Title
Manipulating Core Excitations in Molecules by X-Ray Cavities

Permalink
https://escholarship.org/uc/item/4ck0r7wz

Journal
Physical Review Letters, 126(5)

ISSN
0031-9007

Authors
Gu, Bing
Nenov, Artur
Segatta, Francesco
et al.

Publication Date
2021-02-05

DOI
10.1103/physrevlett.126.053201

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at https://creativecommons.org/licenses/by/4.0/

Peer reviewed
Manipulating Core-Excitations in Molecules by X-ray Cavities

Bing Gu,1,∗ Artur Nenov,2,∗ Francesco Segatta,2 Marco Garavelli,2,† and Shaul Mukamel1,†

1Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, 92697, USA
2Dipartimento di Chimica Industriale “Toso Montanari”, Università degli studi di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy.

Core-excitations on different atoms are highly localized and therefore decoupled. By placing molecules in an X-ray cavity the core-transitions become coupled via the exchange of cavity photons and form delocalized hybrid light-matter excitations known as core-polaritons. We demonstrate these effects for the two inequivalent carbon atoms in 1,1-difluoroethylene. Polariton signatures in the X-ray absorption, two-photon absorption, and multidimensional four-wave mixing, signals are predicted.

Hybrid light-matter states between the material polarization and cavity photon modes, known as polaritons, are created when the light-matter coupling strength g is larger than the decay rate of the cavity mode and the decoherence rate of the molecular transition (the strong coupling regime). When the cavity mode is in the vacuum state, the effective coupling strength for an assembly of N identical molecules is

\[ g = \frac{\sqrt{N}}{\hbar} \frac{\mu_{g}}{\sqrt{\varepsilon_{0} V_{c}}} \]

where \( \varepsilon_{0} \) is the electric permittivity of vacuum, \( \omega_{c} \) the cavity frequency, \( \mu \) the transition dipole moment, and \( V_{c} \) is the cavity mode volume [1]. The \( \sqrt{N} \) factor is responsible for cooperative superradiance [2, 3]. Cavity polaritons in the visible and infrared regime have long been studied in atoms and were recently experimentally reported in molecules [4–11]. Molecular electronic and vibrational polaritons have been experimentally shown to alter the electronic, optical, and chemical properties of molecules including photoisomerization, electronic energy transfer, electron transfer, and ground-state reaction rates [9]. These findings had triggered intensive theoretical investigations [3, 6, 12–30].

Thin-film optical cavities in the hard X-ray regime have been recently employed in the study of collective Mössbauer signals of 57Fe nuclei (14.4keV) [31–33] and tantalum L-edge X-ray spectra (9881 eV) [34]. A \( \sim 41 \) eV effective light-molecule coupling strength for low-finesse X-ray cavities has been reported [34]. X-ray cavities in the soft X-ray regime can be formed by alternating nanometer layers of materials with different indices of refraction, and are on the horizon. For high-reflectivity mirrors, the cavity photon modes satisfy \( n + \frac{1}{2} \lambda_{n} = L \), where \( L \) is the cavity length and \( \lambda_{n} \) the wavelength of the cavity mode. For carbon K-edge (\( \sim 300 \) eV), it corresponds to \( L \sim 10 \) nm.

Here we study molecular polariton effects in the X-ray regime whereby a high-finesse X-ray cavity mode couples to molecular core-excitations. We demonstrate that localized excitations from inequivalent carbon core-orbitals in 1,1-difluoroethylene can be coupled by the exchange of an X-ray cavity photon, leading to hybrid core-excitation with X-ray cavity photon modes. Rich exciton-polariton physics has been observed in the optical regime. This includes long-range transport [35, 36], enhanced optical nonlinearity, modified chemical reactions, polariton lasers, optical transistors, and phase transitions [9]. Our study suggests that similar phenomena may be expected for core-polaritons in the X-ray regime. X-ray cavities enable long-range transport of core-excitations or core-holes despite their highly localized nature as long as the light-matter coupling strength is stronger than their decay rates [35, 36]. We predict signatures of core-polaritons in the X-ray absorption spectrum, in two-dimensional (2D) X-ray four-wave mixing signals: photon echo and double quantum coherence, and in the two-photon absorption. Time-domain 2D spectroscopic techniques provide a versatile tool for exploring the optical properties of matter [37, 38]. Multidimensional X-ray spectroscopy enabled by X-ray lasers [39] can [40–42] capture electron dynamics on the attosecond (as) time scale, and can reveal the correlations among core-excitations.

