Formation and Attosecond Carrier Dynamics of a Two-Dimensional Electron Gas in K/MoS\textsubscript{2}

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Abstract

Electronic interactions associated with atomic adsorbates on transition metal dichalcogenides such as MoS$_2$ can induce massive electronic reconstruction. This offers a powerful handle to tailor the electronic structure of this versatile materials class beyond changes of chemical composition or the creation of van der Waals heterostructures. To take full advantage of this approach, it is important to understand the mechanism and the consequences of the adsorbate-induced reconstruction for carrier dynamics. Here we show by a combination of angle-resolved photoemission and advanced x-ray spectrosopies that potassium intercalation in MoS$_2$ creates a two-dimensional electron gas by forcing orbital rehybridization. The resulting electronic structure resembles that of a monolayer, and the resulting many-body interactions in reduced dimension drastically shorten carrier lifetimes to below 0.5 fs. Together, these observations provide evidence that K intercalation brings about the emergence of new quasi-two-dimensional electronic phases at the surface of a bulk transition metal dichalcogenide.
Two-dimensional electron gases (2DEGs) provide an exquisite test-bed for strongly correlated physics in reduced dimension. In 2D, a balance between fluctuations and order parameter scales gives rise to exotic phenomena, including spin-charge separation, superconductivity and possibly magnetism. Beyond oxide heterointerfaces, 2DEGs have been observed in semiconductor quantum well structures, image potential states, and more recently in black phosphorous. A more detailed understanding of the many-body physics at play may be obtained from the ultrafast dynamics of carriers in a 2DEG, but such studies have so far been mostly restricted to spin scattering and image potential states.

Here, we report on ultrafast carrier dynamics and 2DEG formation in two-dimensional layered transition metal dichalcogenides (TMDs). TMDs have unique layer-dependent electronic properties, including thickness-dependent bandstructure and an indirect-to-direct bandgap transition, topological phases and spin and valley polarization. The rich physics also hold promise for next-generation electronics such as field-effect transistors, light-emitting diodes, photovoltaics, spin- and valley-based devices and quantum information processing. The confinement of the wavefunction to individual layers which is central to many of the unique properties and applications of TMDs also makes them ideally suited to potentially support 2DEGs even in bulk crystals. Indeed, 2DEGs have been reported in electron doped WSe$_2$ as well as monolayer TMDs. Such strong doping may be achieved with alkali adsorbates, which may also induce structural transformations between different polytypes, metal-to-insulator transitions and bandgap renormalization. Though Li adsorbates react with the TMD, more typically alkali dopants adsorb or intercalate, as shown for Na, K, Rb and Cs.
In this work, we demonstrate by angle-resolved photoemission spectroscopy (ARPES) and element- and orbital-selective core-hole clock spectroscopy (CHC)\textsuperscript{41–45} the effect of K-doping induced massive electronic reconstruction and formation of a state resembling a 2DEG. CHC shows that this reconstruction is associated with dramatically increased electron scattering rates at $K\bar{K}$, reducing the lifetime to a few hundred attoseconds. The atom-specificity and orbital-selectivity of CHC spectroscopy reveals that the origin for these changes rests in intralayer orbital rehybridization, increasing quantum confinement of the conduction band wavefunction and creating a quasi-freestanding monolayer-like structure of MoS$_2$. Our study directly demonstrates how reduced screening in the 2DEG of quasi-2D MoS$_2$ increases carrier scattering rates on attosecond time-scales.

