High-Resolution Imaging of C + He Collisions using Zeeman Deceleration and Vacuum-Ultraviolet Detection

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ABSTRACT: High-resolution measurements of angular scattering distributions provide a sensitive test for theoretical descriptions of collision processes. Crossed beam experiments employing a decelerator and velocity map imaging have proven successful to probe collision cross sections with extraordinary resolution. However, a prerequisite to exploit these possibilities is the availability of a near-threshold state-selective ionization scheme to detect the collision products, which for many species is either absent or inefficient. We present the first implementation of recoil-free vacuum ultraviolet (VUV) based detection in scattering experiments involving a decelerator and velocity map imaging. This allowed for high-resolution measurements of state-resolved angular scattering distributions for inelastic collisions between Zeeman-decelerated carbon C(3P_J) atoms and helium atoms. We fully resolved diffraction oscillations in the angular distributions, which showed excellent agreement with the distributions predicted by quantum scattering calculations. Our approach offers exciting prospects to investigate a range of scattering processes with unprecedented precision.
implementation of VUV-based REMPI detection in a crossed beam experiment employing a decelerator and VMI. The C atom is well suited for manipulation using magnetic fields, and thus, we used a Zeeman decelerator to prepare velocity-controlled packets of \(C^1P_j\) atoms with narrow velocity and angular spreads. Despite the challenges arising from the reduced carbon beam density after deceleration and the low VUV power generated by difference frequency mixing, scattered carbon atoms were efficiently detected without ion-recoil by implementing a \((1 + 1)\) (VUV + UV) REMPI scheme. The resulting exceptional resolution allowed us to fully resolve diffraction oscillations, for which excellent agreement was found with simulations based on ab initio calculations of the involved potential energy curves (PECs). Since the use of VUV light for REMPI detection is generally applicable and provides the perspective of recoil-free \(\delta\)-motion, this approach offers exciting prospects to study a large range of collision processes with an unprecedented level of precision.

The recoil-free \((1 + 1)\) (VUV + UV) REMPI scheme for the state-selective detection of \(C^1P_j\) atoms is schematically depicted in Figure 1a. It employs the \(2p^33P_j \rightarrow 2p^23P_j\) transition induced by 166 nm VUV light, which is produced by difference frequency mixing \((2\omega_1 - \omega_2)^{38,39}\) of copropagating \(\lambda_1 = 212.56\) nm (0.5 mJ) and \(\lambda_2 = 296\) nm (0.4 mJ) laser beams focused inside a gas cell filled with 85 mbar krypton. While this transition is well known from precision spectroscopy experiments, it has not been used for REMPI detection in previous scattering experiments. The ion-recoil associated with the excess energy of ionization by, for example, a \(\lambda_1\) or \(\lambda_2\) photon is generally of no particular importance for spectroscopic investigations. When imaging scattering distributions, however, this ion-recoil induces a velocity blurring that washes out the fine structures that can be observed. Therefore, our implementation, which is similar to that of Glab et al., uses \(\lambda_3 \sim 329\) nm light (8.5 mJ, partially focused) for subsequent near-threshold ionization that allows for efficient high-resolution imaging of the carbon atoms.

For the VUV excitation step, the \(2p^33P_j\) intermediate state was chosen to state-selectively detect either the \(C^1P_j\) from the decelerated beam or the \(C^3P_j\) scattering product. The UV laser pulses \((212, 296,\) and \(329\) nm) were generated by frequency doubling or tripling the output of three separate dye-lasers. Optimal time overlap for the 212 and 296 nm laser pulses used to generate VUV light was ensured with the use of a shared Nd:YAG pump laser and suitable delay line. For the 329 nm ionization laser a separate Nd:YAG pump laser was used. The time jitter for each pump laser amounts to less than 1 ns, which is significantly shorter than both the laser pulse duration of around 6 ns full width at half maximum (fwhm) and the expected 2.7 ns lifetime of the \(2p^33P_j\) intermediate state.\(^{32,35}\) The VUV light was not separated from its parent \(\lambda_1\) and \(\lambda_2\) UV beams, and was focused by a MgF₂ lens (focal length \(\sim 275\) mm) at a substantial distance behind the detection region.

