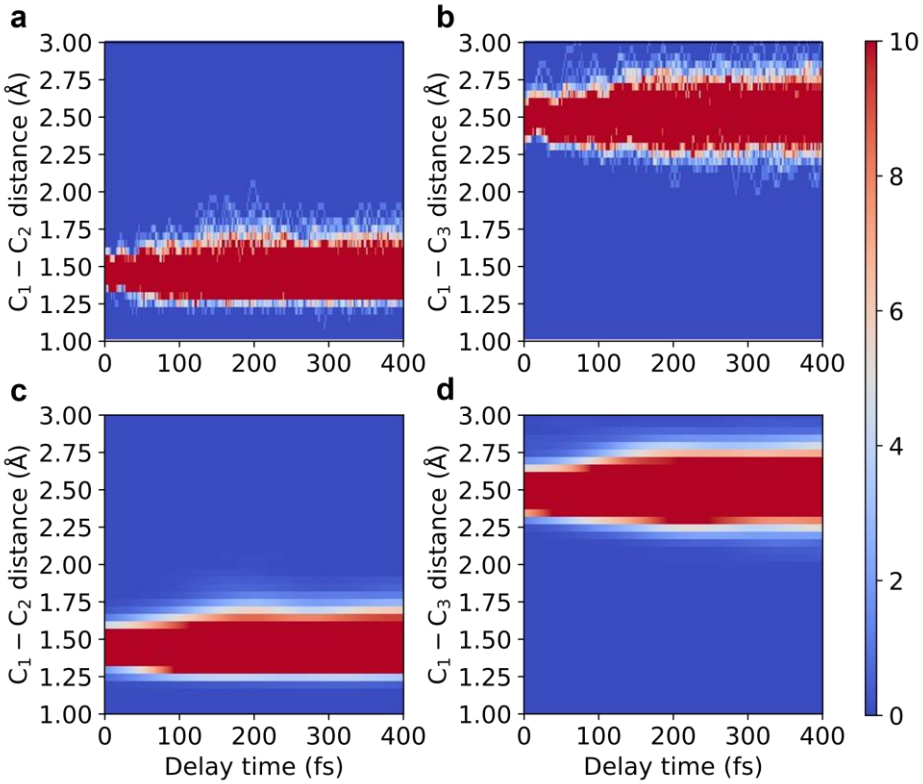

Fig. R3: Simulated evolutions of C_1−C_2 and C_1−C_3 interatomic distances from all 193 trajectories. Atomic labels are shown in Fig. 1b. C_1-C_2 refers to the nearest carbon pair, while C_1-C_3 corresponds to the next-nearest pair. **a** and **c**, The evolution of C_1-C_2 before and after convolution with the instrument response function. **b** and **d**, The evolution of C_1-C_3 before and after convolution with the instrument response function.

Report of the Third Referee

This manuscript describes a cutting-edge ultrafast experiment, using UED to observe the ring opening of cyclohexadiene (CHD) following absorption. This is a "fruit-fly" type photochemical reaction, in that it is very well studied and understood. It is known that relaxation occurs via passage through two conical intersections. Yet passage through the conical intersections has never been directly observed. In this work, it is argued that the authors observe such passage for the first time using a combination of experimental (DBA) and data analysis (super-resolution) methods. This is a very exciting result. The experimental data appears to be of extremely high quality, with high information content and low signal to noise. The theory is done with cutting edge methods (surface hopping, CASPT2). The theory agrees very well with experiment, as presented in figure 4, making a very compelling case that the observed dynamics are precisely what is predicted by theory.

I encourage publication of this work in Nat Comm, but I do suggest that the authors clarify a few points regarding the comparison of theory to experiment before the manuscript is finalized.

Our reply:

We thank the Referee for the positive comments and recommendation for publication.

