PERSPECTIVE

Periodic burst-like photochemical bond splitting in metal carbonyls and cyclohexadiene

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Recently, Schori *et al.*, *Nat. Commun.*, 2025, **16**, 4767 observed by time-resolved X-ray diffraction of Fe(CO)$_5$, excited at 267 nm, a burst-like CO elimination, which was synchronized with a Fe–CO stretch vibration excited in the Franck–Condon region. Another recent work, using time-resolved electron diffraction (Ma *et al.*, preprint, 2025, DOI: **https://doi.org/10.21203/rs.3.rs-6125327/v1**), provided supplementary results. The periodic bursts were predicted before (Banerjee *et al.*, *Nat. Commun.*, 2022, **13**, 1337) by molecular dynamics simulations. They were interpreted by periodic passage of the wave packet from the initially excited bound state to a repulsive state through the crossing of the potentials. Whereas this mechanism is appealing, there are still open questions. Attention is drawn here on two similar cases, which seem more clear-cut: CO elimination from group-6 metal hexacarbonyls such as Cr(CO)$_6$ and the ring opening of 1,3-cyclohexadiene. The comparison not only shows that the phenomenon may be more general but also suggests some additional interpretations concerning conical intersections, slope directions, assignment of oscillations and mechanisms of energy redistribution.

1. Introduction

Great progress has been made in the last decade in time-resolved X-ray and electron diffraction methods to investigate the detailed atomic motions in photochemical reactions. Both, the time resolution and the signal-to-noise ratio were improved by using X-ray lasers and MeV electron beams, respectively. It was known (see, *e.g.*, ref. 1 and 2) that excitation of Fe(CO)$_5$ around 267 nm initially populates a bound metal-to-ligand charge transfer (MLCT) state, from where the wave packet rapidly crosses over to a repulsive (metal-centered, MC, or ligand-field, LF) state. A recent molecular–dynamics calculation[3] predicted that this crossing occurs periodically, synchronously with a Franck–Condon active Fe–C stretch vibration, so that the expulsion of CO molecules is geyser-like; primarily an axial CO is split off, while elimination of equatorial CO is a minority channel and is slightly delayed. The latter was correlated with pseudorotation and the Jahn–Teller effect.

All this was confirmed in a recent time-resolved X-ray diffraction experiment in a cooperation of many institutes.[4] This includes the predicted rotation of the eliminated CO. The authors also determined the energy deposited in this degree of freedom and in translation, and detected coherent oscillations in the product Fe(CO)$_4$. By ultrafast electron diffraction, in another collaboration of many institutes reported in a recent preprint,[5] the bursts of CO were confirmed; in addition, the

polarization dependence pointed to periodic axial expulsion and a delayed equatorial elimination.

It is very appealing and is consistent with common understanding of conical intersections (CoIns) that non-adiabatic transitions are more or less localized on the potentials to the CoIns (or the intersection space) and their immediate neighborhood. Unfortunately, the respective CoIns and the involved coordinates were not yet revealed in calculations and experiments. Whereas some suggestions are attempted here, attention is drawn on the much investigated ring opening of 1,3-cyclohexadiene and also to the photodissociation of Cr(CO)$_6$, which seems simpler than that of Fe(CO)$_5$. The comparison can provide additional insights. Accordingly, this Perspective not only points to the possible generality of periodic bond splitting but also to the potential that CoIns provide for rationalizing a variety of observations.

A review on transient structures in ultrafast photochemical dynamics[6] includes also time-resolved diffraction experiments. It also reports on some early observations of oscillations of small (*e.g.* diatomic) dissociating molecules. A tutorial review on photochemistry of transition metal carbonyls[7] includes ultrafast processes, as does also an earlier review by Long.[8]

2. Periodic passing through the last CoIn in ring opening of 1,3-cyclohexadiene

Photochemical ring opening of 1,3-cyclohexadiene passes from the initially excited 1B state to the (dark) two-electron excited

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2A state and then through the last CoIn to the product *Z*-hexatriene or back to the reactant (see the reviews;[9,10] for quantum-chemical aspects, the recent work of the Barbatti group with the quoted literature may be a starting point[11]). This CoIn (actually two symmetry-equivalent minima in the intersection space) involves a three-electron three-center bond of one CH_2 group with the other end of the molecule (Fig. 1).

When we investigated this reaction[12] by probing with multiphoton ionization mass spectroscopy (time resolution 13 fs), we also detected a coherent oscillation on the 2A potential (ν_3 in Fig. 2), which could be assigned to a ring expansion/contraction vibration. The corresponding coordinate connects the two symmetry-equivalent CoIns (minima in the intersection space) and is one of the two coordinates, spanning the branching space.

The oscillation was seen, because the multiphoton ionization probability is position-dependent and the ionic and neutral potentials are not parallel. Hardtke and coworkers[13] presented an interesting interpretation: every time the wave packet arrives near the 2A/1A CoIn (*i.e.* the S_1/S_0 CoIn), a large part of it falls down to the ground-state surface (1A, S_0). The calculated time-dependent 2A population is shown in Fig. 3 bottom, which can be compared with our measured signal (Fig. 3 top).

The lower part of Fig. 3 shows clearly that the calculated 2A population drops repeatedly in steps, with time distances similar as those of the measured oscillation maxima (upper part of the figure). The population in between the steps is constant. This is not in contradiction with the experimental data: we did not measure populations but the position dependent signals (black dots) and analysed them by the product of an exponential part (dark blue) with an oscillatory part (a sine wave with an overtone, green curve); also the exponential part is supposed to contain a position dependence (dark blue curve).

Another peculiarity of the measured data is worth mentioning: the oscillation (green curve in Fig. 3 top) seems quite pronounced even at times near 300 fs, long after the measured exponential decay time (80 fs) of the 2A state. The actually measured signal (black dots) is weak and is enhanced by dividing through the exponentially decaying part. Also, in the diffraction experiments on $Fe(CO)_5$, stretch oscillations were seen even after the nominal dissociation time for this bond.

We found the idea of non-adiabatic transitions, localized near CoIns, appealing. It is not devaluated by an obvious oversimplification of the assumed potential: it was supposed

Fig. 2 Potentials, wave packet paths and coherent oscillations according to ref. 12. FC is the Franck–Condon region, *p** the pericyclic minimum. The molecular structures at the two CoIns are indicated in Fig. 1. The oscillation leading to periodic bond splitting is ν_3 (140 cm^{-1}, period 240 fs), the lifetime (traveling time) in 2A is 80 fs.

Fig. 3 Top: Signal from the observation window L_3, identified as the 2A (S_1) surface (black dots), which can be simulated by the product of an exponential part (dark blue solid line) with an oscillatory part (Fourier transform in the inset); the 270 cm^{-1} band was ascribed to an overtone of that at 140 cm^{-1} (from ref. 12). Bottom: Calculated 2A populations, showing the steps, when the wave packet comes close to a CoIn (from ref. 13, with permission of ACS).
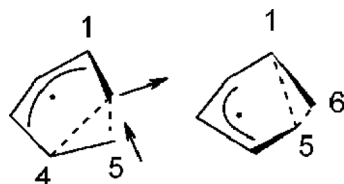