\textit{Results}

\textbf{Valence Band of MoS$_2$ and K/MoS$_2$}

The occupied bandstructure of bulk MoS$_2$ has been well established in both high-resolution experiments\textsuperscript{10} and state-of-the-art computations.\textsuperscript{46} Our ARPES results show good agreement with previous reports (Fig. 1a). In bulk MoS$_2$, the bandgap is indirect and located at $\bar{\Gamma} - \bar{\Sigma}$ with an energy of 1.4 eV, while the direct bandgap of 1.9 eV is at $K$.\textsuperscript{10,12} The valence band supports a spin-orbit splitting of 180 meV at $K$ due to the dominant Mo character at the band edge, which is poorly resolved in our room temperature spectra.
The change of the MoS$_2$ band structure with addition of 0.15 ML K is illustrated in Fig. 1b, and similar data were obtained for other low K coverages. All energy levels shift to higher binding energies, indicative of K-induced $n$-doping. Though matrix element effects suppress the photoemission intensity at $\Gamma$, it is obvious that the bands do not shift rigidly: At $\Gamma$, the binding energy increases by 0.31(2) eV, while at $K$ the shift is 0.72(2) eV. This is a first indication that K atoms do not merely function as $n$-dopants but rather induce a massive reconstruction of the electronic structure in MoS$_2$. We further observe occupation of the conduction band minimum at $K$, creating an approximately direct bandgap system with a bandgap $E_{g,\text{direct}} = 2.0(1)$ eV, as measured from the onsets of both bands. This is another sign of severe electronic reconstruction upon K-doping, since in bulk MoS$_2$ the conduction band minimum is located at $\bar{\Sigma}$ instead of $\bar{K}$. Though the specific changes to the
band structure differ somewhat on a quantitative level, e.g. in the magnitude of the shifts of band extrema at \( \Gamma \) and \( K \), the transition to a direct-gap system and the accompanying electronic reconstruction are reminiscent of electronic structure differences between bulk and monolayer MoS\(_2\).\(^{12}\) In that case, band structure changes are generally believed to be due to quantum-confinement of out-of-plane orbitals at \( \Gamma \) and \( \Sigma \) while leaving the Mo \( d_{x^2−y^2} \) and \( d_{xy} \) in-plane orbitals that dominate the valence band at \( K \) unaffected.\(^{47}\) Addition of potassium atoms to bulk MoS\(_2\) therefore induces layer a measure of decoupling and the emergence of MoS\(_2\) structures that are rather similar to nominally isolated monolayers. True MoS\(_2\) monolayers are normally only accessible by exfoliation or direct growth. Importantly, this decoupling is accompanied by filling of the \( K \)-valley by electrons, creating a state that approximates a multivalley two-dimensional electron gas (2DEG), as also reported for Rb-dosed WSe\(_2\).\(^{26}\)

The majority of K atoms initially adsorb on the surface, followed by prompt intercalation into the layered MoS\(_2\) crystal, as observed in the XPS data (see Supplementary Figure 1). This is supported by both work function and band structure that show no large time-dependent changes, remaining stable over many hours after dosing, and the fact that the K coverages and a temperature of 298 K used here kinetically favor intercalation.\(^{40,48,49}\) Indeed, surface adsorption has been reported to shift the band structure rigidly,\(^{50}\) in contrast to our findings. K intercalation is also supported by theoretical predictions\(^{51,52}\) and previous electronic structure investigations.\(^{35}\)

Our ARPES results are in good agreement with other reports on alkali dosing of transition metal dichalcogenides. While ARPES clearly demonstrates the strong electronic reconstruction upon K dosing, and suggests the formation of a 2DEG, it does not provide a
microscopic mechanism for this effect. Mechanistic insights can however be obtained from element-selective x-ray spectroscopy to resolve carrier dynamics with attosecond resolution.

**Conduction Band of MoS$_2$ and K/MoS$_2$**

As a first step we investigate the XA spectra of MoS$_2$ on the Mo M$_{2,3}$ edges (primarily $3p \rightarrow 4d$) to map the conduction band region (Fig. 2). Upon K intercalation, the intensity decreases and shifts by 0.39(2) eV towards lower photon energies. This is likely due to filling of the conduction band states, thus lowering the density of states and reducing