When scanning the \(\lambda_3\) ionization laser wavelength after VUV excitation, see Figure 1b, a clear step in the ion yield was observed for the threshold of both the \(2^3P_{1/2}\) ionic ground state, as well as the \(2^3P_{3/2}\) state of the ion that lies just 63.42 cm\(^{-1}\) higher in energy.\(^{44}\) Furthermore, just above the \(2^3P_{3/2}\) threshold a series of sharp peaks can be observed that correspond to resonant excitation to autoionizing Rydberg states.\(^{46}\) While these resonances provide a strong enhancement in signal level just above the ionization threshold, many of them lead to a small increase in blurring of the VMI images. This blurring is attributed to the expected long lifetimes of these Rydberg states that can lead to an effective enlargement of the ionization volume. In combination with the already large laser-overlap volume (several mm in each dimension), this poses especially demanding conditions for accurate velocity mapping. However, the resonance at \(\lambda_{\text{res}} = 328.5079\) nm, indicated by the arrow in Figure 1b, was found to give a significant increase in ion yield while causing only a marginal increase in image blurring. At this peak, the ratio of the signal levels with the \(\lambda_{\text{res}}\) laser on and off was found to be around 33:1, which gives a lower bound for the ratio between signal from low-recoil near-threshold ionization and the high-recoil contribution from ionization by the \(\lambda_1\) and \(\lambda_2\) laser beams copropagating with the VUV light. It should be noted that separation of the VUV light from its parent UV beams by suitable dichroics should effectively eliminate the high-recoil contribution, and would allow for the use of stronger VUV radiation to increase the ion yield while maintaining low overall recoil.

To illustrate the improvement in image resolution afforded by the implementation of the \((1 + 1)\) REMPI scheme, the
packet of C(3P_1) atoms exiting the decelerator with a mean longitudinal velocity of v^l = 300 m/s was velocity map imaged both with and without the addition of the λ_{33.4} laser after VUV excitation, as well as with a conventional (2 + 1) REMPI detection scheme. The results are depicted in Figure 1c–e. For (2 + 1) REMPI detection, a 280.31 nm laser (10.5 mJ, partially focused) was used to induce the 2p^3P_1 \rightarrow 2p^3P_0 transition and subsequently ionize the atom, as schematically depicted in Figure 1a. The image noise arising from the ionization of background gas was found to be strongly increased for (2 + 1) REMPI detection in comparison with the VUV-based detection schemes. To suppress this noise, the \(^{13}\)C isotope was used when employing the (2 + 1) REMPI scheme, while the naturally most abundant \(^{12}\)C isotope was used for the images recorded with VUV radiation. Both isotopes are transmitted through the Zeeman decelerator with near-identical efficiency. The laser powers were attenuated for each beamspot image such that less than one ion per shot was recorded on average. The 36 m/s recoil for the (2 + 1) REMPI detection of \(^{12}\)C causes the ion signal to appear on a ring centered around the mean velocity of the decelerated beam, and with a radius corresponding to the recoil velocity (see Figure 1c). The intensity distribution along the ring depends on the initial orbital of the ejected electrons as well as the laser polarizations. Similarly, when ionizing by \(\lambda_1\) and \(\lambda_2\) after VUV excitation, two concentric rings are observed that correspond to \(^{12}\)C recoil velocities of 39 and 17 m/s, respectively (see Figure 1d). By contrast, when employing the \(\lambda_{33.4}\) light for near-threshold ionization after VUV excitation, which reduces the \(^{12}\)C ion-recoil to <0.9 m/s, a small and well-defined spot is observed in the VMI image that reflects the velocity spreads of the Zeeman decelerated VMI beam itself (see Figure 1e). The low VUV power generated by difference frequency mixing suppressed the absorption of another VUV photon after VUV excitation, and signals from this high-recoil ionization process could not be distinguished.

The near-threshold (1 + 1′) REMPI scheme implemented here appeared remarkably efficient. The (1 + 1′) scheme provided a similar ion yield as the conventional (2 + 1) REMPI scheme, while a strong decrease in ionization of background gas was observed. Together, this resulted in a significantly better signal-to-noise ratio in the scattering images captured with the (1 + 1′) (VUV + UV) detection method. These observations show that, despite the low VUV power, VUV + UV detection as employed here can provide a promising path to recoil-free detection of species for which near-threshold (UV + UV′) REMPI schemes are either unavailable or experience strong (UV + UV) competition associated with large ion recoil.

