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Observation of laser-assisted electron scattering in superfluid helium

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Abstract

Laser-assisted electron scattering (LAES), a light-matter interaction process that facilitates energy transfer between strong light fields and free electrons, has so far been observed only in gas phase. Here we report on the observation of LAES at condensed phase particle densities, for which we create nano-structured systems consisting of a single atom or molecule surrounded by a superfluid He shell of variable thickness (32–340 Å). We observe that free electrons, generated by femtosecond strong-field ionization of the core particle, can gain several tens of photon energies due to multiple LAES processes within the liquid He shell. Supported by 3D scattering simulations, these results provide the first insight into the interplay of LAES energy gain/loss and dissipative electron movement in a liquid. Our results reveal that LAES could significantly increase the temporal resolution of ultrafast electron microscopy, potentially to the attosecond regime.

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17 Introduction

18 The investigation of atomic-scale processes with high spatio-temporal resolution is key to the understanding and
19 development of materials. While pulsed light sources have been developed to provide attosecond temporal resolution¹,
20 the diffraction limit of light waves prohibits the improvement of the spatial resolution below the ten-nanometer range.
21 Electron probes, in contrast, allow for subatomic spatial resolution due to their picometer deBroglie wavelength,
22 and can, in principle, achieve the temporal resolution of light pulses. Time-domain shaping of electron pulses
23 is based on the transfer of energy between electromagnetic radiation and free electrons, which is manifested in
24 various phenomena, such as bremsstrahlung, Smith-Purcell radiation², Cerenkov radiation³, or Compton scattering⁴.
25 Electron-photon coupling is furthermore key to the development of novel light sources like free electron lasers⁵ or
26 high-harmonic generation⁶, and to ultrafast structural probing like high-harmonic spectroscopy⁷ or laser-induced
27 electron diffraction⁸. While few- and sub-femtosecond electron pulses^{9,10} and pulse trains^{11,12} could be generated
28 through light-field manipulation, the time resolution achievable with these electron pulses suffers from velocity
29 dispersion and Coulomb repulsion¹⁰. Consequently, spatial separation of pulse shaping and structural probing in
30 ultrafast electron microscopy (UEM) setups^{13–18} leads to broadening of electron pulses during delivery to the sample,
31 limiting the temporal resolution currently to about 80 fs¹⁹.

32 LAES is a light-matter interaction process that holds promise to increase the temporal resolution of electron probes
33 by combining velocity modulation and structural probing within the investigated sample. In LAES, free electrons
34 that scatter off neutral atoms or molecules in presence of a strong laser field, can increase (inverse bremsstrahlung)
35 or decrease (stimulated bremsstrahlung) their kinetic energy by multiples of the photon energy ($\pm n\hbar\omega$)^{20–22}. Struc-
36 tural information of the scattering object is encoded in the angular distribution of the accelerated/decelerated
37 electrons^{20,23}. Importantly, the energy modulation only takes place during the time window in which the short laser
38 pulse overlaps with part of the much longer electron pulse within the sample. LAES can thus be viewed as an optical
39 gating technique that allows to record scattering-snapshots at precisely defined times. The capability of LAES to
40 analyze structural dynamics with subparticle spatial resolution (~ 1 pm) at timescales of electron dynamics (< 10 fs)
41 was recently demonstrated in the gas-phase^{20,23}. However, in contrast to other strong-field phenomena²⁴, LAES has
42 evaded observation in the condensed phase so far, so that its potential for advancing the time resolution of structural
43 probing through UEM and other techniques remains unexplored.

Here, we demonstrate that LAES can be observed at condensed phase particle densities of $2 \cdot 10^{22} \text{ cm}^{-3}$, for which we create core-shell nanostructures, consisting of a single atom/molecule located inside a superfluid He droplet (He_N)^{25,26}. This system provides three unique advantages: First, the droplet size and thus the LAES interaction shell thickness underlies a well defined distribution, the mean of which can be varied with Angstrom resolution²⁵. Second, the high strong-field ionization threshold of He²⁷ enables high laser intensities to increase the LAES probability without solvent ionization. Third, energy dissipation of electrons propagating inside He_N is very low²⁸. We have chosen the experimental conditions to work in the multiple scattering regime in order to characterize the interplay of LAES acceleration/deceleration and dissipative electron movement within the He shell; as a consequence, our experiment does not provide information about the electron angular distribution.