![Figure 2. X-ray absorption spectra of MoS$_2$ (black) and 0.2 ML K on MoS$_2$ (gray). Intensity is normalized with respect to the incident X-ray photon flux, $I_0$. The XA spectrum shows the spin-orbit components of Mo, M$_3$ ($3p_{3/2}$) and M$_2$ ($3p_{1/2}$).](image-url)
The conduction band of MoS\textsubscript{2} is composed of strongly hybridized Mo 4\textit{d} \otimes S 3\textit{p} \otimes S 3\textit{s} orbitals, with contributions from Mo 5\textit{p} as well, as determined by polarization-dependent XAS investigations of Mo L\textsubscript{2,3} by Li \textit{et al.}\textsuperscript{53} and from group theoretical considerations.\textsuperscript{54} The conduction band at \textit{\Gamma} is comprised mainly of Mo \textit{d}_{\textit{x}^2-\textit{y}^2} and \textit{d}_{\textit{xy}} orbitals, hybridized with S \textit{p}_x, \textit{p}_y orbitals, while at \textit{\bar{K}} and \textit{\bar{M}} the lowest few conduction bands support out-of-plane \textit{d} and \textit{p} character oriented along the \textit{z}-axis (surface normal).

\textbf{Resonant enhancement of Mo 3\textit{d} core-level}

To obtain the dynamics of conduction band electrons, we monitor the decay of the excited state using core-hole-clock spectroscopy (CHC). CHC is a rather general approach in which carrier lifetimes are retrieved from resonant photoemission spectroscopy intensity measurements.\textsuperscript{41} Specifically, while scanning an x-ray light source over the Mo M\textsubscript{2,3} absorption edge and following resonant excitation of the core electron to the conduction band (\textit{Mo} 3\textit{p} \rightarrow 4\textit{s}, 4\textit{d}), we monitor the photoemission intensity associated with specific decay channels of the core-excited electron from the conduction band. Comparison of this intensity in MoS\textsubscript{2} vs. K/MoS\textsubscript{2}, in relation to the known lifetime of the Mo 3\textit{p} core hole, enables us to obtain excited state dynamics with element- and orbital-specificity and on attosecond time-scales.\textsuperscript{55}

The scheme used here is shown in Fig. 3: Resonant excitation from Mo 3\textit{p} levels to the conduction band of MoS\textsubscript{2} (Fig. 3a) is followed by an Auger-like decay that results in a one-hole final state in the Mo 3\textit{d} manifold (Fig. 3b). In the CHC experiment, this participator decay channel manifests as resonant enhancement of photoemission from Mo 3\textit{d} levels. If on the time-scale of the Auger decay lifetime the excited electron escapes the potential exerted by the core hole e.g. due to delocalization or electron-electron scattering,
the expected resonant photoemission enhancement is however suppressed (Fig. 3c). The excited state decays instead via normal Auger processes. Consequently, Mo 3d photoemission appears with an intensity comparable to direct photoemission at similar photon energies. Resonant photoemission intensities therefore directly encode the dynamics of carriers.

Figure 3. CHC scheme for measuring attosecond conduction band dynamics in MoS2. a) Resonant excitation from Mo 3p to the conduction band of MoS2. b) Auger-like participator decay resulting in final state with Mo 3d hole. c) The excited electron delocalizes into the conduction band before core-hole decay, and normal Auger processes drive the system to its ground state. $\tau_{c-h}$ is the core-hole lifetime, and $\tau_{CB}$ is the lifetime of a conduction band electron.
We first analyze the resonant photoemission spectra and intensities. Fig. 4 shows the resulting resonant photoemission map for MoS\(_2\) and K/MoS\(_2\), together with the x-ray absorption spectrum of Mo 3\(p\) (M\(_{2,3}\)) in MoS\(_2\). Here, the photoemission spectrum is monitored in the Mo 3\(d\) region as a function of excitation energy. The photoemission maps exhibit for both samples strong resonant enhancement of both Mo 3\(d_{3/2}\) and 3\(d_{5/2}\) features across the Mo M\(_2\) and M\(_3\) edges. Also present at lower binding energy is a feature associated with resonant photoemission from S 2\(s\). For a more quantitative analysis, we focus in the remainder on the M\(_3\) edge to avoid interference from the K N-edge at 410 eV.