We consider a system of N molecules coupled to a single X-ray cavity mode described by the Hamiltonian

\[ H = H_{CM} + H_{LM}(t) + H_{C} \]

where the \( n \)-th molecular Hamiltonian

\[ H_{CM}^{(n)} = \sum_{j \in \{1,2\}} \hbar \omega_{j} \langle j^{(n)} | \hat{J}_{\mu}^{(n)} | j^{(n)} \rangle \hat{J}_{\mu}^{(n)} \]

the cavity Hamiltonian \( H_{C} = \hbar \omega_{c} a^\dagger a \), and the cavity-molecule coupling \( H_{CM} = \sum_{n=1}^{N} -\mu^{(n)} \cdot \hat{E} (r_{n}, t) \). Here \( \mu^{(n)} \) is the transition dipole moment and \( \hat{E} (r) = i \frac{\hbar \omega_{c}}{2\varepsilon_{0} V_{c}} e_{\epsilon} e^{ik_{c} \cdot r} + H.c. \) is the electric field operator where \( a \) (\( a^\dagger \)) is the boson annihilation (creation) operator for the cavity mode, \( k_{c}, e_{\epsilon} \) are the cavity mode wave vector and polarization, respectively, H.c. stands for the Hermitian conjugate. We focus on the single- and double-core carbon K-edge excited states, labeled \( e \) and \( f \), respectively. Double-core excitations of the same carbon atom are excluded, as they are blue-shifted by tens of eV with respect to doubly core-excited states on different atoms [43]. This shift can be attributed to the reduced electron shielding caused by the first core-excitation which shifts a second core-excitation from the same atom to the blue. The electric-dipole coupling \( H_{LM}(t) \) describes the interaction of the molecules with external laser pulses.

For \( N > 1 \) and \( | \vec{k}_{c} \cdot (\vec{r}_{n} - \vec{r}_{m}) | \ll 1 \), it is con-
convenient to introduce the collective core-exciton states $|E_{\sigma k}\rangle = \frac{1}{\sqrt{N}} \sum_{\alpha=1}^{N} e^{i k n} \alpha g^{(1)}(\alpha) \ldots g^{(n-1)}(\alpha) g^{(n+1)}(\alpha) \ldots$ describing a superposition of a single excitation shared by all molecules and similarly $|F_{\mu k}\rangle$, where $k = 2\pi j/N, j = 0, \ldots, N-1$. Here $\alpha$ and $\mu$ run over the singly and doubly excited states, respectively. Up to double excitations, the cavity-molecule coupling can be represented by (see Sec. S1 for details)

$$H_{CM} = \sum_{\alpha} \sqrt{N} \kappa_{\alpha g} |E_{\alpha 0}\rangle \langle G| a + \sum_{k, \mu, \alpha} \kappa_{\mu e} |F_{\mu k}\rangle \langle E_{\alpha k}| a$$

$$+ \sum_{n \neq m, \alpha, \gamma} \kappa_{\alpha g} |e^{(n)}_{\alpha} e^{(m)}_{\beta}\rangle |e^{(m)}_{\beta}\rangle a + H.c.$$

(1)

where $|G\rangle = |g^{(1)} \ldots g^{(N)}\rangle$. Equation (1) implies that the transition from the ground-state to the delocalized core-exciton states $|E_{\alpha 0}\rangle$ is enhanced by $\sqrt{N}$ whereas the coupling between excited states $|E_{\alpha k}\rangle$ and $|F_{\mu k}\rangle$ does not show such cooperativity [3]. The bright state $|E_{\alpha 0}\rangle$ is invariant under exchange of any two molecules. The dark states $|E_{\alpha k}\rangle, k \neq 0$ do not contribute to the absorption spectrum. Nevertheless, the transitions between the single-polariton and the dark biexciton states are coupled to the cavity mode by the $|F_{\mu k}\rangle \langle E_{\alpha k}| a + H.c.$ term even for $k \neq 0$. Note that bright polariton states can relax to the dark states due to e.g. vibronic couplings, disorder, and cavity loss [3, 44]. The third term in Eq. (1) represents the coupling between the singly and doubly core-excited states from different molecules (Sec. S1).