Results

Observation of multiple LAES events

To measure the energy gain of electrons through LAES within the liquid He shell, we perform strong-field photoionization with femtosecond laser pulses and compare two photoelectron spectra that are recorded under the same laser pulse conditions: First, the above threshold ionization (ATI) spectrum of a bare, gas-phase atom/molecule and, second, the LAES spectrum obtained with the same atom/molecule embedded inside a He_N . The He droplets, which have a radius of a few nanometer, are created by supersonic expansion of He gas through a cryogenic nozzle and loaded with single dopant atoms or molecules through the pickup technique^{25,26}, as described in the Methods section below. Figures 1a-c show the two types of spectra for three species: Indium (In) atoms, xenon (Xe) atoms, and acetone (AC) molecules. For all three species, the LAES spectrum shows significantly higher electron energies than the ATI spectrum, and both types of spectra—ATI and LAES—show equidistant signal modulations with a peak distance of 1.55 eV, corresponding to the central laser wavelength of 800 nm (1.55 eV photon energy). Closer inspection of the area-normalized spectra shows that, in addition to the higher energies of the LAES spectrum, the ATI signal exceeds the LAES signal at low energies up to $\sim 5 \text{ eV}$, indicating a shift of the electron energy distribution towards higher kinetic energies due to the presence of the He shell. The energy increase of the fastest electrons exceeds 20 eV in all three cases, which is far beyond the $10 U_P$ energy gain limit for a single scattering event according to the strong-field Kroll-Watson approximation³⁰ (U_P is the ponderomotive energy, see parameters

70 above Figures 1a-c). Thus, a significant fraction of the electrons must encounter multiple LAES events within the
71 liquid He shell.

72 In order to investigate the influence of the dopant species that serves as electron source through strong-field ionization,
73 we compare the In, Xe and AC spectra (Figures 1a-c). We use a higher laser intensity I for Xe and AC due to
74 the higher ionization energy E_I , compared to In, which is reflected by ATI spectra that extend to higher energies.
75 Smoothed LAES and ATI spectra are compared in Figure 1d. The similarity of the Xe and AC spectra, for which
76 a very similar laser intensity was used, indicates that the species from which the electrons originate has very little
77 influence. Instead, the LAES energy gain is larger for Xe and AC (e.g., at a signal level of 10^{-3} : 25-30 eV gain),
78 compared to In (20 eV gain), because of the higher laser intensities used for Xe and AC. These observations indicate
79 that the laser intensity dictates the energy gain.

80 In addition to the LAES energy gain, insight into the dissipative electron movement within the liquid He shell can
81 be obtained from the equidistant peak structure of the LAES spectra (Figures 1a-c). Kinetic energy of an electron
82 can be dissipated to the He droplet through binary collisions with He atoms and through a collective excitation of
83 the droplet. While elastic collision with a He atom reduces the electron kinetic energy by $\sim 0.06\%$ due to energy and
84 momentum conservation, collective He_N excitations carry < 2 meV energy²⁶. The pronounced contrast of the LAES
85 peaks in Figure 1 thus demonstrates that energy dissipation plays a subordinate role compared to LAES energy
86 gain for the relatively small droplets ($R_d \approx 45 \text{ \AA}$ radius) used in these measurements. Furthermore, the absence
87 of a kink in the yield at or above 20 eV, the energy threshold of electronic He excitations³¹, shows that inelastic
88 interactions are insignificant, which is in agreement with the much lower cross section for inelastic as compared to
89 elastic interaction²⁹.

Figure 1: Comparison of electron spectra obtained by strong-field ionization with 800 nm light (1.55 eV photon energy) of different species in gas-phase (ATI spectra, black) and inside He $_N$ (LAES spectra, red): **(a)** In atoms, **(b)** Xe atoms, **(c)** acetone (AC) molecules. The spectra are area-normalized in order to account for the reduced ionization energy inside a He $_N$ ²⁸. Above each plot the values of the ionization energy, E_I , laser intensity, I , ponderomotive potential, U_P , and droplet radius, R_d , are listed. **(d)** ATI spectra (dashed lines) and LAES spectra (solid lines) as in a-c but with 3 eV binning (left ordinate), and cross section for total elastic electron scattering of electrons and He (gray line, right ordinate)²⁹.