![Figure 4. Resonant photoemission contour plots (normalized intensity) of a) MoS\(_2\) and b) K/MoS\(_2\). c) Mo M\(_{2,3}\) XA spectrum, showing regions where resonantly enhanced photoemission may be expected.](image)

We extract the normalized photoemission intensity of the Mo 3\(d\) features from spectral fits of the photoemission spectra. Fig. 5a,b shows representative spectra at \(\hbar\omega = 391\) eV for both MoS\(_2\) and K/MoS\(_2\). For K/MoS\(_2\), the Mo 3\(d\) features are slightly asymmetric, necessitating the inclusion of a small shoulder feature indicative of a small fraction of partially reduced MoS\(_2\). Fig. 5d,e shows the evolution of the normalized Mo 3\(d_{5/2}\) and 3\(d_{3/2}\) photoemission intensities, excluding the minor contribution from reduced MoS\(_2\),
as a function of excitation energy and in comparison to the M₃ edge XAS in Fig. 5c. As already visible in Fig. 4, K intercalation suppresses photoemission for both photoemission channels, hence indicating that K intercalation and the associated electron density shorten the lifetime of electrons in the conduction band.

K intercalation promotes carrier delocalization

The core-hole decay of the Mo 3p₃/₂, has a known lifetime of \( \tau_{c-h} = \frac{1}{k_{c-h}} = 299 \) as (Ref. [56]) and is independent of the chemical environment.⁴¹ It functions as a natural clock against which electron dynamics in the conduction band can be measured in a competitive

Figure 5. Resonant enhancement of Mo 3d photoemission upon excitation at the Mo M₃ edge, for MoS₂ and K/MoS₂. Representative spectra at \( \hbar \omega = 391 \) eV for a) MoS₂ and b) K/MoS₂. A normal Auger feature was included in the fit as well, here appearing at binding energies above 232 eV, and a small contribution of reduced Mo accounts for the slightly asymmetric peak shape in K/MoS₂. c) Close-up of M₃ XAS. Normalized resonant intensities for MoS₂ and K/MoS₂ for d) Mo 3d₅/₂ and e) Mo 3d₃/₂. The error bar represents uncertainties in the x-ray intensity, obtained from Au 4f₇/₂ photoemission spectra acquired concurrently.
kinetics scheme (Fig. 3 and Supplementary Figure 2): The competition of core-hole decay vs. delocalization and scattering processes in the conduction band determines the intensity of the observed Mo 3d participator. We conservatively estimate that a signal-to-noise ratio of 10 is needed to differentiate intensities, which translates to an observable range of carrier lifetimes times of $0.1 \tau_{c-h} \leq \tau_{CB} \leq 10\tau_{c-h}$, where $\tau_{CB} = \frac{1}{k_{CB}}$ is the lifetime of carriers in the conduction band. We thus expect to be able to observe processes on time-scales from $30$ as to $3.0$ fs. Assuming first-order rate laws for all decay processes, $\tau_{CB}$ is obtained from the measured resonant photoemission intensities of the Mo 3d participator in MoS$_2$, $I_{MoS_2}^M$, and $I_{loc}$, the resonant photoemission intensity associated with a fully localized conduction band electron that undergoes exclusively core-hole decay:\[^41]\]

$$
k_{CB} = k_{c-h} \frac{I_{loc} - I_{MoS_2}}{I_{MoS_2}}
$$

In order to estimate $I_{loc}$, we make use of the known carrier lifetime in the conduction band of MoS$_2$ of $1.25$ fs.\[^57\] Though this measurement was obtained on the S K-edge, two resonant Auger studies of c(4x2)S / Ru(0001) probing core-holes on different edges found comparable carrier delocalization times, independent of the edge.\[^58\] We thus take the carrier lifetime of MoS$_2$ as $\tau_{CB} = 1.25$ fs, which is also consistent with the width of the XAS spectrum, and use this to estimate $I_{loc}$ of a putative fully localized Mo 3d$^{3/2}$ participator from Eqn. (1). The resonant photoemission intensities for the Mo 3d$^{3/2}$ and 3d$^{5/2}$ participator
in Fig. 5e,d are then used to extract the carrier lifetimes for MoS$_2$ and K/MoS$_2$ excited on the Mo M$_3$ edge, as shown in Fig. 6 and tabulated at the Mo M$_3$ edge in Table 1.