Figure 1 depicts the ground state structure of 1,1-difluoroethylene optimized at the Møller-Plesset second-order perturbation level, and compares the simulated and experimental X-ray absorption near edge structure (XANES) in the [280, 296] eV spectral range. This molecule has two inequivalent carbon atoms with bound pre-edge transitions separated by a few eV. The electronic structure computations are detailed in Sec. S2, and the spectroscopic simulations in Sec. S3 [45]. The simulated XANES spectrum (without any shift) is in excellent agreement with experiment in the [280, 296] eV spectral range. The spectrum has four main features. The 285.6 eV and 289.5 eV peaks are associated with excitations from the 1s core orbitals of the carbon atoms in the CH$_2$ and CF$_2$ groups to the anti-bonding $\pi^*$ orbital, respectively. A broader peak at 293 eV, arises from a pair of close lying transitions from CH$_2$ to Rydberg (Ry) orbitals. Finally, we find a red shoulder to the 289.5 eV band at 288.4 eV, associated with a transition from CH$_2$ to a $\sigma^*$ anti-bonding orbital localized in the CH$_2$ fragment. The $\sim 4$ eV energy splitting between the CH$_2$ $\rightarrow \pi^*$ and CF$_2$ $\rightarrow \pi^*$ peaks shows that functionalization with electron withdrawing groups such as fluorine makes core-excitations more energy-costly, thus inducing a few eV blue-shift. The K-edge spectrum is dominated by the core-excitations of CH$_2$.

In the X-ray cavity, the core-excitations are modified by coupling to the cavity mode. Figure 2 (top) illustrates the XANES of core-polaritons at cavity frequencies $\omega_c = 290$ eV close to the CF$_2$ $\rightarrow \pi^*$ excitation for varying coupling strength. At $\sqrt{N} = 2.45$ eV/Debye (eV/D), we observe a vacuum Rabi splitting of two polariton peaks. The transition dipole is in the order of 0.1 D. The Rabi splitting is increased with the coupling strength, and the lower polariton further mixes with CH$_2$ excitations leading to enhancement and redshift of the CH$_2$ $\rightarrow \pi^*$ transition.

To unveil the polaritonic nature of the core-excitations in the X-ray cavity, we have decomposed each polariton state into the CH$_2$, CF$_2$ and the cavity photon components. These are depicted in the lower panels in Fig. 2. Since the core-excitations localized at CH$_2$ and CF$_2$ are decoupled, each excitation is either purely CH$_2$ or CF$_2$ type. To decompose the polariton states, we introduce the projection operators $P_{\sigma} = \sum_{\alpha \in \sigma} |e_{\alpha}\rangle \langle e_{\alpha}|$ where $\sigma = \{\text{cavity photon, CH}_2, \text{CF}_2\}$. The $\sigma$-component in a polariton state $|\Psi\rangle$ is computed as $P_{\sigma}|\Psi\rangle = \langle \Psi|P_{\sigma}|\Psi\rangle$. As shown in Fig. 2, without cavity ($g = 0$), all excitations are either purely CH$_2$ (yellow) or CF$_2$ (purple) type. As the coupling is turned on, the two $\sim 290$ eV excitation contain mixed CF$_2$ and photon (brown) character, reflecting a hybridization of the CF$_2$ $\rightarrow \pi^*$ and the cavity photon, resembling the polariton states in a Jaynes-Cummings model. As $g$ increases, the polariton states further mix with CH$_2$-excitations, leading to delocalized core-excitations from both CH$_2$ and CF$_2$. The delocalization can be clearly observed in the decomposition of the polariton states $\sim 290$ eV. These delocalized excitations involving both C atoms arise from an effective coupling between their core excitations induced by exchanging cavity photons even when the cavity is in the vacuum state. When the cavity frequency is detuned far from any resonance in the bare XANES $\omega_c = 288$ eV (bottom row of Fig. 2), no substantial changes in the spectrum are observed at $g = 2.45$ eV/D. Nevertheless, as $g$ gets stronger, we observe similar delocalized core-excitations involving both CH$_2$ and CF$_2$ at e.g. 290 eV.
excitations from the same carbon atom do not cancel the
anharmonic citations of CH2.