90 Droplet size effects

91 We now investigate the influence of the He shell thickness on the LAES spectrum in order to deepen our insight
92 into the interplay of light-induced energy gain/loss and dissipative energy losses. The He droplet approach allows to
93 change the He shell thickness around the atom/molecule to be ionized by varying the droplet source temperature.
94 Since LAES processes require electron–He scattering in presence of laser light, information about the electron transit
95 time through the He shell can be gained from the droplet-size dependence of the LAES spectra. Figure 2a shows
96 LAES spectra obtained with In atoms inside He droplets with radii from $R_d = 32 \text{ \AA}$ to $R_d = 340 \text{ \AA}$. The energy
97 gain continuously increases with the He shell thickness for the accessible range of droplet radii. The maximum
98 kinetic energy doubles from 50 eV for the smallest droplets to 100 eV for the largest ones, compared to a maximum
99 energy of the ATI spectrum of about 15 eV. This continuous increase provides a first indication that the transit time
100 distribution, which is a result of stochastic electron trajectories, is comparable to the laser pulse duration, at least
101 up to $R_d \approx 76 \text{ \AA}$.

102 While the LAES energy gain is restricted to the time window of the laser pulse, the electron dissipates energy as
103 long as it propagates within the He droplet. Since the energy transfer in single collisions with He atoms is low,
104 energy dissipation influences the modulation contrast of the LAES signal. A close-up of the LAES spectra in the
105 low-energy region in Figure 2b allows to evaluate the dependence of this contrast on the droplet size. We find
106 that the contrast decreases steadily from the smallest droplets, where it equals the contrast of the gas-phase ATI
107 peaks, until it vanishes completely for the largest droplets. We ascribe this blurring to energy dissipation of the
108 electron within the He shell, which has increasing influence on the spectra for larger droplets. Despite the energy
109 dissipation, the thickest He shell ($R_d = 340 \text{ \AA}$) supports the highest LAES energy gain, emphasizing the dominance
110 of the light-driven electron energy modulation over dissipative energy loss.

Figure 2: Dependence of LAES spectra on the droplet size, for droplet radii between $R_d = 32 \text{ \AA}$ and $R_d = 340 \text{ \AA}$ (R_d values are calculated from the mean values of the droplet size distributions²⁵). The spectra are obtained with In atoms at $I = 1.1 \cdot 10^{13} \frac{\text{W}}{\text{cm}^2}$ and show a pronounced increase of the LAES energy gain with He shell thickness. Additionally, the gas-phase ATI spectrum is shown for comparison. The abrupt increase of the droplet radius to $R_d = 340 \text{ \AA}$ for the lowest droplet source temperature ($T_0 = 10 \text{ K}$) is due to the changing character of the supersonic expansion from sub- to supercritical in this temperature regime²⁵. (b) Close-up of the low-energy region of (a).

3D scattering simulation

For further insight into the electron propagation through the He shell, we perform simple 3D elastic scattering simulations, without considering the light field. From these simulations we obtain estimations for the transit time and the number of electron–He scattering events. Figures 3a and b show the ratios of ejected electrons over time for $E_{\text{kin}} = 2 \text{ eV}$ and $E_{\text{kin}} = 10 \text{ eV}$, each for different droplet sizes. It can be seen that the probability for electron ejection within the time span of the laser pulse (25 fs) depends strongly on the droplet size, in particular for 2 eV electrons. This droplet size dependency is also reflected by the corresponding probability distributions of scattering events within 25 fs (insets of Figure 3a,b): The lower maximum of the double peak structure represents electrons that are ejected within 25 fs, while the upper maximum represents electrons that are inside the droplet after this

time. We note that the actual time span for LAES is shorter than the pulse duration since the ionization is most likely around the pulse maximum, which might add to the uncertainty of the values discussed here, but does not influence the obtained trends.

The mean number of scattering events within 25 fs (Figure 3c) is predicted to increase with droplet size for all kinetic energies, eventually leveling off. Interestingly, in the biggest droplets 10 eV electrons experience more collisions than 2 eV electrons, because they propagate longer distances in larger droplets and thus undergo more collisions, despite their lower scattering cross section (Figure 1d).