The packets of C(3P_1) atoms that exit the decelerator with various selected longitudinal velocities (v^l) were characterized by recording their time-of-flight (TOF) profiles and by imaging their velocity distributions using VMI in combination with the low-recoil REMPI scheme. The TOF profiles are depicted in Figure 2 and show excellent agreement with the profiles obtained from numerical particle trajectory simulations that take into account the forces exerted on the C(3P_1) atoms by the space- and time-dependent fields inside our Zeeman decelerator apparatus. The VMI images were recorded at the peaks of the TOF profiles and thus capture the velocity distributions of the most intense part of the packets (see Figure 1e for the example of v^l = 300 m/s). From these images, the velocity distributions in both the longitudinal (∥) and transverse (⊥) direction were extracted and fitted with a Gaussian function. The resulting fwhm velocity spreads are summarized in Table 1 and show good agreement with the values extracted from the simulations.

The well-controlled packets of Zeeman-decelerated C(3P_1) atoms in combination with the efficient low-recoil detection are an ideal starting point for a high-resolution crossed-beam scattering experiment. To demonstrate this, we recorded scattering images for de-excitation C(3P_1) + He → C(3P_0) + He collisions (see Figure 3) at three different collision energies (E_{coll}), see Figure 3a–c. The images are presented such that the relative velocity vector is directed horizontally, with forward scattering angles positioned at the right side of the image, see Figure 3d. Small segments of the images are masked where the initial atomic beam gives a contribution to the signal. Besides the strong scattering ring corresponding to 3P_1 → 3P_0 de-excitation, a weak outer ring is observed for the 3P_1 → 3P_0 channel, which arises from the significantly lower density of C(3P_1) that is codecelerated with the C(3P_0) atoms. The two rings are well separated due to the high image resolution.

In each of the recorded scattering images, a clear oscillatory pattern can be observed by virtue of the exceptional resolution afforded by the combination of Zeeman-deceleration, VMI, and near-threshold ionization used in the experiment. These oscillations result from the quantum mechanical nature of the atoms that leads to diffraction of matter waves during the collision. The angular scattering distributions, shown in Figure 3a–c, are retrieved from the experimental image intensities within a narrow annulus around the observed rings and can be directly compared to the distributions obtained from simulated images. Our image simulations are based on theoretical state-to-state cross sections acquired from quantum mechanical close-coupling (QM CC) calculations that use state-of-the-art ab initio C–He PECs in combination with the particle trajectory simulations on our Zeeman decelerator apparatus. The simulated images are shown next to the experimental ones, and are analyzed analogously to their experimental counterparts to acquire predicted angular scattering distributions that take into account the spatial, temporal, and velocity spreads of the used atomic beams, as well as kinematic effects.
on the scattering distributions. Our measurements are in excellent agreement with the simulated distributions, which confirms the high quality of the PECs used in the scattering calculations.

A qualitative understanding of the diffraction oscillations follows from a semiclassical picture in which a matter wave scatters on a structureless target. Within a hard-sphere model, the angular spacing between diffraction peaks can be approximated by $\Delta \theta = \pi/(kR)$, in which $k$ denotes the wavenumber of the incoming wave and $R$ is the radius of the sphere. The collision energy is related to $k$ through $\hbar k = \sqrt{2\mu E_{\text{coll}}}$, where $\mu$ is the reduced mass of the system.

Table 1. Experimental (Exp.) and Simulated (Sim.) Longitudinal ($\sigma_v^i$) and Transverse ($\sigma_v^s$) FWHM Velocity Spreads of the Packets of C($^3P_1$) Exiting the Zeeman Decelerator with Different Mean Longitudinal Velocities ($v^l$)\textsuperscript{a}

| $v^l$ (m/s) | fwhm $\sigma_v^i$ (m/s) | fwhm $\sigma_v^s$ (m/s) |
|------------|--------------------------|--------------------------|
| 700        | 15.6                     | 10.0                     |
| 600        | 13.4                     | 9.7                      |
| 500        | 12.2                     | 11.5                     |
| 450        | 9.2                      | 10.9                     |
| 400        | 11.7                     | 7.7                      |
| 350        | 6.7                      | 8.9                      |
| 300        | 4.8                      | 7.8                      |
| 250        | 4.1                      | 8.0                      |

$^a$The possible contribution of residual ion-recoil to the experimental velocity spreads is not included in the simulations.