The 2D PE signals are displayed in Fig. 3. There are three contributions to the spectra: stimulated emission (SE) and ground-state bleaching (GSB) (the first two diagrams in Fig. S1), and the excited state absorption (ESA, the last diagram in Fig. S1). The four XANES features discussed earlier give rise to four traces along \( \Omega_1 \) (i.e., CH2 excitations at 285.6 eV, 288.4 eV and 293.0 eV and CF2 excitations at 289.5 eV) with a characteristic cross peak pattern, that reflects the correlation between various transitions. The cross peaks result from the fact that they share a common ground state, and that the core excitations are both anharmonic \( \omega_{fe} \neq \omega_{cg} \) and coupled \( \omega_{fg} \neq \omega_{eg} + \omega_{c'g} \). ESA signals related to double core-excitations from the same carbon atom do not cancel the respective GSB and SE signals, consequently, cross-peaks appear symmetrically below and above the diagonal. Transitions involving CH2 and CF2 cores are quartically coupled due to spatial vicinity of the two carbons, i.e., excitations of CH2 core depends on the occupation number in CF2. The associated ESA exhibit a \( \sim 1.5 \) eV red-shift (289.6 eV/284.0 eV and 285.6 eV/288.0 eV) or a blue-shift (289.6 eV/294.5 eV and 293.0 eV/291.0 eV) with respect to the corresponding off-diagonal GSB which makes the ESA appear in the 2D spectra. At \( g = 2.45 \) eV/D, the polariton splitting is reflected in the additional cross peaks between the polariton states and bare molecular states. Similar features are seen in the stronger coupling case shown in Fig. 3 where additional hybrid polariton states

![FIG. 2. XANES of 1,1-difluoroethylene in an X-ray cavity for varying coupling strength. Lower panels show the decomposition of each polariton state into CH2, CF2 and photon components. The top row is for cavity frequency \( \omega_c = 290 \) eV close to a specific transition, and the bottom row for cavity frequency \( \omega_c = 288 \) eV detuned from the main core-transitions. The dependence on \( N \) is solely through the (collective) coupling strength \( g\sqrt{N} \).

For nonlinear X-ray signals, we focus on the single-molecule \( N = 1 \) strong coupling case. Single-molecule strong coupling requires a substantial field enhancement, and its realization may benefit from an ensemble of auxiliary emitters [47]. The signals for large \( N \) can depend on many collective dark states that are neglected here. Doubly core-excited dark states \( \left| e^{(n)}_a e^{(m)}_g \right> \) in different molecules also need to be taken into account. Such states do not show up in bare nonlinear spectroscopy due to destructive interference [48, 49]. The cavity mode mediates an effective coupling even for otherwise non-interacting molecules, and the two-core-exciton states from different molecules will influence the bipolariton manifold. Below \( g, e, f \) label the ground, single-polariton, two-polariton states, respectively, see Fig. 3 for the level scheme.

We have computed time-domain heterodyne-detected 2D X-ray four-wave mixing signals of core-polaritons. These allow us to track the time-evolution of the polariton states and reveal correlations between transitions. The total electric field is decomposed into three pulses \( E(t) = E_3(t) + E_2(t + T_2) + E_1(t + T_1 + T_2) \) where \( T_j \) is the time-delay between the \( j \)-th and \( j + 1 \)-th pulse. Labeling the wave vectors of the incoming pulses as \( \mathbf{k}_j \), we first discuss photon echo (PE) signal at \(-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3\).

The 2D PE spectra are sketched by the Liouville space pathways represented by Feynman diagrams [37], depicted in Fig. S1. The 2D correlation spectra are obtained by Fourier transforming the delays \( T_1 \) (coherence time) and \( T_3 \equiv t \) (detection time) in the polarization \( S_{PE}(\Omega_3, \Omega_1; T_2) = \int_0^\infty dT_1 \int_0^\infty dT_3 \langle P_{PE}(T_3, T_2, T_1) \rangle e^{i\omega_0 T_3 + i\Omega_1 T_1} \).
containing excitations from both carbon atoms are created.