Fig. 1 Structures at the two symmetry-equivalent CoIns, indicating the three-electron three-center bonds with the C atoms 6 above 5 and 4, and 5 below 6 and 1, respectively. The first structure is shown in ref. 13 with rendered atoms. The arrows show the conversions between the two structures and thus the coordinate connecting the two CoIns.
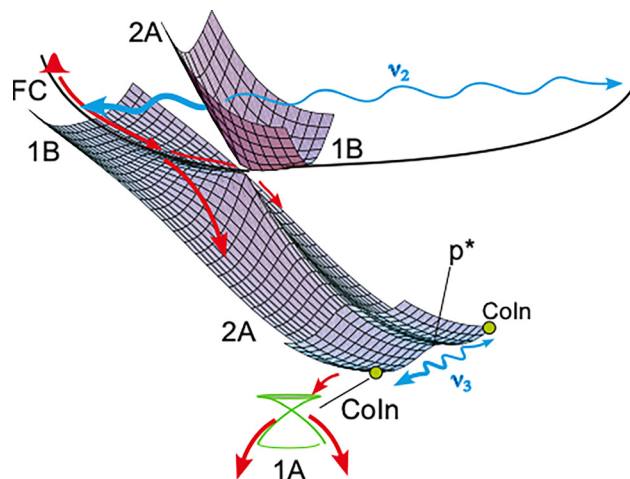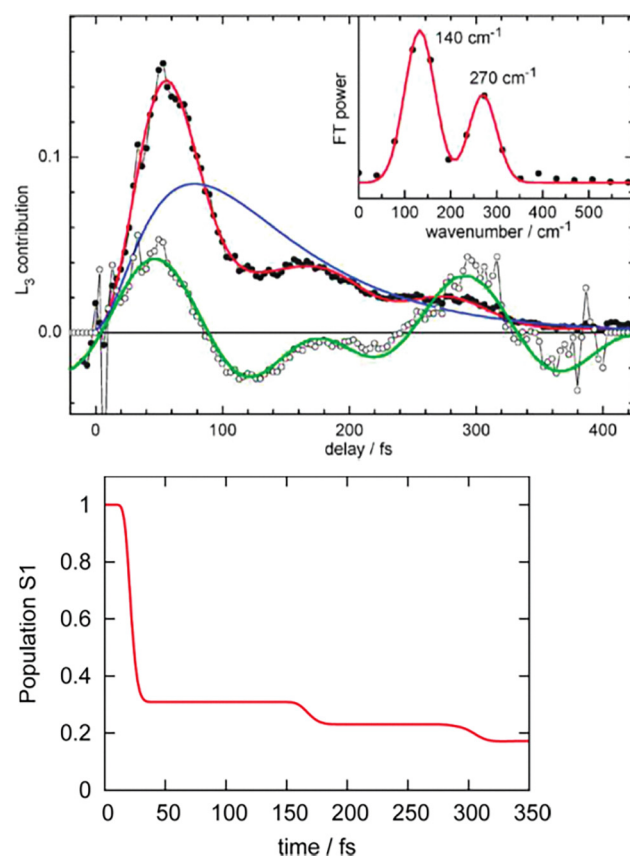
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to be completely flat along a certain angle coordinate, with the consequence that also *E*-hexatriene (along with the *Z*-isomer) was among the predicted products.[13] This was, however, never observed.

Finally, an early observation is worth mentioning here: after arriving to the ground state surface, the wave packet is still very compact (not longer than 20 fs), as found, when it passed through a resonance (in the *Z*-hexatriene ion) with the probe laser.[14] It should also be realized that high-frequency oscillations (also in the following examples) are only resolvable, if the wave packet is temporally compact.

3. Oscillations and pathways in photodissociation of Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$

As in the other binary metal carbonyls, in Cr(CO)$_6$ and heavier homologs there are two groups of low-lying excited states: the MLCT states are non-dissociative, and the two of T_{1u} symmetry (in the symmetry group O_h) carry most of the oscillator strength; excitation in the weaker long-wavelength tail of the UV spectrum also leads to MLCT states (T_{2u}, E_u and A_{1u}) in transitions, which borrow their intensity from the allowed T_{1u} states. The MC states are repulsive. The lowest of them is just above the lowest T_{1u} state (see *e.g.* ref. 15).

On extension of one Cr–CO bond, the lowest MLCT state (T_{2u}) was calculated[15–17] to split, with the lowest component becoming repulsive. This can be considered a result of an avoided crossing with an MC state that comes steeply down along this coordinate; after passing this region, a wave packet would have MC character. The other MLCT states remain bound. On excitation of a higher MLCT state (*e.g.* T_{1u} near 270 nm), it was believed that the molecule first relaxes down to the T_{2u} state and then dissociates. In our early time-resolved work on M(CO)$_6$ photodissociation,[18,19] we adopted this view. If the T_{2u} state is excited directly (at long wavelength), one should expect in this mechanism one time constant less (that for $T_{1u} \rightarrow T_{2u}$ relaxation, for example) than for shorter wavelengths. However, we saw the same number of time constants, independently of wavelength.[20,21] We concluded, the mechanism is the same: from every initially excited MLCT state the molecule goes directly within a first time (τ_1) to a repulsive MC potential, where it dissociates within τ_2 to the (excited state of the) unsaturated carbonyl M(CO)$_5$. This is illustrated for three initial states in Fig. 4.

The calculations along a pure M–CO stretch coordinate show that the lower MLCT states soon become repulsive, as said above. That is, the molecule passes over an avoided crossing to the lowest MC state. From a higher MLCT state, such as that near 270 nm, the molecule would then have to jump from an upper curve to the lower one near this avoided crossing. This is not possible in femtoseconds, as we argued in ref. 21. Instead, it must follow a (steeper) continuous path. In addition to M–CO stretch, it must involve another coordinate of the
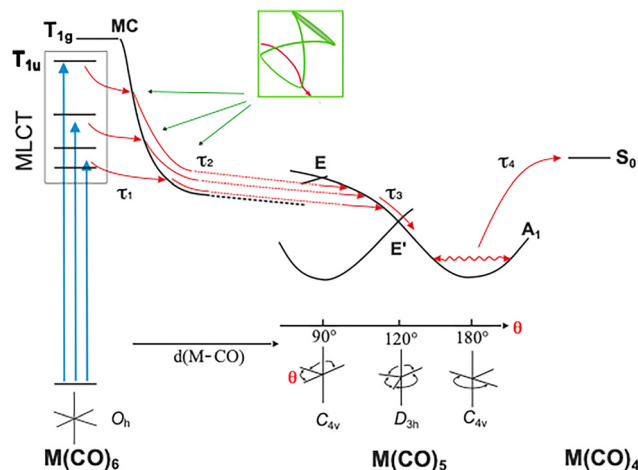

Fig. 4 Schematic potentials and paths for photodissociation of M(CO)$_6$, using three different photolysis wavelengths, as discussed in ref. 20 and 21. The time constants τ_1 to τ_4 are 12.5, 18, 40 and 930 fs, respectively, for Cr(CO)$_6$ photolysed at 270 nm; they slightly depend on the photolysis wavelength and the metal carbonyl.[20] It is worth noting that a slightly higher-lying nondegenerate state (A$'_1$ in D_{3h}) of Cr(CO)$_5$ may also be accessible; pseudo-Jahn–Teller interaction with E$'$ can occur by distortion along the same distortion (θ) and thus contribute to the indicated relaxation path.[22,23] – Elimination of a second CO, which is due to excess energy in the primary product and occurs on a picosecond time scale, is shown for completeness and not discussed in the text.

branching space, the direction of strongest non-adiabatic coupling (NAC).

This is what Fig. 4 (inset) indicates for the crossing-over from the MLCT states to the repulsive MC potential for a path surrounding a CoIn. The deflection is towards the NAC vector. Also, what is denoted for simplicity as M–CO stretch in the figure, must contain admixtures of other coordinates. We also argued in ref. 21 that the NAC vector involves some M–C–O bending and is related to Jahn–Teller distortion.