Table 2. Parameters Used for and Following from the Hard-Shell Model\textsuperscript{a}

| $E_{\text{coll}}$ (cm$^{-1}$) | $R$, $^3\Sigma$ PEC ($a_0$) | $R$, $^3\Pi$ PEC ($a_0$) | $\Delta \theta$ hard shell, $^3\Sigma$ PEC (deg) | $\Delta \theta$ hard shell, $^3\Pi$ PEC (deg) | $\Delta \theta$ QM CC calculations (deg) |
|-------------------------------|-----------------------------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| 32.5                          | 5.0                         | 6.1                         | 28                             | 23                             | 26                             |
| 53.1                          | 4.8                         | 5.9                         | 23                             | 19                             | 20                             |
| 91.2                          | 4.7                         | 5.6                         | 18                             | 15                             | 15                             |

$^a$For the experimental collision energies ($E_{\text{coll}}$), the radius ($R$) of the sphere, and the angular spacing ($\Delta \theta$) between the diffraction oscillations following from the QM CC calculations and the hard-shell model with the two potential energy curves (PECs) are listed.

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combination of Zeeman deceleration, VMI, and near-threshold VUV-based REMPI detection allows for high-resolution measurements that provide a sensitive test for theoretical models. The resolution attained here is similar to the resolution achieved in crossed beam experiments that use Stark decelerated NO radicals, which currently defines the state of the art in this type of experiments.21,22,45,46

Our approach opens new vistas to study interesting collision phenomena in a wide variety of systems, for example, the observation of predicted scattering resonances in the ICSs and accompanying rapid changes of structure in the DCs of low energy C(3P) + H2, as well as C(3P) + H2 de-excitation collisions.28,29 Moreover, inelastic scattering of C(3P) atoms with complex molecules like O2 and NO could be investigated in collisions.28,29 Additionally, since a large variety of chemically relevant species are amenable to Zeeman or Stark deceleration16 for theory. Additionally, since a large variety of chemically relevant species interact, thus providing a further challenge for theory. Additionally, since a large variety of chemically relevant species is amenable to Zeeman or Stark deceleration16 and the use of VUV light provides the perspective of recoil-free REMPI detection for many species, the combination of techniques demonstrated here offers new and exciting prospects to study a large range of collision processes with an unprecedented level of precision. Noteworthy species like OH, CO, NH3, and CH3 possess well-known VUV transitions,47–50 although for some the intermediate state is strongly predissociative, and it remains to be seen how efficient and state-selective near-threshold multicolor REMPI schemes are best implemented for these species. Furthermore, making use of the recently reported near-threshold VUV-based REMPI schemes for H/D52 or O(3P) atoms,52 our approach provides a pathway to high-resolution and low-energy investigations of elementary reactive scattering processes that produce O or H atoms, such as C + O2 → CO + O53,55,54 or complex-forming reactions between Zeeman decelerated atoms and H2 molecules.55–57