Finally, we look into the dissipative electron movement and therefore consider 5 eV electrons and the scattering event distribution after ejection from the droplet (long interaction times, not restricted to 25 fs, Figure 3d). Comparing these distributions to the mean number of scattering events within the pulse duration in figure 3c, it is obvious, that for the biggest droplets, the majority of scattering events happen after the laser pulse.

Figure 3: 3D simulation of electron trajectories inside a He droplet for different kinetic energies E_{kin} and different droplet radii R_d in similarity to Tulsy et al.³². An ensemble of $1 \cdot 10^5$ electrons is considered. **(a)** Probability that an $E_{\text{kin}} = 2 \text{ eV}$ electron has been ejected as function of time T for different R_d . Inset: Probability density of the number of scattering events within 25 fs for $E_{\text{kin}} = 2 \text{ eV}$. **(b)** Same as (a) but for $E_{\text{kin}} = 10 \text{ eV}$. **(c)** Mean number of scattering events within 25 fs [c.f., insets in (a) and (b)] as function of the droplet radius for $E_{\text{kin}} = 2, 5, 10, 20, 50, 100 \text{ eV}$. Vertical lines indicate the R_d -values that are considered in (a) and (b). **(d)** Probability distribution of total scattering events, i.e., without temporal limit, for $E_{\text{kin}} = 5 \text{ eV}$.

Discussion

Comparison of strong-field ionization spectra of atoms/molecules in gas phase and inside He droplets reveals that the presence of a nanometer-thick layer of superfluid He around the ionized particle leads to a significant increase of the electron kinetic energies. The following observations, in combination with predictions from 3D scattering simulations, lead us to the conclusion that the electron acceleration is due to multiple LAES processes within the He layer: (i) The energy gain strongly increases with droplet size (Figure 2). This behavior observed for strong-field ionization is in contrast to weak-field ionization inside He droplets, where the photoelectron spectrum is droplet-size independent because it is influenced only by the structure of the immediate environment of the dopant, the solvation shell³³. In the current situation, the energy gain of the electron is related to the number of light-mediated binary electron–He-atom collisions at a distance from the remaining ion, which increases with growing droplet size. (ii) Comparison for three different species shows that the laser intensity has the strongest influence on the LAES energy gain, while the ionization energy plays a negligible role (Figure 1). This is explicable by an increased LAES probability due to increased photon flux. (iii) The upper limit of the energy gain by far exceeds the maximum light-field energy of $10 U_P$ that can be transferred to an electron in a single scattering event³⁰. Multiple scattering events are in agreement with our simulations, which predict a broad distribution ranging up to several tens of scattering events even within the smallest droplets (Figure 3).

For the applicability of LAES in UEM, the interplay of LAES energy gain/loss and dissipative energy losses as a function of the thickness of the material is a crucial factor. We gain insight into the electron transit time through the He shell, as well as the number of dissipative electron–He-atom collisions, by comparing the droplet-size dependence of the LAES spectra to the scattering simulations. In the experiment we observe that the LAES energy gain increases continuously over the whole range of investigated droplet sizes ($R_d = 32 \text{ \AA}$ to $R_d = 340 \text{ \AA}$, Figure 2). This is in agreement with the simulations, which predict that the mean number of collisions within 25 fs, increases up to the largest droplets used in the experiment ($R_d = 340 \text{ \AA}$), most dominantly for higher electron energies. Consequently, the average transit time of the observed ensemble is on the order of the laser pulse duration. The LAES interaction time is determined by the droplet size in small droplets and by the laser pulse duration in large droplets (Figure 3).