![Figure 6. Carrier lifetimes of MoS$_2$ and K/MoS$_2$. a) Mo M$_3$ XA spectrum. Carrier lifetimes of b) MoS$_2$ and c) K/MoS$_2$ calculated from Mo 3d resonant intensities and their uncertainties.](image)

**Table 1. Ultrafast carrier delocalization times of MoS$_2$ and K/MoS$_2$ (peak values, see Fig. 6).**

| XP feature | $\tau_{CB} = k_{CB}^{-1}$, MoS$_2$ (fs) at $\hbar \omega \sim 391$eV | $\tau_{CB} = k_{CB}^{-1}$, K/MoS$_2$ (as) at $\hbar \omega = 391$eV |
|------------|-------------------------------------------------|-------------------------------------------------|
| Mo 3d$_{5/2}$ | $1.24 \pm 0.34$ | $368 \pm 60$ |
| Mo 3d$_{3/2}$ | $1.25 \pm 0.62$ | $459 \pm 159$ |
The carrier lifetimes drop from approximately 1.25 fs to 300 – 500 as in K/MoS₂, approximately 3 × shorter than for MoS₂, and indicating that K intercalation generates additional pathways for inelastic scattering of conduction band electrons. Both participator channels, Mo 3d₃/₂ and 3d₅/₂, exhibit a qualitatively similar decrease; the difference stems largely from different energy-dependent partial photoionization cross-sections.⁵⁹

Discussion

The combination of ARPES and CHC spectroscopy indicates that K intercalation causes a strong electronic reconstruction, accompanied by the formation of a 2DEG and significantly shorter electronic lifetimes in the conduction band. The element- and orbital-selectivity of the x-ray spectroscopy help distinguish between different possible mechanisms at the root of these strong electronic changes.

A number of studies have demonstrated that alkali atom dosing induces a structural phase transition from the standard 2H- to 1T-MoS₂,³²,⁶⁰ triggered by intralayer atomic gliding. Signatures of this transition to the metallic 1T phase can be readily observed in XPS,⁶¹ manifesting e.g. as shifts in the Mo 3d levels by several eV. We do not observe such changes in the XPS. Moreover, though charge-density wave formation and suppression by alkali adsorbates has been observed in other van der Waals layered materials,³⁹ there is no indication of such a phase transition in the ARPES data. We may therefore exclude structural phase transformations as the source of the 2DEG formation.

Previous work showed that layered van der Waals materials are effectively two-dimensional on short time-scales, i.e. intralayer electron-transfer is approximately 10 × faster than interlayer electron transfer, \( k_{\text{intra}} \approx 10k_{\text{inter}} \).⁴³ It is conceivable that K
intercalation further separates adjacent MoS$_2$ sheets, thus further decoupling individual layers. Such simple “layer decoupling” is however unable to account for the observed shortened lifetimes upon K intercalation: Under the assumption of first-order kinetics inherent to CHC, and assuming the two rates $k_{\text{intra}}$ and $k_{\text{inter}}$ to be independent, the total rate $k_{\text{tot}}$ for conduction band electron transfer in real space is $k_{\text{tot}} = k_{\text{intra}} + k_{\text{inter}}$; simple layer decoupling due to increased separation of MoS$_2$ sheets by K intercalation would reduce $k_{\text{inter}}$ and therefore decrease $k_{\text{tot}}$, contrary to our observations of shortened carrier lifetimes and increased $k_{\text{CB}}$.