It may be useful to remember that each of the six symmetry-adapted M–CO stretch coordinates a_{1g}, e_g and t_{1u} is a linear combination of local stretches. Conversely, a local stretch can be considered a superposition of these normal coordinates. (Because t_{1u} also contains C–M–C bending, another bending coordinate will be needed for compensation.) Excitation will involve the Franck–Condon active delocalized a_{1g} stretch ("breathing") coordinate, whereas near a CoIn the motion becomes local, involving a single CO only (or the mentioned superposition of normal modes). Because most excited states are degenerate, the Jahn–Teller active coordinates e_g and t_{2g} will also contribute some Franck–Condon activity. Such considerations immediately rationalize, why all these modes were observed in resonance Raman spectroscopy of M(CO)$_6$ (as overtones only, if required by symmetry).[24–27]

The early Jahn–Teller (JT) distortion has two interesting consequences:

– The C–M–C bending caused by the t_{2g} distortion may also cause some M–C–O kink. Then, when antibonding is switched on between M and C, the CO molecule will begin to rotate. This was in detail predicted by Crespo-Otero and Barbatti.[15]

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Conversely, one can conclude from the rotationally excited CO observed in photofragment spectroscopy[28] and diode laser spectroscopy[29] that M–C–O bending or the Jahn–Teller distortion begins before CO expulsion.

– When one M–CO bond is already extended (*i.e.* after crossing over to the lowest MC potential, symmetry E in C_{4v}), an additional JT distortion becomes active:[15–17] it corresponds to pseudorotation of the free unsaturated metal carbonyl $M(CO)_5$. Along this path, this molecule passes from the initially formed excited state through a CoIn to its ground state. There, a coherent oscillation is observed along this coordinate, stimulated by the slope through this CoIn. We observed this oscillation also, if $Cr(CO)_6$ was excited at a long wavelength (345 nm), where the energy is not sufficient to produce $Cr(CO)_5$ in its excited state (E) in square-pyramidal form (which is the ground-state equilibrium structure),[20,21] see Fig. 4. Therefore, we concluded that the (JT induced) pseudorotation begins, before dissociation is complete.[20,21] This was confirmed by calculation.[15] – It is suggestive that this early pseudorotation is switched on by the surrounding of the CoIn between MLCT potentials of various symmetries and the lowest MC potential (symmetry T_{1g}): the non-adiabatic coupling vector contains displacements of t_{2u} symmetry, just right for pseudorotation.

In the unsaturated $Mo(CO)_5$ and $W(CO)_5$, we saw two of the four possible CMC bending vibrations (besides overtones and combination vibrations and besides MC stretch vibrations, see the end of the next section, where we come back also to the following issues), symmetry types a_1 and b_2 in C_{4v} (square pyramidal structure).[21] Their superposition just generates pseudorotation. They are the result of decomposing the vector (symmetry e′) of passage through the D_{3h} CoIn.[21] Thus, this mechanism neatly explains that just these oscillations are excited, and conversely, their observation supports the relaxation path. Furthermore, as explained in Section 4.4 of ref. 21, this path also explained photochemical observations such as the *cis* effect in photosubstitution, which were not fully understood before. We could also infer that redistribution of energy in this time range is phase-coherent and by far not fills the full phase space, and that triplets do not take part (Sections 4.6 and 4.5 of ref. 21).

In the work with the different wavelengths,[20,21] we used much shorter pulses (10 fs) than before. Thus, we could resolve also a coherent oscillation with higher frequency (around 400 cm^{-1} for $Cr(CO)_6$) than those detected before. By its frequency, it must be a (Franck–Condon active) M–C stretch vibration. We found such oscillations not only in in the Franck–Condon region but – with slightly different frequencies – also in the subsequent three observation windows: on the repulsive (MC) potential (*i.e.* during dissociation) and in S_1 and S_0 of the dissociation product. (The simulation of Crespo-Otero and Barbatti also show – in their Fig. 8 – an oscillation with such a frequency, which extends from the Franck–Condon region to the dissociation product.[15]) For interpretation, why the oscillation survives even dissociation, we pointed to the fact that only one of the six M–C bonds is split and suggested that the oscillating wave packet simply propagates on the changing potential (for details, see ref. 20).

Also an alternative interpretation was briefly considered: when the wave packet crosses over to another potential, an M–C vibration is stimulated anew, by the local slope, although synchronized with the incoming wave packet. In fact, on simulating the S_1/S_0 relaxation of the dissociation product $Cr(CO)_5$, Worth and coworkers found that the slope through the CoIn not only stimulates the pseudorotation vibration but also a Cr–C stretch (period 80 fs).[22] If such an entering on a dissociative potential, synchronized with an M–C stretch oscillation, is very sudden, this mechanism is closely related to the burst-like photodissociation of $Fe(CO)_5$ (see Introduction) and the stepwise ring-opening of cyclohexadiene (Section 2).

So, is there any evidence that the entering to the repulsive potential is in fact sudden? In cyclohexadiene, the wave packet enters to the CoIn through the upper funnel, through which it falls within less than one vibrational period, as is generally the case.[30] But in $Cr(CO)_6$, the wave packet surrounds the CoIn, where the crossing is avoided. Such avoided crossing normally means a less sudden change of electronic character; often they even involve an activation energy. The calculations in fact show a smooth change of slopes in this region.[15,17] A closer inspection, however, reveals that this happens within a bond lengthening of the order of 0.1 Å. A direct evidence is due to photofragment spectroscopy:[28] it shows that the CO ejection is an impulsive process ("half collision"). Not only the M–C repulsion is suddenly switched on (after M–C–O bending by Jahn–Teller activity) but also the CO bond is suddenly shortened (eventually to that of free CO), perhaps in a time shorter than a vibrational period. Only in this way it was possible to explain the high (but unequal) energies deposited in translation, vibration and rotation of the CO. (In photodissociation of $Fe(CO)_5$, even a vibrational inversion was observed in the CO product.[31]) Also the short dissociation times we measured (τ_2 in Fig. 4) imply an impulsive process: they are only a fraction of the period of an M–C stretch vibration.

In an investigation by time-resolved valence photoelectron spectroscopy (photon energy 23 eV) and accompanying molecular–dynamics calculations (similar to those of Banerjee *et al.*[3]), Schröder *et al.* focused on differences in photodissociation of $Cr(CO)_6$ and $Fe(CO)_5$ (the dynamics in the latter is slower) and their interpretation.[32] But remarkably, they also found a common feature: the periodic bursts of CO were also seen in the molecular–dynamics simulations of $Cr(CO)_6$ (they were not seen in the photoelectron spectra due to insufficient time resolution). This fully confirms the considerations above.

In view of the many states and crossings of potentials, it may be asked, whether really only few states contribute to the reaction path. This problem is the same in $Fe(CO)_5$ and will be discussed in the end of the next section.

In passing, one can also clarify a source of surprise in the photofragment work:[28] the authors wondered, why only a relatively small fraction of the "available" energy is found (as translation, vibration and rotation) in the ejected CO, although the conservation of momentum would predict that most energy is imparted to the light fragment. However, the heavier fragment $M(CO)_5$ is produced in its electronically excited state

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S_1 (Fig. 4), so that the available energy is much smaller than expected.

4. Periodic bursts of CO ejection from iron carbonyl

The recent time resolved X-ray and electron diffraction[4,5] and the preceding molecular dynamics calculations[3] revealed new details on the path of photodissociation of $Fe(CO)_5$. The comparison with $Cr(CO)_6$ and heavier homologs (Section 3) can provide additional insight.