1. It is a little difficult for me to understand the claim that the conical intersections themselves are directly observed. The theory agrees well with experiment, and theory suggests that the reaction occurs through conical intersections. But it is not obvious to me that one can see a clear signature of a conical intersections here (such as geometric phase). IAM does not contain any information about changes in the electronic wave functions. Would the dynamics look different, for example, if they were totally adiabatic?

Our reply:

We thank the Referee for the question. We agree with the referee that the information of structural evolution alone is insufficient to confirm the presence of CI. Our claim to have observed CI dynamics are aided by the simulation and the measured inelastic scattering signal.

We captured structural features near the CIs in real space using a model-free inverse transform technique with high spatial resolution, which reveal characteristic peaks in the Δs-PDF near two specific pair distance. Leveraging the temporal resolution of our instrument, we successfully extract the pair density changes induced by the passage of the nuclear wave packet through these two regions. By comparing with theoretical simulations, we identified these structural signatures as markers that allow us to determine, in real space, the precise time at which the wave packet traverses the CI region. It is noteworthy that adiabatic process can lead to similar structural evolutions. Therefore, to directly attribute the observed dynamics to a CI, it

is essential to simultaneously observe changes in both the nuclear and electronic degrees of freedom. In this work, we qualitatively analyzed the excited-state population using the inelastic scattering signal. We find that the onset of its decay coincides closely with the second CI passage time obtained from the structural dynamics. This temporal correlation between electronic and structural changes provides additional evidence of CI dynamics. With further improvements in the temporal resolution and signal-to-noise ratio of ultrafast electron diffraction (UED), it may be possible to detect coherence arising from the geometric phase near the CI.

To clarify this, we added following sentences into the main text:

"Moreover, the extracted CI_2 passage time closely matches the onset of the decay in the inelastic scattering signal, indicating simultaneous changes in both the nuclear and electronic degrees of freedom. This temporal coincidence provides further evidence that the observed dynamics are governed by the conical intersection."

2. Was the super-resolution inversion performed using Natan's software or the author's own implementation? Is there software widely available for this technique? For reproducibility's sake and for comparison to future theory, it would be useful if the software were made available one way or another.

Our reply:

Thanks for the suggestion. This super-resolution technique was implemented using our own code based on the methodology described in Natan's work. We will upload and open-source the code upon acceptance of the manuscript.

Report of the Fourth Referee

The work "Super-resolution femtosecond electron diffraction reveals electronic and nuclear dynamics at conical intersections" by Xiang et. al. describes a new way to study the photodynamics at conical intersection using femtosecond electron diffraction techniques. Both experimental measurements and computational simulation were used to investigate the ring-opening reaction of 1,3-cyclohexadiene. The combination of both experiment and theory makes this approach an interesting tool for the study of photodynamic processes. The manuscript is well written, still I have a few open questions/comments that should be addressed before publication.

Our reply:

We thank the Referee for their thorough review and insightful comments. We are grateful for the positive assessment on significance of our work. We have addressed the referees concerns in the revised manuscript.

1. The authors use the standard 6 electrons in 6 orbitals (6e, 6o) active space combined with a triple zeta basis set. One issue of CAS-Methods is the issue of intruder states, which increases with basis set size and with the use of diffuse basis sets. Did the authors encounter this issue or was the real shift of 0.5 Hartree enough to prevent this for the used triple zeta basis set?

Our reply:

We thank the Referee for pointing out this critical question. The intruder state problem (ISP) is indeed a well-known issue in CAS-based perturbation methods. In this work, ISP was prevented by applying an appropriate level shift during the calculations. To ensure reliable and quantitatively accurate descriptions of the low-lying excited states, we employ a real shift value of 0.5 Hartree. To assess the robustness of this choice, we conducted benchmark calculations on several key geometries using different shift parameters (0.3, 0.5, and 0.6 Hartree), as summarized in Table R1. The results indicate that the excitation energies are only marginally affected by variations in the shift value, thereby validating our choice of 0.5 Hartree.