Finally, we want to focus on the dissipative electron movement. Considering purely elastic scattering (Figure 3d), on

158 average, 5 eV electrons undergo 10 collisions inside the smallest droplets ($R_d = 32 \text{ \AA}$), resulting in an energy loss of
 159 30 meV (0.06% energy loss per collision). Inside the largest droplets ($R_d = 340 \text{ \AA}$) they loose, on average, 2 eV after
 160 830 elastic collisions. Comparing these values to the 1.55 eV distance of LAES peaks, the signal contrast is expected
 161 to be the same as that of the gas-phase ATI spectrum for the smallest droplets, while it can be expected to fully smear
 162 out for the largest droplets, in agreement with our measurements in Figure 2b. However, the simulated electron
 163 energy loss of 130 meV (45 collisions) for $R_d = 76 \text{ \AA}$, seems insufficient to explain the observed $\sim 50\%$ contrast
 164 reduction (around $E_{\text{kin}} = 5 \text{ eV}$) in figure 2b. This discrepancy points towards shortcomings of the simulation that
 165 are currently neglected: excitation of collective droplet modes^{25,26}, transit-time increase due to Coulomb interaction
 166 between the ion core and the electron, or additional blurring of the LAES peaks due to sequential energy-gain–
 167 energy-loss processes with varying U_P . Nevertheless, the most important observation is that the largest He droplet
 168 (thickest He layer, $R_d = 340 \text{ \AA}$) yields the fastest electrons, proving that energy gain through multiple LAES
 169 processes effectively dominates energy dissipation for propagation distances of several tens of nanometers.

170 In conclusion, we have demonstrated that LAES can be observed with femtosecond laser pulses in the condensed
 171 phase at particle densities of $2 \cdot 10^{22} \text{ cm}^{-3}$. This demonstration shows that LAES can be used in the condensed phase
 172 to merge temporal selection via velocity modulation of electrons with ultrashort laser pulses (as demonstrated here),
 173 and structural analysis that can be extracted from the electron angular distributions^{20,23}. While it is encouraging
 174 that in superfluid He LAES energy modulation dominates energy dissipation of electrons, it will be important to
 175 investigate this ratio for other materials, which is enabled by the He droplet approach through the creation of core–
 176 shell systems^{34,35}. Photoionization of the core will allow to observe LAES-acceleration and energy dissipation within
 177 the shell material. Furthermore, extension to a pump-probe configuration with few-cycle pulses ($\sim 5 \text{ fs}$ duration)
 178 should enable the tracing of electron propagation within the target material. In view of UEM, our results suggest
 179 that LAES can increase the temporal resolution of electron probes through optical gating with ultrashort laser
 180 pulses.

181 Methods

182 Helium nanodroplet generation and particle pickup

183 We generate superfluid helium nanodroplets (He_N) in a supersonic expansion of high-purity He gas through a cooled
184 nozzle ($5\,\mu\text{m}$ diameter, 40 bar stagnation pressure) into vacuum. Variation of the nozzle temperature between
185 10 and 20 K allows us to change the mean droplet size in the range of $\bar{N} = 3.0 \cdot 10^3 - 3.7 \cdot 10^6$ He atoms per
186 droplet²⁵, corresponding to a droplet radius of $R_d = 32 - 340\,\text{\AA}$. After formation, evaporative cooling results in
187 superfluid droplets at a temperature of about 0.4 K. We load the droplets with single atoms or molecules by passing
188 them through a resistively heated pickup oven (In), or a gas pickup cell (Xe, acetone). While pickup conditions
189 are optimized for single atom/molecule pickup, we found that the generation of dimers and larger complexes has
190 negligible effects on the LAES spectrum.

191 Strong-field photoionization and detection of LAES spectra

192 We ionize the guest atom/molecule inside a droplet with femtosecond laser pulses from an amplified Ti:sapphire
193 laser system (800 nm center wavelength, 25 fs pulse duration, 3 kHz repetition rate, 1 mJ maximum pulse energy),
194 which we focus to obtain intensities of $I \leq 3 \cdot 10^{13} \frac{\text{W}}{\text{cm}^2}$, as indicated on top of Figures 1a-c. The pulse duration
195 is measured with a single-shot autocorrelator and the intensity is calibrated using the U_P energy shift of electrons
196 generated by ATI of H_2O at a pressure of $1 \cdot 10^{-7}$ mbar³⁶. Laser-ionization of the doped droplets takes place
197 inside the extraction region of a magnetic-bottle time-of-flight spectrometer and electron spectra are computed from
198 flight-time measurements^{28,37}. We compare LAES spectra of atoms/molecules inside the droplets to ATI spectra
199 of bare atoms/molecules, which we obtain as effusive beam from the pickup cell by blocking the He droplets. The
200 measurement chamber is operated at a base pressure of 10^{-10} mbar.