As in the other binary metal carbonyls, in $Fe(CO)_5$ MLCT states are bound and, with suitable symmetry, carry most of the intensity; the MC states are repulsive. Near 4.6 eV there are two MLCT states (A_2'' and E' in D_{3h}) which can be excited by wavelengths near 270 nm; according to ref. 2 the oscillator strength by far favors A_2''. In contrast to $M(CO)_6$, iron carbonyl has an MC state (E') also below this energy,[1,2] which can even be directly excited in a weak transition. It is usually assumed (also by us ref. 33) that this state is intermediate between an initially excited higher MLCT state and the ejection of a CO. Indeed, Kunnus and coworkers could distinguish by X-ray anti-Stokes Raman scattering with high time resolution the initially excited MLCT state from the intermediate MC state.[34]

In semiclassical molecular dynamics calculations,[3] based on TDDFT surfaces, Banerjee and coworkers found that by 267 nm one excites the (non-degenerate) A_2'' state; they find there a coherent Fe–C stretch oscillation, which leads to synchronized ejection of an axial CO, and these molecules are rotationally excited. A minority channel also splits off an equatorial ligand with a small delay; it is correlated with a beginning pseudorotation (which exchanges axial and equatorial ligands); this distortion is attributed to a Jahn–Teller effect in the low-lying MC state (symmetry type E'). The preferentially axial dissociation is ascribed to the population of the metal centered $14a_1'$ orbital, which is axially antibonding.

Admirably detailed results were obtained along this line by X-ray diffraction (time resolution 60 fs) by Schori and coworkers.[4] They found the predicted bond-length oscillations in axial direction with the synchronized bursts of rotating CO, which happen each time when an adiabatic MLCT → MC transition occurs according to their interpretation[4] and the molecular dynamics calculations.[3] They could determine energies deposited in translation, vibration and rotation of CO. The anisotropy supports initial excitation of the A_2'' state and that dissociation favors an axial CO. A more isotropic CO extrusion with picosecond delay was ascribed to further dissociation of the primary product $Fe(CO)_4$. In this unsaturated carbonyl, also coherent oscillations were detected and identified as C–Fe–C bending modes.

A recent electron diffraction work with less time resolution (150 fs)[5] focuses more on the anisotropy. At times from 350 to 700 fs, the dissociation is nearly isotropic. The authors ascribe this result to pseudorotation accompanying dissociation, just as predicted. (At times before 300 fs – before the window of

measurements –, anisotropies consistent with axial dissociation cannot be excluded and even are suggested by back-extrapolation of the anisotropy data in their Fig. 4. So, there is not necessarily a discrepancy with the X-ray diffraction results of ref. 4) At earlier times (before 200 fs), the Fe–C oscillation could not be temporally resolved. But its presence was detected indirectly, by its mean square amplitude. The authors interpret their results by assuming that the MLCT surface crosses with an MC potential, which falls down from a higher energy on Fe–C extension (similarly as in $M(CO)_6$, Section 3); depending on the energy, at which the wave packet crosses this intersection space, axial or equatorial dissociation is suggested to follow. The energy in the active coordinate could either depend on the excitation wavelength (266 nm were used as in the X-ray experiment) or – according to the authors – after a preceding vibrational energy redistribution.

These new results combined with some of previous investigations (Section 3) allow for a few more conclusions on the reaction path and slope directions.

4.1. Before and during dissociation

The prompt CO ejection, synchronized with a Franck–Condon active Fe–C stretch oscillation, requires an easily accessible conical intersection (CoIn) for the non-adiabatic MLCT → MC relaxation. The accessibility will be facilitated, if a (local) Fe–C stretch is contained in its branching space. This assumption seems plausible in view of the repulsive nature of the MC surface and as to infer from the potentials, which avoid crossing in this direction. The rotation of the expelled CO requires that an Fe–C–O bending occurs, before repulsion sets in. For the axial ligand, it would have e' symmetry. On surrounding the CoIn, the wave packet is deflected towards the non-adiabatic coupling vector. This vector (coupling the states E' MLCT with E' MC or A_2'' MLCT with E'' MC) indeed contains an e' coordinate, which is suggested here to involve both, C–Fe–C and Fe–C–O bending. Such an e' coordinate will also be Jahn–Teller active in E' and E'' states. Furthermore, it is just the pseudorotation of $Fe(CO)_5$, discussed in the three recent works.[3–5]

As to judge from vibrational frequencies,[35] pure bending is slower than stretching by a factor of about 5. The slowness of bending can hence explain the observed[5] and calculated[3] slight delay of the equatorial dissociation in the minority channel, which is mediated by pseudorotation (*i.e.* a bending motion) in the parent molecule.[3,5] (The delay of 250 fs suggested in ref. 5 seems, however, too high in view of the short dissociation times reported by us ref. 33, see Fig. 5) Hence, it is not necessary to postulate[5] different energies of two crossing points of the intersection space (although the crossing locations may be displaced from each other).

In our earlier study,[33] we assumed that besides the A_2'' state also the E' MLCT state (with nearly equal energy[2]) is excited at 267 nm. (Now the anisotropy found by Schori *et al.*[4] is evidence for population of A_2'' alone. And as said, the oscillator strengths by far favor the A_2'' over the E' state.[2]) We also postulated a rapid
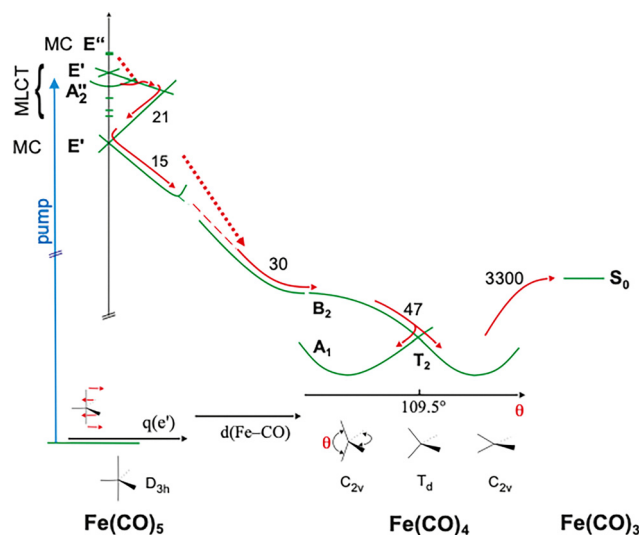
Fig. 5 Suggested potentials and paths for $Fe(CO)_5$ photodissociation, with our previously measured[33] time constants (in fs). The sequence of excited states qualitatively follows the calculation of Malcomson et al.,[2] though the energetic distance of A_2'' and E' (nearly degenerate in the calculation) is enlarged for reasons of visibility. Pseudorotation is denoted $q(e')$ in the parent molecule and θ in $Fe(CO)_4$. For the times up to dissociation, two paths are suggested: the solid arrows (preferred in the text) lead via the lowest MC state, whereas the (interrupted) dotted arrow would lead around a crossing with the steeply descending potential from the higher MC E'' state; this latter path would be analogous to $Cr(CO)_6$, shown in Fig. 4. For the CoIn in $Fe(CO)_4$, we (as others) assumed tetrahedral geometry (T_d) and a triply degenerate electronic state (T_2); Paterson et al. point out that their calculations predict a degenerate (E) and a nondegenerate (A_1) state lying nearby, which may influence details of the relaxation path.[23] – Elimination of a second CO, which is due to excess energy in the primary product and occurs on a picosecond time scale, is shown for completeness but is not discussed in the text.

exchange of population between the two states via a CoIn that arises, because the E' surface is Jahn–Teller split along an e' distortion. Such a flow (though unidirectional) could also be active with excitation of A_2'' alone; this is one modification of Fig. 5 compared to ref. 33. The path can then lead further down via another CoIn with the E' MC surface, which is also Jahn–Teller split.[33]

This mechanism provides a non-adiabatic continuous path (solid arrows) from the initial MLCT A_2'' state to the low-lying MC E' state (and an early Fe–C–O bending). A continuous path – as opposed to jumps over avoided crossings – is necessary to explain the short times. An alternative continuous path is indicated by the interrupted dotted line: relaxation via an MC surface that falls down from the higher E'' state, similar as in $M(CO)_6$ (Section 3, Fig. 4). It was also considered theoretically[2] and was assumed in in the electron diffraction.[5] In this case one would expect only a single time constant for the $A_2'' \rightarrow$ MC relaxation, in contrast to the two indicated in Fig. 5. This is well conceivable: when (in the work with the different wavelengths[20,21]) we improved the time resolution for $Cr(CO)_6$, it turned out that one of the time constants measured before was due to an unresolved highly damped coherent oscillation. This may be the case also for $Fe(CO)_5$.