Moreover, electronic structure calculations often fail to converge or yield unphysical results in the presence of intruder states. However, we did not observe such failures in the nonadiabatic simulations, suggesting that the ISP did not pose a significant problem in our study.

To clarify this, we added following sentences into the Methods section (Geometries simulations):

“The absence of convergence failures due to intruder states in the subsequent nonadiabatic simulations further confirms the robustness of the chosen level shift value.”

Table R1. Relative energies of the two lowest excited states at several geometries with respect to the ground state minimum under different level-shift values.

Level-shift (Hartree)	State	S_0-min	CI_1	CI_2
0.3	S_1 (eV)	4.826	4.158	3.647
	S_2 (eV)	6.221	4.192	5.794
0.5	S_1 (eV)	4.954	4.235	3.672
	S_2 (eV)	6.294	4.235	5.886
0.6	S_1 (eV)	5.017	4.256	3.694
	S_2 (eV)	6.319	4.276	5.930

2. In equation 5 the formula is given with which the diffraction signals of the simulated nuclear structures are computed. However it is not clear to me, how the f_i(s) are computed from the simulation data. Could the authors explain these in more detail?

Our reply:

In this study, the simulated diffraction patterns are obtained using the independent atom model (IAM), which neglect the effects of chemical bonding and electron redistribution during the reaction. Accordingly, we employed the IAM model in our theoretical diffraction simulations to analyze structural dynamics. In this model, the atomic form factors (f_i)—i.e., the standard elastic electron scattering amplitudes for each atom—can be obtained from tabulated data [Wilson et al., International Tables for Crystallography: Volume C-Mathematical, Physical and Chemical Tables, Vol. C, p. 992 (1999)] or computed by ELSEPA program [Salvat et al., Elsepa—dirac partial-wave calculation of elastic scattering of electrons and positrons by atoms, positive ions and molecules, Computer Physics Communications 165, 157–190 (2005)]. The ELSEPA program is employed in this work.

We have included this information in the revised manuscript.

3. The authors write that the location of the first CI is an issue, due to the absence of wave packet bifurcation. From a theoretical point of view, the wave packet should always bifurcate at a conical intersection. Could the authors elaborate how they mean this?

Our reply:

We thank the referee for pointing out this inaccurate description in the original manuscript. The referee is correct that in theory the wave packet should always bifurcate at a conical intersection. This is indeed one signature that has been used to identify CIs when a measured ΔPDF divides into two branches at some point, a

feature that has been utilized in previous studies. However, such a signature does not always manifest in all scenarios of bifurcation. For example, if the two bifurcated pathways exhibit similar structural changes, or if one of the pathways has a very small branching ratio, the measured ΔPDF may not clearly indicate a CI. This is what we observed in the first CI, so alternative methods are needed to identify it, this is where the analysis in Figure 4 becomes useful.

To clarify this, we have revised the relevant descriptions in the main text to avoid confusion:

"such protocol cannot be applied to locate the first CI due to the absence of a pronounced bifurcation of the structural pathway in the observed ΔPDFs."

4. To estimate the quantum yield, the author compute ΔsM with the simulated results obtained at varying quantum yields. However it is not clear to me, how the simulated results at varying quantum yields were obtained? Could the authors describe this in more detail?

Our reply:

We thank the referee for the question. Simulations corresponding to different quantum yields were obtained by resampling from the set of 193 computed trajectories, in which a specified number of ring-opening and ring-closing trajectories were randomly selected to match the desired yield. To ensure statistical convergence, multiple resampling iterations were performed, and as many trajectories as possible were included in the averaging process.

To clarify this, we have included this part of the response in the Methods section (Quantum yield and excitation ratio estimation).

5. The authors write, that they use a narrow excitation energy window with a ~2 nm FWHM. In my opinion it would help the reader if the excitation energy window would be also given in eV, as this makes it easier to estimate the energy window.