### EXPERIMENTAL METHODS

A beam of carbon atoms, C(3P), with a mean velocity of around 550 m/s was generated by running an electric discharge through an expansion of 2% CO seeded in krypton (see Figure 4), using a Nijmegen pulsed valve (NPV) with discharge assembly.46 After the expansion, the majority of the carbon atoms resided in the 3P0 ground state spin–orbit level, while the 3P1,2 levels were much less populated. This beam of carbon atoms then passed a skimmer and entered the Zeeman decelerator, of which a detailed description is given elsewhere.60 Briefly, it consists of an alternating array of pulsed solenoids and permanent magnetic hexapoles that allow independent control over the longitudinal and transverse motion of paramagnetic species, respectively. The decelerator contains a total of 100 solenoids and 101 hexapoles and was operated at a repetition rate of 20 Hz. Each coil can be pulsed once to either accelerate or decelerate the packet of C atoms as it passes the coil (acceleration or deceleration mode). Double pulses can be used (hybrid mode), for example to increase contrast in the TOF profiles for mild deceleration or to guide the packet through the decelerator at a constant speed (guiding).59 The C atom 3P1 state has a magnetic moment of 1.5 μB and splits into mJ = 0, ±1 components in the presence of a magnetic field, with mJ the projection of the total electronic angular momentum j on the space-fixed z-axis. The mJ = 1 component was effectively manipulated with the decelerator. Similarly, the 3P2 state has a magnetic moment of 3 μB and splits into five components, that is, mj = 0, ±1, ±2. Although the C(3P2, mJ = 1, 2) components were codecelerated with the C(3P1, mJ = 1) atoms, their density in the beam was significantly lower. While the 3P0 state had a much higher initial population, it only has an mJ = 0 component, which is almost insensitive to magnetic fields. The resulting free flight through the decelerator heavily reduced the 3P0 atom density, such that its final contribution was negligible. Thus, after the decelerator a beam of mainly C(3P1) atoms was obtained with controlled velocity and narrow angular and velocity spreads. A series of 13 additional hexapoles guided the packets of C(3P1) atoms toward the interaction region, where they were intersected by a beam of He atoms at an angle of 46° about 368.5 mm from the decelerator exit. The He beam was produced using an Even–Lavie valve (ELV) that was cryogenically cooled to control the mean velocity, thus changing the mean collision energy to 32.5, 53.1, or 91.2 cm−1 when intersected by the packets of C(3P1) atoms that were decelerated to a final velocity of 350 m/s. After scattering, the product C(3P0) atoms were state-selectively ionized using a near-threshold (1 + 1′) (VUV + UV) REMPI scheme, and detected with the use of high-resolution VMI ion optics that allows for accurate mapping of large ionization volumes.60

![Figure 4. Schematic depiction of the crossed-beam setup. The used combination of Zeeman deceleration, (1 + 1′) (VUV + UV) near-threshold REMPI detection and VMI allowed for high-resolution imaging of C atom scattering distributions after interaction with He.](https://doi.org/10.1021/acs.jpclett.1c03643)
Because of the obtained narrow velocity spreads of the decelerated C atoms the scattering signal arising from the contribution of decelerated initial C(3P) could be well separated from the main C(3P) contribution.

■ THEORETICAL METHODS

In a full description of the collision process including the electronic fine-structure of the C atom, the states in the C(3P)+He arrangement are described by the quantum number \( j \) which corresponds to the total electronic angular momentum of the \( ^3P \) carbon atom (\( j = L + S \) with \( L \) and \( S \) the electronic orbital and spin angular momenta, respectively). For the collision energy spreads as a Gaussian distribution. The calculations were performed with the C-HIBRIDON package.\(^{62} \) The calculations were performed with the spin-hybridization method of Pouilly et al.\(^{61} \) implemented in the HIBRIDON package.\(^{62} \) The calculations were performed with C–He PECs of Bergeat et al.\(^{24} \) calculated using the spin-polarized valence quintuple-zeta (aug-cc-pV5Z) basis set completed with additional 3s 3p 2d 2f 1g midbond functions.\(^{64} \) The asymptotic experimental spin–orbit splitting of C(\( ^3P \)) (\( \Delta_{SO} = 16.4167 \text{ cm}^{-1} \) and \( \Delta_{j \pi} = 43.413 \text{ 50 cm}^{-1} \))\(^{65} \) was used in the computation of energy levels and in the quantum scattering calculations. In all calculations, the propagation was performed for \( R \) ranging from 2.5 to 80 Bohr, with \( R \) the interatomic C–He distance. The reduced mass of the C–He complex is \( \mu = 3.001 \text{ u.} \) At each collision energy, the maximum value of the total angular momentum \( J_{\text{max}} \) was set large enough to converge the integral and differential cross sections within 0.001 \( \text{Å} \). The effective DCs that were used as input for the image simulations were constructed from the computed DCs by taking into account the experimental collision energy spreads as a Gaussian distribution.

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Notes

The authors declare no competing financial interest.

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