In Fig. 5, a path following the solid arrows is preferred, because the molecular dynamics calculation of Banerjee et al. supports the way through the low-lying MC state.[3] Unfortunately, this calculation did not deliver details of the path such as CoIns. (In their figure, they even indicate a vertical MLCT → MC relaxation, obviously only symbolically, because in the text they speak about crossings.) – Direct excitation of the E' MC state at long wavelength could decide between the two alternative paths.

The coordinates indicated at the bottom of Fig. 5 are not a full description: in order that a path be continuous, it must intersect with the intermediate potential surfaces (belonging to the indicated intermediate states). But surface crossing might be avoided, if one does not allow for deviations from strictly following of one single coordinate such as Fe–C stretching.

4.2. Processes in the primary product $Fe(CO)_4$

In the binary metal carbonyls $M(CO)_n$ we investigated (brief review:[36]), photochemical splitting off of one CO produces the unsaturated carbonyl $M(CO)_{n-1}$ in its first excited singlet state S_1. (Note also the recent review on ultrafast photochemistry of metal carbonyls in the gas phase by Ramasesha et al.[37]) Whereas the primary product from $Ni(CO)_4$ shows a long-lived luminescence,[38,39] the others are very short-lived. They can relax down to S_0 via a symmetry-induced CoIn, following Jahn–Teller active coordinates, which correspond to pseudorotation. The slope on this path stimulates coherent oscillations in S_0 (Section 3), which in turn indicate the direction of the slope. Although we saw such oscillations only, if the coordination number of the unsaturated carbonyl was 5, we suggested[33] the same mechanism also for $Fe(CO)_4$ (Fig. 5), assuming that its spectrum does not provide sensitivity for our probe wavelength (800 nm) to detect oscillations. According to coupled-cluster calculations,[2] the spectrum of $Fe(CO)_4$ is in fact very flat in this region, so that vibrations in the lower state are not expected to modulate the signal.

The scheme with an initially formed short-lived excited singlet state (S_1, $^1B_2$ in C_{2v}) and a lower-lying S_0 ($^1A_1$) seems accepted, sometimes modified by addition of the slightly lower triplet ground sate (T_1, $^3B_2$) or consideration of bimolecular addition reactions, such as in ref. 40–42. Nevertheless, it is highly satisfactory and valuable that the time-resolved X-ray diffraction[4] now detected the expected coherent oscillations with wavenumbers mainly near 78 cm^{-1} (satellites near 31 and 110 cm^{-1} in their Fig. 3). They identify the main spectral peak as C–Fe–C bending vibration. In their supplementary note 7, they calculate all five such bending vibrations and assign also the peak at 31 cm^{-1} to such a mode in S_0. To explain also higher frequencies in the observations, they calculated also vibrations in S_1 and T_1 and suggested that these two states also contribute with 29 and 14%.

However, the S_1 state is too short-lived (47 fs in Fig. 5) for an oscillation with period near 400 fs (wavenumber 80 cm^{-1}), and the triplet is formed with delay only (from S_0,[41,42] or not at all in the gas phase[33,43]). And in contrast to S_1 and T_1, for an oscillation in S_0, there is a plausible excitation mechanism:

the slope along pseudorotation in passing through the S_1/S_0 CoIn, as said. An assignment of the observed oscillation spectrum may be possible, if combination vibrations (e.g., $110 \approx 78 + 31$ for their wavenumbers) and more overtones are taken into account; after all, the potential is very anharmonic. For illustration and further conclusions, let us look again to results for $M(CO)_5$, M = Cr, Mo, W.

4.3. Further comparison with the oscillations in the unsaturated group-6 carbonyls

Fig. 6 (from ref. 21) shows a spectrum of the oscillations in $Mo(CO)_5$ (measured as the indicated ion in this example) after dissociation of the hexacarbonyl at 341 nm. It is better resolved than the iron carbonyl spectra of ref. 4, because we measured the time-dependent data over longer times (up to 5 ps). Probably it well shows the idea of overtone and combination vibrations of the two strong (red) bands. (The peak at 420 cm^{-1} – if real – may be an M–C stretch. In $Cr(CO)_5$ it is much stronger).

In Fig. 4 and 5, the pseudorotation potentials are indicated as a function of a single coordinate. At least two are needed to show the nature as rotation. Fig. 7 shows such a potential of $Cr(CO)_5$ qualitatively (for quantitative CASSCF calculations see ref. 16) as function of two angular coordinates (details in ref. 21, triangular coordinates are explained in ref. 19). One can recognize the threefold symmetry. (The full symmetry of the potential in the case of $CrCO)_5$ is that of the CoIn, D_{3h}, with C_{4v} minima and C_{2v} transition states; the pseudorotation potential of $Fe(CO)_4$ is even more symmetric than that of the CoIn – O_h versus T_d –, with C_{2v} minima and C_s transition states, (see ref. 23).

A ring-like motion above the barriers in the moat (circular channel) represents a hindered pseudorotation. The solid arrows show a path of the wave packet that excites just two of the bending vibrations (confirmed by CASSCCF calculations[16]), one radial (a_1 in C_{4v}) in the moat, the other circular (b_2, in two of the three minima). The paths along the broken arrows cause mainly radial (umbrella) vibrations. The paths differ by how much the molecule has undergone pseudorotation already
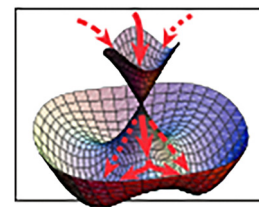

Fig. 7 Illustration of a pseudorotation potential with different paths such as in $Cr(CO)_5$ (from ref. 21).

during or before dissociation (see the three paths in Fig. 4). – It is suggested that a similar scheme applies to $Fe(CO)_4$, although the moat looks a little different.[23]

It may be nice that such a model can explain that two (just two) bending vibrations are excited and that we can conversely conclude on the slope direction. But there are also tangible photochemical implications: according to ref. 21, it rationalizes orientation effects in a low-temperature matrix or the limited quantum yield of recombination with CO. Furthermore, the cis effect in photosubstitution of $LM(CO)_5$ became eventually clear, as already mentioned (Section 3). On the one hand, pseudorotation has been invoked before for interpretation[44] (or in Long's review of 2010[8]). But it was a puzzle, why it stops after one step and does not continue (so: why not all minima in Fig. 7 are populated). The answer is that pseudorotation is driven by the passing through the CoIn, which occurs only once, and that apparently the excess energy is immediately channeled to different degrees of freedom. The latter point is worth a separate discussion.

4.4. Intramolecular vibrational relaxation? Even with decoherence?

Such processes are assumed in the diffraction works and the molecular dynamics simulations,[3–5] perhaps only an unfortunate choice of words. For example, a flow of energy from the initial axial C–Fe–C oscillation to a pseudorotation coordinate is assumed in the electron diffraction work[5] to result from decoherence. Instead, this Perspective explains excitation of pseudorotation by forces, that is, by slopes along Jahn–Teller or non-adiabatic-coupling coordinates. The following briefly summarizes a discussion in ref. 21, which concludes that there is no sub-ps decoherence.