Instead, we make use of the element- and orbital-specificity of CHC spectroscopy to identify the mechanism for 2DEG formation. The $p$-polarized x-ray excitation probes predominantly out-of-plane Mo orbital constituents of the conduction band. In combination with the atomic selection rule of $\Delta \ell = \pm 1$, excitation from the Mo $3p$ core levels accesses preferentially out-of-plane $d$-orbitals such as $4d_{z^2}$. A group theory-based orbital decomposition of the MoS$_2$ conduction band indicates that such orbitals occur primarily at $\bar{K}$ and $\bar{M}$, and thus the CHC spectroscopy preferentially probes electron dynamics in these two regions. The $\bar{K}$ valley is also the region in the Brillouin zone of increased electron density upon potassium intercalation, and hence the most significant region for understanding the electronic reconstruction and the associated conduction band electron dynamics.

The out-of-plane character of the orbitals probed in our experiment accesses Mo orbitals that are hybridized with S ligand orbitals. Thus, an increase of $k_{\text{CB}}$ is the result of rehybridization and stronger mixing between Mo $4d_{z^2}$ and S $3p$ orbitals in K/MoS$_2$. In real space, this results in increased electron-electron interactions, i.e. increased scattering rates,
within a single MoS$_2$ layer (increased $k_{\text{intra}}$), and provides additional decay channels of the excited state. The decreased electronic lifetime in the doped MoS$_2$ involves thus both an increased phase-space for electron scattering and an increased scattering cross-section. The electron-doping induced many-body interactions cause rehybridization towards an electronic structure that resembles more closely that of the MoS$_2$ monolayer, which is the source of the strong electronic reconstruction and appearance of a direct bandgap in the ARPES data. At the same time, the increased intralayer interactions occur at the expense of interlayer coupling, confining the electrons more strongly to a single MoS$_2$ sheet and creating the observed 2DEG-like state.

Conclusion

We demonstrate with a combined ARPES and CHC study that K intercalation in MoS$_2$ leads to massive electronic reconstruction and 2DEG formation due to out-of-plane orbital rehybridization. The increased conduction band electron density and quantum confinement to a single MoS$_2$ layer causes dramatically increased electronic scattering rates with lifetimes reduced by a factor $\sim 3$ to approximately 300 – 500 attoseconds. Such fast electron scattering is a hallmark of reduced screening that accompanies confinement of layered van der Waals materials in the 2D limit. Evidently, this confinement-induced reduced screening is not offset by the doping-induced increased carrier density, and is rather the result of many-body interactions induced by filling of the $\bar{K}$-valley upon doping. Our study also shows that the ultrafast carrier dynamics of MoS$_2$ can be tailored rather simply, and opens opportunities for investigating the consequences of intercalation- or adsorption-induced inversion symmetry breaking and the possibility of spin-splitting on ultrashort time-scales.$^{34}$
Methods

Synthetically grown bulk 2H-MoS2 was purchased from 2D Semiconductors. The
MoS2 crystal was cleaved by mechanical exfoliation in a protective atmosphere before
introduction to an ultrahigh vacuum preparation chamber. Sample integrity was verified by
x-ray photoemission spectroscopy (XPS) of Mo 3d\textsubscript{5/2} and 3d\textsubscript{3/2} features, by sharp and intense
valence band features without an underlying defect background, and a work function of 5.2
eV. K deposition (SAES Getters) was calibrated on clean Cu(111), where the evolution of
the electronic structure as a result of alkali adsorbates has been studied in detail,\textsuperscript{62–64} and is
reported in fractions of a putative monolayer (ML).