201 3D scattering simulations

202 For the 3D scattering simulations, we assume an ensemble of electrons with a fixed kinetic energy E_{kin} . The
203 ensemble with an isotropic distribution of initial directions propagates from the droplet center and scatters elastically
204 until it finally exits the droplet. We assume binary electron-He collisions of mono-energetic electrons and neglect
205 acceleration/deceleration due to LAES, as well as momentum transfer in elastic scattering events and inelastic
206 interactions. The propagation distance before a scattering event, s is chosen from the exponential distribution
207 $N(x) = N_0 \cdot e^{-n\sigma x}$ (Lambert-Beer law) as $s = -\frac{\log(R)}{(n\sigma)}$, with R uniformly distributed within the interval $[0,1]$. Values
208 for the elastic scattering cross section σ and angular distribution $\frac{d\sigma}{d\Omega}$ are taken from Ref.³⁸ for electron energies up

209 to 10 eV and from Ref.³⁹ for faster electrons. A constant He density of $n = 2.18 \cdot 10^{22} \frac{\text{Atoms}}{\text{cm}^3}$ ⁴⁰ is assumed.

210 Data availability

211 The data measured, simulated, and analyzed in this study are available from the corresponding author on reasonable
212 request.

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217 Author contributions

218 M.K. conceived and designed the experiment with contributions of L.T. and M.K.-Z. ; P.H. built the experimental
219 setup with contributions of B.T. and M.K.; L.T. B.T., and M.S. performed the experiment; L.T. performed the
220 simulations with contributions of P.H.; L.T., B.T., M.K., and M.K.-Z. analyzed the data; all authors contributed to
221 the interpretation of the results; L.T., and M.K. wrote the paper.

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Figures

Figure 1

Comparison of electron spectra obtained by strong-field ionization with 800 nm light (1.55 eV photon energy) of different species in gas-phase (ATI spectra, black) and inside HeN (LAES spectra, red): (a) In atoms, (b) Xe atoms, (c) acetone (AC) molecules. The spectra are area-normalized in order to account for

the reduced ionization energy inside a HeN28. Above each plot the values of the ionization energy, E_i , laser intensity, I , ponderomotive potential, U_P , and droplet radius, R_d , are listed. (d) ATI spectra (dashed lines) and LAES spectra (solid lines) as in a-c but with 3 eV binning (left ordinate), and cross section for total elastic electron scattering of electrons and He (gray line, right ordinate)29.

Figure 2

Dependence of LAES spectra on the droplet size, for droplet radii between $R_d = 32 \text{ \AA}$ and $R_d = 340 \text{ \AA}$ (R_d values are calculated from the mean values of the droplet size distributions25). The spectra are obtained with In atoms at $I = 1.1 \cdot 10^{13} \text{ W/cm}^2$ and show a pronounced increase of the LAES energy gain with He shell thickness. Additionally, the gas-phase ATI spectrum is shown for comparison. The abrupt increase of the droplet radius to $R_d = 340 \text{ \AA}$ for the lowest droplet source temperature ($T_0 = 10 \text{ K}$) is due to the

changing character of the supersonic expansion from sub- to supercritical in this temperature regime²⁵.

(b) Close-up of the low-energy region of (a).

Figure 3

3D simulation of electron trajectories inside a He droplet for different kinetic energies E_{kin} and different droplet radii R_d in similarity to Tulskey et al.³². An ensemble of $1 \cdot 10^5$ electrons is considered. (a) Probability that an $E_{kin} = 2 \text{ eV}$ electron has been ejected as function of time T for different R_d . Inset:

Probability density of the number of scattering events within 25 fs for $E_{\text{kin}} = 2$ eV. (b) Same as (a) but for $E_{\text{kin}} = 10$ eV. (c) Mean number of scattering events within 25 fs [c.f., insets in (a) and (b)] as function of the droplet radius for $E_{\text{kin}} = 2; 5; 10; 20; 50; 100$ eV. Vertical lines indicate the R_d -values that are considered in (a) and (b). (d) Probability distribution of total scattering events, i.e., without temporal limit, for $E_{\text{kin}} = 5$ eV.