– In the example of $Mo(CO)_5$, about 2.25 eV ($18\,000 \text{ cm}^{-1}$) of the S_1 electronic energy is converted to kinetic energy, i.e. to vibrations. But only a small fraction is observed as pseudorotation oscillation: the wave packet remains clearly below the barriers (calculated around 0.5 eV for $Cr(CO)_5$[16]); near or above the barriers, the frequencies would be very different. Obviously, most energy goes to other vibrational degrees of freedom. In a first calculation, using trajectory surface hopping and CASSCF surfaces, Paterson, Hunt and Robb confirmed that the wave packets arrive in a minimum of the moat and remain trapped there.[16] In a wave packet dynamics calculation (taking into account also pseudo-Jahn–Teller interaction with a higher, non-degenerate state) Worth, Welch and Paterson found no

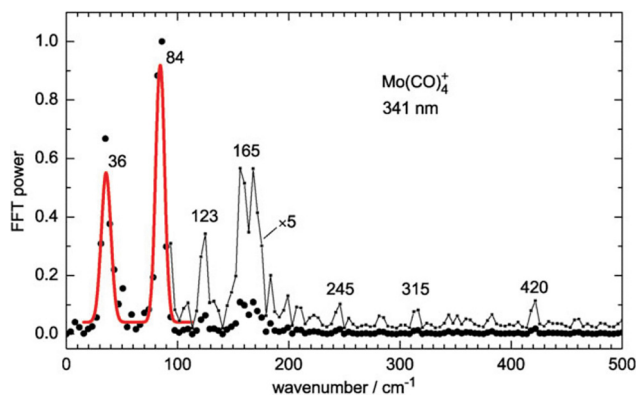
Fig. 6 Fourier transform spectrum ("FFT power") of coherent oscillations (wavenumbers in cm^{-1}) in $Mo(CO)_5$ as detected by the $Mo(CO)_4^+$ ion (from ref. 21). $Mo(CO)_5$ was generated by photolysis of $Mo(CO)_6$ at 341 nm.

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trapping;[22] the authors discuss the origin of the difference. But one may guess that the later work took just too few degrees of freedom into account.

A popular model (Redfield model, used for example for describing electron-transfer processes[45]) assumes a bath (with 58 of the 60 vibrational degrees of freedom), which can take over the energy from the observed 2 modes. The relaxation would be exponential, and the energy distribution in the bath is statistical, with the full phase space being used. But the coherent oscillations can be observed over more than 5 ps (dephasing time 1–1.5 ps). If the initially fast relaxation continued (over >30 time constants), only 3.3% (= 2/60) of the energy would be left in the pseudorotation. We suggested instead, the leakage rate varies locally and is fastest, where suitable anharmonicities are largest, probably near the CoIn.

Furthermore:

– It is hard to imagine an interacting bath with statistical fluctuations that would not disturb the vibrational coherence of the observed oscillations. (But the Redfield model can handle coherences: in ref. 45 an assumed electronic coherence was included.) The system-bath model would also hardly explain, why the Cr–C stretch dephases much faster than pseudorotation.[21]

– The lack of equipartition is demonstrated by the fact that even not all symmetry-equivalent minima are populated (Fig. 7).

Instead of a system-bath model, we drew the attention to the fact that on its way downhill the wave packet repeatedly changes direction (which is kind of local cross anharmonicity). This already leaves some energy in other modes, without equipartition and with keeping some phase relationship. So, in some sense, photochemistry is coherent in the time range below a few picoseconds. The phenomenon of extremely non-exponential relaxation and of long-lived coherences seems general. We observed quite a number of similar cases. They are compiled in ref. 46. It is also possible in much larger molecules: Boeije and Olivucci compiled a number of examples, where coherent effects strongly influence the quantum yields of cis–trans isomerization of rhodopsin-type molecules.[47]

5. Conclusions

The given examples suggest two main messages: (1) the observed periodic bond splittings may be more general and can be explained by sudden non-adiabatic transitions at conical intersections (CoIns). (2) CoIns with the slopes nearby can rationalize a variety of observed phenomena. Conversely, such considerations support the suggested structures of CoIns, the directions of slopes and the pathways.

The periodic burst-like splitting of a bond, triggered by (and synchronous with) a preceding coherent oscillation as found by ref. 3–5 in photodissociation of $Fe(CO)_5$, seems to be a more general phenomenon. This is suggested by a comparison with group-6 metal hexacarbonyls and with ring opening of cyclohexadiene. The phenomenon is interpreted here by a sudden non-adiabatic transition to the repulsive potential, which is localized at or near a CoIn. For cyclohexadiene, the last CoIn is

well documented; the wave packet enters into the funnel-like upper part of it and passes through it in less than a vibrational period.

For the metal carbonyls, the early CoIns (between the bound MLCT potentials and the repulsive MC potentials) are not known. Quantum chemical calculations to characterize them or even more of the intersection space, including the directions of slopes in the branching space, would be desirable. Here some experimental observations are used to make some suggestions.

In contrast to cyclohexadiene, the early path in metal carbonyls leads around the lower cone of a CoIn, that is *via* an avoided crossing. Such a path is not necessarily fast, in particular if associated with activation energy. But indeed, their dissociation sets in very suddenly (it occurs impulsively). Evidence is based on the fragment energy distribution from resonance Raman spectroscopy $(M(CO)_6)$ and photofragment spectroscopy $((MCO)_6$ and $Fe(CO)_5)$, and for $Fe(CO)_5$ from the new measurements of time-resolved diffraction, of course. A further support of the impulsive nature is due to the short times (30 to 50% of a period of an M–C stretch vibration), which we measured and assigned to times for dissociation, see Fig. 4 and 5.

The rotation of the ejected CO must be due to an early (slight) M–C–O bending. Just such a distortion is plausible for a Jahn–Teller effect in the dissociative (degenerate) MC state. The same distortion is expected as part of the non-adiabatic coupling vector of the MLCT/MC CoIn, that is the direction of deflection of the wave packet surrounding the CoIn. Furthermore, it is the pseudorotation coordinate for both, the intact metal carbonyl and the primary product. – In $Fe(CO)_5$, the main channel was found to be axial dissociation,[3,4] and a minority channel towards equatorial dissociation was found to be slightly delayed; the latter was correlated with an early beginning of pseudorotation due to the Jahn–Teller distortion[3] (or, as suggested here, also by the non-adiabatic coupling vector). Here it is suggested to attribute the delay to the slower evolution of this preceding bending compared with stretching.

It is very satisfactory that in the primary product $Fe(CO)_4$, the time resolved X-ray diffraction[4] revealed the same type of coherent oscillations (namely pseudorotation; the authors speak only about C–Fe–C bending), which we found in all studied metal carbonyls, whose coordination number is higher by 1. It is here again pointed out that the oscillation is triggered by the slope of the path through the S_1/S_0 CoIn. Compared with the equilibrium geometry in S_0, this CoIn has a structure with higher symmetry and is Jahn–Teller induced.

In view of the many excited states and the many crossings before, during and after dissociation, one may ask, whether it makes sense to assign a definite path (curved but one-dimensional, except a few branchings at CoIns or on ridges) to the wave packet. However, if many states participate, perhaps even with equipartition, it is hard to imagine coherent oscillations, some of which have dephasing times of >1 ps. Also, rationalization of the early pseudorotation would certainly be more difficult. A more direct indication is the fact that after dissociation only two of the 4 or 5 bending modes were excited,

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those corresponding to pseudorotation. And most directly: only part of the symmetry-equivalent minima in the pseudorotation moat are populated; this is neatly rationalized by the pathway approach (Fig. 7) and is supported by photochemical observations (Section 4 near Fig. 7). Instead of vertical relaxation, controlled by matrix elements and densities of states, it was suggested in 1998 that in ultrafast reactions the path of the wave packet is controlled by CoIns and slopes of the potential surfaces.[48] A continuous path is suggested also, if initially a higher state than S_1 is excited; if crossing of intermediate and lower potentials is fast (which depends on velocity and relative slopes), population transfer to such potentials can be negligible. The metal carbonyls may be prototypes of such cases. They can also serve as model cases, where slopes control the reaction paths. Understanding them better would probably also provide more insight into wavelength dependences of metal carbonyl photochemistry (see, *e.g.*, ref. 49).