Our reply:

We thank the referee for the suggestion. The excitation energy window is 4.39-4.46 eV. We have included this information in the revised manuscript.

Response to Review for
"Super-resolution femtosecond electron diffraction reveals electronic and nuclear dynamics at conical intersections"

June 25, 2025

Report of the First Referee

We appreciate the authors' comprehensive response to the original review, and we acknowledge that most of the concerns raised, particularly those regarding structural modeling (Point 1), simulation–experiment mismatch (Point 2), and colorbar consistency (Point 4), have been addressed effectively and with clarity. However, regarding Point 3, we find the response concerning the claim that Δs-PDF "clearly resolves" the diagonal C–C atomic pair distance R3 (~2.8 Å) from R2 (~2.4 Å) remains only partially convincing. The authors assert that the Δs-PDF resolves these pair distances due to its sparse reconstruction capabilities and provide Fig. R1 to support this claim.

Yet, even in Fig. R1, the ΔPDF exhibits a broadened and asymmetric negative feature near ~2.5 Å. This signal alone suggests overlapping contributions that could be analyzed using signal decomposition techniques such as Gaussian fitting, as potentially arising from multiple nearby pair distances, including R3. That is, the ΔPDF appears to contain enough information to infer such structures, even without invoking sparsity-based inversion. If so, the advantage of Δs-PDF lies not in its exclusive ability to resolve these distances, but rather in offering an alternative reconstruction formalism that emphasizes automation and sparsity-based regularization.

Most importantly, we would like to emphasize the interpretive caution that must accompany any sparsity-based representation. In cases such as wavepacket delocalization or vibrationally hot molecular states, where the pair distribution is physically broadened, the Δs-PDF may approximate this spread-out distribution using multiple discrete peaks. These discrete peaks, while mathematically well-defined, do not necessarily imply the presence of multiple distinct physical structures. This may lead to an "illusion of resolution," in which the sparse reconstruction yields artificially fine structural features that may not correspond to real, distinguishable atomic arrangements.

Our reply:

We thank the Referee for the insightful clarification regarding both the capabilities and limitations of the super-resolution technique. To improve the accuracy of our description of the Δs-PDF, we have revised the relevant parts of the manuscript according to the referee's suggestions.

To prevent overinterpretation, we strongly encourage the authors to clarify in the manuscript that:

1. The resolution of R3 in Δs-PDF arises from a sparsity-constrained mathematical

inversion, and does not in itself prove the existence of a well-separated structural signal at that distance.

2. In situations involving broadened or delocalized wavefunctions, such as those arising from vibrational excitation or wavepacket spreading, the Δs-PDF may represent a continuous distribution using multiple discrete points, which should not be over-interpreted as indicating distinct structural populations.

3. The Δs-PDF formalism offers clear practical advantages in regularization and visualization, but its physical interpretability depends critically on the sparsity and localization of the underlying pair distributions.

We emphasize that the Δs-PDF remains a valuable approach, particularly in sparse conditions, but its advantage over standard ΔPDF-based analysis should be framed in terms of algorithmic benefits and practical implementation, rather than being interpreted as inherently offering superior spatial resolution.

Our reply:

We thank the Referee for the suggestion. We have revised the descriptions as follows:

"However, the pair density changes around two interatomic distances could not be extracted directly using the conventional PDF analysis."

"Notably, the Δs-PDF suggests a peak near R_3 at ~2.8 Å, distinct from R_2 at ~2.4 Å in Fig. 3a, as a result of the sparsity-based reconstruction. We note that in the case of broadened or delocalized nuclear wave packets, the resulting Δs-PDF could exhibit multiple adjacent discrete points representing a broad continuous distribution, which does not necessarily indicate a well-separated atom pair at that specific distance. Nevertheless, even when the sparsity condition is compromised, the Δs-PDF still serves as a practical tool for robustly deconvolving the conventional ΔPDF and extracting localized variations in pair density."