We now turn to the double quantum coherence (DQC) signal at $k_1 + k_2 - k_3$ [50–54], represented by the diagrams shown in Fig. S2. The correlations between single- and two-polaritons can be obtained either by Fourier transform of the time-delays $T_3$ and $T_2$ at a fixed $T_1$, $S_{\text{DQC}}(\Omega_3, \Omega_2; T_1)$ or by Fourier transform of the time-delays $T_1$ and $T_2$ at a fixed $T_3$ $S_{\text{DQC}}(\Omega_2, \Omega_1; T_2)$. In DQC, the polariton system is in the coherence $\langle e \rangle$ or $\langle g \rangle$ during $T_1$, and is then promoted to $\langle f \rangle$ or $\langle g \rangle$ during $T_2$. The system can be either $\langle f \rangle \langle e \rangle$ or $\langle e \rangle \langle g \rangle$ for the detection time $T_3$. The peaks in $S_{\text{DQC}}(\Omega_2, \Omega_1; T_3)$ reveal correlation between $\omega_{eg}$ and $\omega_{fg}$. For a harmonic system where $\omega_{fg} = \omega_{eg}$ and for uncorrelated transitions where $\omega_{fg} = \omega_{eg} + \omega_{eg}$, the DQC signal vanishes as the two contributions to DQC interfere destructively. This makes DQC suitable for resolving anharmonicities and correlated transitions.

The DQC $S_{\text{DQC}}(\Omega_2, \Omega_1; T_3)$ are shown in Fig. 4 for varying cavity coupling strengths. The vertical axis shows the doubly core-excited states $\langle f \rangle$ that can be reached from $\langle g \rangle$ through an excited state $\langle e \rangle$. Prominent contributions at $\Omega_1/\Omega_2 = 285.6\text{ eV}/573.9\text{ eV}$ and 289.5 eV/573.9 eV arise due to the coupling of CH$_2$ to $\pi^*$ (285.6 eV) and CF$_2$ to $\pi^*$ (289.5 eV) transitions to the CH$_2$CF$_2 \Rightarrow \pi^*$ transition [55]. Similarly, peaks at 289.5 eV/584.1 eV and 293.0 eV/584.1 eV arise due to the coupling of CF$_2$ to $\pi^*$ (289.5 eV) and CH$_2$ to Ry (293.0 eV) transitions to the CH$_2$, CF$_2 \Rightarrow \pi^*$, Ry transition. In the strong coupling regime, the polariton states manifest as a doublet around $\Omega_1 = 290$ eV. Additional peaks are clearly observed between these single-polariton states and the $f$-manifold. Core-polaritons also modulate the doubly core-excited states by mixing them with the two-cavity-photon state and single-core-excitation single-cavity-photon state. For example, a noticeable red-shift can be observed for the CH$_2$CF$_2 \Rightarrow \pi^*$ transition from the slices of the DQC at $\Omega_1 = 285.5$ eV.

The correlations between $\omega_{fe}$ and $\omega_{fg}$ are revealed in the DQC signal $S_{\text{DQC}}(\Omega_3, \Omega_2; T_1)$ displayed in Fig. 4 (bottom row). States from the doubly excited manifold coupled to the singly excited manifold are characterized through a set of four peaks along $\Omega_3$ for a given $\Omega_2$ value [56]. For example, the quartet of peaks along the $\Omega_2 = 573.9$ eV are associated with two peaks at 285.6 eV and 289.5 eV coinciding with the CH$_2\rightarrow \pi^*$ and CF$_2 \rightarrow \pi^*$ transitions and two red-shifted peaks at 284.4 eV and 288.3 eV corresponding to the CH$_2\rightarrow \pi^*$ with CF$_2$ excited and CF$_2 \rightarrow \pi^*$ with CH$_2$-excited. [57] The 1.2 eV splitting between each pair of corresponds to the value of the quartic coupling between both transitions. Under strong coupling, core-polariton doublets can be observed along $\Omega_3$ due to the $\omega_{fe}$ resonances. The splitting does not directly correspond to the polariton resonances because both $e$ and $f$ manifolds are modified by the cavity mode.

Similar information about the correlations of single and double excitations as provided by DQC can be extracted from the two-photon absorption signal, discussed in Sec. S4. This signal does not require coherent X-ray pulses and is thus easier to implement experimentally.