On the other hand, there must be a mechanism carrying energy out from the observed degree of freedom to unobserved ones: the 2 eV of electronic energy released in the $S_1 \rightarrow S_0$ relaxation through the CoIn in Fig. 7 is by far not fully converted to pseudorotation vibrations; otherwise, the barriers (*ca.* 0.5 eV in $Cr(CO)_5$) would be easily overcome, the last minimum would be populated and the frequencies would be very different. This outflow must be initially coherent, and development of decoherence takes more than a few picoseconds, as discussed in Section 4.4, which points also to a compilation of similar cases. A calculation capable of revealing details of such processes would be desirable. Such a calculation could perhaps also answer the question, how the wave packets can stay very compact in time (as in all examples above) after passing so many very anharmonic regions.

Apart from the periodic bond splitting, another common feature of the presented examples is the fact that the oscillation takes place along a vibrational coordinate that leads directly to a CoIn. Near the CoIn the normal coordinate breaks down to a local coordinate, which is contained in the branching space. A referee pointed to the periodic predissociations observed by the Zewail group in diatomics such as NaI[50] (see also Section 5.1 in the review,[6] where further original work is quoted). The vibrational coordinate in the bound ionic state leads to a crossing with a repulsive covalent state, where part of the wave packet leaks through. But although the vibrational coordinate points to the region of non-adiabatic transition, there is no CoIn in diatomic molecules. (As said, CoIns are one focus of the present Perspective).

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this paper.

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References

1 O. Rubner, V. Engel, M. R. Hachey and C. Daniel, A CASSCF/MR-CCI study of the excited states of $Fe(CO)_5$, *Chem. Phys. Lett.*, 1999, **302**, 489–494.

2 T. Malcomson, R. G. McKinlay and M. J. Paterson, One- and two-photon-induced photochemistry of iron pentacarbonyl ($Fe(CO)_5$): insights from coupled cluster response theory, *ChemPhotoChem*, 2019, 825–832.

3 A. Banerjee, M. R. Coates, M. Kowalewski, H. Wikmark, R. M. Jay, P. Wernet and M. Odelius, Photoinduced bond oscillations in ironpentacarbonyl give delayed synchronous bursts of carbonmonoxide release, *Nat. Commun.*, 2022, **13**, 1337.

4 A. Schori, E. Biasin, A. Banerjee, S. Boutet, P. H. Bucksbaum, S. Carbajo, K. J. Gaffney, J. M. Glownia, R. W. Hartsock, K. Ledbetter, A. Kaldun, J. E. Koglin, K. Kunnus, T. J. Lane, M. Liang, M. P. Minitti, J. T. O'Neal, R. M. Parrish, F. Poitevin, J. M. Ruddock, S. Nelson, B. Stankus, P. M. Weber, T. J. A. Wolf, M. Odelius and A. Natan, Real space observation of the dissociation of a transition metal complex and its concurrent energy redistribution, *Nat. Commun.*, 2025, **16**, 4767.

5 J. Yang, H. Ma, J. Pedro Nunes, A. Banerjee, M. Centurion, K. Hegazy, R. Li, Y. Liu, X. Shen, X. Wang, S. Weathersby, P. Wernet, T. J. A. Wolf and M. Odelius, Berry pseudorotation enabled photodissociation of $Fe(CO)_5$ observed by ultrafast electron diffraction, 2025, DOI: **10.21203/rs.3.rs-6125327/v1**, preprint.

6 A. Ischenko, P. M. Weber and R. J. D. Miller, Transient structures and chemical reaction dynamics, *Russ. Chem. Rev.*, 2017, **86**, 1173–1253.

7 J. J. Turner, M. W. George, M. Poliakoff and R. N. Perutz, Photochemistry of transition metal carbonyls, *Chem. Soc. Rev.*, 2022, **51**, 5300–5329.

8 C. Long, Photophysics of CO loss from simple metal carbonyl complexes, *Top Organomet. Chem.*, 2010, **29**, 37–71.

9 S. Deb and P. M. Weber, The ultrafast pathway of photoninduced electrocyclic ring-opening reactions: the case of 1,3-cyclohexadiene, *Ann. Rev. Phys. Chem.*, 2011, **62**, 19–39.

10 B. C. Arruda and R. J. Sension, Ultrafast polyene dynamics: the ring opening of 1,3-cyclohexadiene derivatives, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4439–4455.

11 I. Polyak, L. Hutto, R. Crespo-Otero, M. Barbatti and P. J. Knowles, Ultrafast photoinduced dynamics of 1,3-cyclohexadiene using XMS-CASPT2 surface hopping, *J. Chem. Theory Comput.*, 2019, **15**, 3939–3940.

12 K. Kosma, S. A. Trushin, W. Fuß and W. E. Schmid, Cyclohexadiene ring opening observed with 13 fs resolution: coherent oscillations confirm the reaction path, *Phys. Chem. Chem. Phys.*, 2009, **11**, 172–181.

23542 | *Phys. Chem. Chem. Phys.*, 2025, **27**, 23534–23544

This journal is © the Owner Societies 2025

13 J. B. Schönborn, J. Sielk and B. Hartke, Photochemical ring-opening of cyclohexadiene: quantum wavepacket dynamics on a global ab initio potential energy surface, *J. Phys. Chem. A*, 2010, **114**, 4036–4044.

14 W. Fuß, W. E. Schmid and S. A. Trushin, Time-resolved dissociative intense-laser field ionization for probing dynamics: femtosecond photochemical ring opening of 1,3-cyclohexadiene, *J. Chem. Phys.*, 2000, **112**, 8347–8362.

15 R. Crespo-Otero and M. Barbatti, $Cr(CO)_6$ photochemistry: semi-classical study of UV absorption spectral intensities and dynamics of photodissociation, *J. Chem. Phys.*, 2011, **134**, 164305.

16 M. J. Paterson, P. A. Hunt, M. A. Robb and O. Takahashi, Non-adiabatic direct dynamics study of chromium hexacarbonyl photodissociation, *J. Phys. Chem. A*, 2002, **106**, 10494–10504.

17 S. Villaume, A. Strich, C. Daniel, S. A. Perera and R. J. Bartlett, A coupled cluster study of the electronic spectroscopy and photochemistry of $Cr(CO)_6$, *Phys. Chem. Chem. Phys.*, 2007, **9**, 6115–6122.

18 S. A. Trushin, W. Fuß, W. E. Schmid and K. L. Kompa, Femtosecond dynamics and vibrational coherence in gas phase UV photodecomposition of $Cr(CO)_6$, *J. Phys. Chem. A*, 1998, **102**, 4129–4137.

19 S. A. Trushin, W. Fuß and W. E. Schmid, Conical intersections, pseudorotation and coherent oscillations in ultrafast photodissociation of group-6 metal hexacarbonyls, *Chem. Phys.*, 2000, **259**, 313–330.

20 S. A. Trushin, K. Kosma, W. Fuß and W. E. Schmid, Wavelength-independent ultrafast dynamics and coherent oscillation of a metal-carbon stretch vibration in photodissociation of $Cr(CO)_6$ in the region of 270–345 nm, *Chem. Phys.*, 2008, **347**, 309–323.

21 K. Kosma, S. A. Trushin, W. Fuß, W. E. Schmid and B. M. R. Schneider, Photodissociation of group-6 hexacarbonyls: observation of coherent oscillations in an antisymmetric (pseudorotation) vibration in $Mo(CO)_5$ and $W(CO)_5$, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13197–13214.