X-ray absorption (XAS) and resonant photoemission (RPES) spectra were obtained
at Stanford Synchrotron Radiation Lightsource on beamline 8-2 (SLAC National
Accelerator Laboratory), with all experiments carried out at room temperature. XA spectra
were performed in total electron yield (TEY) mode using the drain current. XP and RPE
spectra were acquired with a double-pass cylindrical mirror analyzer for kinetic energy
discrimination of photoelectrons. The electric field of the near-grazing incidence x-ray beam
was linearly polarized in the horizontal plane, and excites thus predominantly transitions
that are polarized along the surface normal (z-axis). XP and RPE spectral resolution was
approximately 0.5 eV, with a pass energy of 25 eV. The base pressure of the analysis
chamber remained below 7 x 10\textsuperscript{-9} mbar throughout all measurements. Absolute energy
calibration and global vacuum level corrections were obtained from an Au film on a Si
wafer, and spectral intensities were calibrated against the incident X-ray photon flux (I\textsubscript{0})
measured on a gold grid upstream from the analysis chamber. All X-ray spectra were
corrected by subtraction of a linear background with a Shirley or integrated background.
Angle-resolved photoemission spectra (ARPES) were collected in a VG EscaLab MK II photoelectron spectrometer at room temperature with a base pressure of $2 \times 10^{-10}$ mbar. All measurements shown here were taken along the $\Gamma - \bar{K}$ direction with an acceptance angle of $\pm 1.5^\circ$ and a sample bias of -3 V, and using a He I source (SPECS 10/35, $\hbar \omega = 21.22$ eV) mounted at a 30° angle of incidence. ARPES data were processed using the curvature method.\textsuperscript{65}

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Contributions

C.N.E. and S.L.Z. carried out the experiments, C.N.E., J.P. and A.C. analyzed the results, and O.L.A.M. conceived and designed the experiments. C.N.E., D.L.N. and O.L.A.M. wrote the manuscript and discussed the results.

Competing interests

The authors declare no competing financial interests.
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Potassium Intercalation

To understand the fate of the K adsorbate, we performed x-ray photoemission spectroscopy (XPS) of 0.2 ML K on MoS$_2$ at a photon energy of 600 eV at grazing incidence angle (Supplementary Figure 1). The C 1s signal remains, indicative of a small amount of adventitious carbon on the MoS$_2$ crystal surface from cleaving and vacuum environment. In contrast, the K 2p peak diminishes promptly. In the chosen combination of photon energy and incidence angle, XPS is exquisitely surface sensitive with a measurement depth of a no more than one MoS$_2$ layer. The XP spectra demonstrate therefore unequivocally that K atoms do not stay as surface adsorbates but rather intercalate and diffuse irreversibly into the crystal to a depth of at least one layer. There are no further changes to the XP or resonant photoemission spectra over the course of the measurement period, indicating that initial
intercalation is fast while diffusion throughout the crystal is slow. This is also supported by the absence of any K 2p signatures after further cleaves of the MoS2 crystal.

![Supplementary Figure 1. X-ray photoemission spectra of K/MoS2 as a function of time.](image)

**Core-Hole Clock Spectroscopy Scheme of Competitive Kinetics**

Core-hole clock spectroscopy (CHC) may be readily interpreted in the framework of a scheme of two levels (ground state $|0\rangle$ and core-excited state $|1\rangle$) coupled to a continuum of states $|k\rangle$ composed of electronic states with crystal momentum $k$ (Supplementary Figure 2). Assuming that all decay channels are independent and that coherences can be neglected due to decay into dense continua, the decay of the core-excited state $|1\rangle$ may occur through a number of Auger decay processes with a combined rate $k_{c-h}$, or by delocalization into the continuum of electronic states $\{|k\}\rangle$ in the solid and characterized by rate $k_{CB}$. If $k_{CB} \ll k_{c-h}$, resonant excitation of $|1\rangle$ enhances the intensity
of the photoemission features associated with the Auger-like decays, while such enhancement is suppressed if instead $k_{CB} \gg k_{c-h}$. The competition of these two decay processes, governed by the relative magnitude of the two rate constants, determines therefore the intensity of the associated spectroscopic features in the resonant photoemission spectra.

Supplementary Figure 2. Principle of CHC to determine lifetimes. The relative magnitude of the two rate constants $k_{c-h}$ and $k_{CB}$ determines the intensity of associated Auger features in the resonant photoemission map.