In summary, we have demonstrated how molecular core-excitations can be manipulated by coupling to the vacuum field in an X-ray cavity. Localized excitations from the two carbon atoms in 1,1-difluoroethylene are coherently coupled by the exchange of an X-ray cavity photon creating hybrid delocalized excitations. We identified the spectroscopic signatures of core-polaritons in XANES, two-photon absorption, and multidimensional X-ray spectroscopic signals. XANES directly probes the hybrid core-polariton states with the polariton effects manifested as mode splitting, redistribution of oscillator strength, and line shifts, depending on the cavity frequency and coupling strength. Correlation between polaritonic excitations are revealed by the PE, and information about the two-polariton manifold can be readily extracted from the DQC and two-photon absorption signals. This study shows how to manipulate core-excitations in molecules by strong coupling to a cavity in the X-ray regime. Many interesting phenomena dis-
covered for exciton-polaritons in the optical regime such as long-range transport [35], modified chemical reaction rates [58], enhanced nonlinearity [36] suggest analogous extensions for core-polaritons in the X-ray regime. Relaxation dynamics of core-polaritons is also expected to differ significantly from the bare core-excitations. Collective effects found in Mössbauer resonance in iron including electromagnetically induced transparency and Lamb shift [32, 33] may show up in molecules as well.

\[ g = 0 \quad g = 2.45 \text{ eV/D} \quad g = 4.89 \text{ eV/D} \]

FIG. 4. 2D double quantum coherence spectra \( S_{DQC}(\Omega_2, \Omega_1; T_3) \) (upper row) and \( S_{DQC}(\Omega_2, \Omega_3; T_1) \) (lower) in an X-ray cavity with \( \omega_c = 290 \text{ eV} \) at different coupling strengths \( g \) as indicated. A small time delay \( 10^{-5} \text{s} \) is used for both \( T_3 \) and \( T_1 \) to avoid cancellation of the two DQC diagrams.

ACKNOWLEDGMENTS

We thank Dr. Stefano M. Cavaletto for helpful discussions and Dr. Ralf Röhrsberger for valuable feedback. M.G., A.N., F.S., and S.M. acknowledge support from the Chemical Sciences, Geosciences, and Bio-sciences division, Office of Basic Energy Sciences, Office of Science, U.S., Department of Energy, through Award No. DE-SC0019484. B.G. acknowledges the support from the National Science Foundation Grant CHE-1953045.

Courtney A. DelPo, Bryan Kudisch, Kyu Hyung Park, Saeed-Uz-Zaman Khan, Francesca Fassioli, Daniele

(2016).


See Supplemental Material for details of the electronic structure and spectroscopic computations, which includes Refs. [59–72].


Here => indicates a double excitation.


Here, the brackets indicate that the core-excitation occurs in the presence of a core-excited carbon.


Ignacio Fdez. Galván, Morgane Vacher, Ali Alavi, Celestino Angeli, Francesco Aquilante, Jochen Autschbach, Jie J. Bao, Sergey I. Bokarev, Nikolay A. Bogdanov, Rebecca K. Carlson, Liviu F. Chibotaru, Joel Creutzberg, Jie J. Bao, Sergey I. Bokarev, Nikolay A. Bogdanov, Re-bec-kah. Carlson, Liviu F. Chibotaru, Joel Creutzberg, Niko Dattani, Mickael G. Delcey, Siija S. Dong, Andreas Drew, Leon Freitag, Luis Manuel Frutos, Laura Gagliardi, Frédéric Gendron, Angelo Giussani, Letícia González, Gilbert Grell, Meiuyan Guo, Chad E. Hoyer, Marcus Johansson, Sebastian Keller, Stefan Knecht, Goran Kovachević, Erik Källman, Giovanni Li Manni, Marcus Lundberg, Yingjin Ma, Sebastian Mai, João Pedro Malhado, Per Ake Malmqvist, Philipp Marquetand, Stefanie A. Mewes, Jesper Norell, Massimo Olivucci, Markus Oppel, Quan Manh Phung, Kristine Pierlout, Felix Plasser, Markus Reiser, Andreas M. Sand, Igor Schapiro, Prachi Sharma, Christopher J. Stein, Lasse Krågh Sørensen, Donald G. Truhlar, Mihkel Ugandi, Liviu Ungur, Alessio Valentini, Steven Vancollie, Valera Veryazov, Oskar Weser, Tomasz A. Wesolowski, Per-Olof Widmark, Sebastian Wouters,