22 G. A. Worth, G. Welch and M. J. Paterson, Wavepacket dynamics study of $Cr(CO)_5$ after formation by photodissociation: relaxation through an $(E + A) \times e$ Jahn–Teller conical intersection, *Mol. Phys.*, 2006, **104**, 1095–1105.

23 R. G. McKinlay and M. J. Paterson, in *The Jahn–Teller effect, fundamentals and applications for physics and chemistry – Springer series in Chemical Physics*, ed. H. Köppel, R. Yarkony and H. Barentzen, Springer, Berlin Heidelberg, 2009, 97, pp. 311–344.

24 D. Adelman and D. P. Gerrity, UV resonance Raman studies of group 6 transition-metal carbonyls: evidence of Jahn–Teller distortion in excited states of the lowest allowed charge-transfer transitions, *J. Phys. Chem.*, 1990, **94**, 4055–4060.

25 A. G. Joly and K. A. Nelson, Metal carbonyl photochemistry in organic solvents: femtosecond transient absorption and preliminary resonance Raman spectroscopy, *Chem. Phys.*, 1991, **152**, 69–82.

26 S.-B. Ko, S.-c Yu and J. B. Hopkins, Ultrafast investigation of vibrational relaxation and solvent coordination following photodissociation of $Cr(CO)_6$, *Bull. Korean Chem. Soc.*, 1994, **15**, 762–765.

27 S.-C. Yu, S.-B. Ko and J. B. Hopkins, Investigation of the reaction coordinate for dissociation in $Cr(CO)_6$ using resonance Raman spectroscopy, *Bull. Korean Chem. Soc.*, 1995, **16**, 1043–1045.

28 J. P. Holland and R. N. Rosenfeld, Energy disposal in the photofragmentation of $W(CO)_6$: experimental observations and physical models, *J. Chem. Phys.*, 1988, **89**, 7217–7225.

29 J. P. Holland and R. N. Rosenfeld, A time-resolved tunable diode laser study of the photodissociation dynamics of $W(CO)_6$, *Chem. Phys. Lett.*, 1988, **145**, 481–485.

30 U. Manthe and H. Köppel, Dynamics on potential energy surfaces with a conical intersection: adiabatic, intermediate, and diabatic behavior, *J. Chem. Phys.*, 1990, **93**, 1658–1669.

31 R. L. Whetten, K.-J. Fu and E. R. Grant, Photodissociation of $Fe(CO)_5$: excited state lifetimes and energy disposal, *J. Chem. Phys.*, 1983, **79**, 4899–4911.

32 H. Schröder, M. R. Coates, R. M. Jay, A. Banerjee, N. L. A. N. Sorgenfrei, C. Weniger, R. Mitzner, A. Föhlisch, M. Odelius and P. Wernet, Different photodissociation mechanisms in $Fe(CO)_5$ and $Cr(CO)_6$ evidenced with femtosecond valence photoelectron spectroscopy and excited-state molecular dynamics simulation, *J. Phys. Chem. Lett.*, 2024, **15**, 11830–11838.

33 S. A. Trushin, W. Fuß, K. L. Kompa and W. E. Schmid, Femtosecond dynamics of $Fe(CO)_5$ photodissociation at 267 nm studied by transient ionization, *J. Phys. Chem. A*, 2000, **104**, 1997–2006.

34 K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, S. Grübel, M. Schol, D. Nordlund, W. Zhang, R. W. Hartsock, K. J. Gaffney, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, S. Techert, W. Werncke, M. Odelius and A. Föhlisch, Anti-Stokes resonant X-ray Raman scattering for atom specific and excited state selective dynamics, *New J. Phys.*, 2016, **18**, 103011.

35 V. Jonas and W. Thiel, Theoretical study of the vibrational spectra of the transition metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt), *J. Chem. Phys.*, 1995, **102**, 8474–8483.

36 W. Fuß, S. A. Trushin and W. E. Schmid, Ultrafast photochemistry of metal carbonyls, *Res. Chem. Intermed.*, 2001, **27**, 447–457.

37 K. Ramasesha, D. R. Carlson and S. Bandaranayake, Ultrafast photochemistry of gas-phase transition-metal carbonyls, *Chem. Phys. Rev.*, 2025, **6**, 021307.

38 W. Fuß, W. E. Schmid and S. A. Trushin, Ultrafast photodissociation dynamics of $Ni(CO)_4$, *J. Phys. Chem. A*, 2001, **105**, 333–339.

39 N. Rösch, M. Kotzian, H. Jörg, H. Schröder, B. Rager and S. Metev, On visible transients in gas phase UV photolysis of transition metal compounds: experimental and theoretical results in $Ni(CO)_4$, *J. Am. Chem. Soc.*, 1986, **108**, 4238–4239.

This journal is © the Owner Societies 2025

Phys. Chem. Chem. Phys., 2025, **27**, 23534–23544 | **23543**

40 K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, K. J. Gaffney, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. De Groot, S. Techert, M. Odelius, P. Wernet and A. Föhlisch, Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of Fe(CO)$_5$ and Fe(CO)$_4$ EtOH, *Struct. Dyn.*, 2016, **3**, 043204.

41 J. Troß, J. E. Arias-Martinez, K. Carter-Fenk, N. C. Cole-Filipiak, P. Schrader, L. M. McCaslin, M. Head-Gordon and K. Ramasesha, Femtosecond core-level spectroscopy reveals involvement of triplet states in the gas-phase photodissociation of Fe(CO)$_5$, *J. Am. Chem. Soc.*, 2024, **146**, 22711–22723.

42 N. C. Cole-Filipiak, J. Troß, P. Schrader, L. M. McCaslin and K. Ramasesha, Ultrafast photodissociation of gas-phase iron pentacarbonyl probed with ultrafast infrared spectroscopy, *J. Chem. Phys.*, 2021, **154**, 134308.

43 H. Ihee, J. Cao and A. H. Zewail, Ultrafast electron diffraction of transient Fe(CO)$_4$: determination of molecular structure and reaction pathway, *Angew. Chem., Int. Ed.*, 2001, **40**, 1532–1536.

44 J. K. Burdett, J. M. Grzybowski, R. N. Perutz, M. Poliakoff, J. J. Turner and R. F. Turner, Photolysis and spectroscopy with polarized light: key to the photochemistry of Cr(CO)$_5$ and related species, *Inorg. Chem.*, 1978, **17**, 147–154.

45 D. Egorova and W. Domcke, Coherent vibrational dynamics during ultrafast electron-transfer reactions: quantum dynamical simulatons within multilevel Redfield theory, *Chem. Phys. Lett.*, 2004, **384**, 157–164.

46 W. Fuß, Where does the energy go in fs-relaxation?, *Chem. Phys.*, 2013, **425**, 96–103.

47 Y. Boeije and M. Olivucci, From a one-mode to a multi-mode understanding of conical intersection mediated ultrafast organic photochemical reactions, *Chem. Soc. Rev.*, 2023, **52**, 2643–2687.

48 W. Fuß, S. Lochbrunner, A. M. Müller, T. Schikarski, W. E. Schmid and S. A. Trushin, Pathway approach to ultrafast photochemistry: potential surfaces, conical intersections and isomerizations of small polyenes, *Chem. Phys.*, 1998, **232**, 161–174.

49 A. J. Lees, Quantitative photochemistry of organometallic complexes: insight to their photophysical and photoreactivity mechanisms, *Coord. Chem. Rev.*, 2001, **211**, 255–278.

50 A. H. Zewail, Femtosecond Transition-state Dynamics, *Faraday Discuss. Chem. Soc.*, 1991, **91**, 207–237.

23544 | *Phys. Chem. Chem. Phys.*, 2025, **27**, 23534–23544

This journal is © the Owner Societies 2025