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Research paper

Time-resolved photoelectron spectroscopy of nitrobenzene and its aldehydes

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1. Introduction

The excited state dynamics of ortho-nitrobenzaldehyde (2-NBA) has recently received major interest [1–9], especially as a model system for excited state hydrogen transfer dynamics which plays

an important role in many biological systems [10-12]. Upon excitation to the first ${}^{1}\pi\pi^{*}$ band in the liquid phase at 258 nm [1], the molecule decays to the lowest lying ${}^{1}n\pi^{*}$ state within 50 fs thereby performing a twisting motion at the NO₂ group. From there, it first re-planarizes [2] before returning to the ground state under hydrogen transfer from the aldehyde to the nitro group within 400 fs [1,3,4] via the formation of a ketene called azinic acid (2KAA, see Fig. 1 for an explanation of the abbreviations) [5,13,14]. This ketene further decays to a nitroso acid (2NsoBA) via a lactone intermediate (TS(OH)). The lifetime for the lactone formation is solvent dependent and ranges from 60 ps to 2 ns for 2-butanol and tetrahydrofuran, respectively [7]. In contrast, meta- and para-

ABSTRACT

We report the first femtosecond time-resolved photoelectron spectroscopy study of 2-, 3- and 4nitrobenzaldehyde (NBA) and nitrobenzene (NBE) in the gas phase upon excitation at 200 nm. In 3and 4-NBA, the dynamics follow fast intersystem crossing within 1-2 picoseconds. In 2-NBA and NBE, the dynamics are faster (\sim 0.5 ps). 2-NBA undergoes hydrogen transfer similar to solution phase dynamics. NBE either releases NO2 in the excited state or converts internally back to the ground state. We discuss why these channels are suppressed in the other nitrobenzaldehydes.

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nitrobenzaldehvde (3- and 4-NBA) are thought to undergo ultrafast intersystem crossing (ISC) with a quantum yield close to unity within 1.4 and 1.8 ps, respectively [1,15]. In the gas phase, these processes are potentially suppressed by alternative reaction paths known from nitrobenzene (NBE) which splits off either NO₂ in the S_1 state (FB + NO₂) or - after rearrangements in the triplet state (FPhN) - NO [16]. Both dissociation channels are also open upon return to the ground state. Here, NO dissociation is favored by a roaming type dissociation [17]. The NO₂ yield increases with increasing excitation energy [17-19]. As a reference for the remainder of the publication, we list the various relaxation pathways for NBE [20]:

$$C_6H_5NO_2 + h\nu \to C_6H_5NO + O(^3P) \tag{1}$$

$$\rightarrow C_6 H_5 + NO_2 \tag{2}$$

 \rightarrow [C₆H₅ONO] \rightarrow C₆H₅O + NO $(\mathbf{3})$

$$\rightarrow C_5 H_5 + CO + NO \tag{4}$$

In the present study, we report time-resolved photoelectron spectroscopy experiments on NBE, 2-, 3-, and 4-NBA in the gas phase following 200 nm excitation. These studies aim to examine the influence of the aldehyde group on the fast nitrogen oxide





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Fig. 1. Possible reaction paths of 2-nitrobenzaldehyde upon photoexcitation.

release channels and to disentangle the influence of the solvent on the initial dynamics of the NBAs. We also briefly consider the related species benzaldehyde (BA). We have chosen a high excitation energy (6.2 eV, which is more than 2.5 eV above the S₁ state of all molecules [3,16]) (i) in order to prepare the same excited state in all molecules, (ii) because of a low cross section at longer excitation wavelengths, and (iii) to examine the influence of excitation to higher lying states on the dynamics of a molecule. Our analysis is supported by ab initio quantum chemistry calculations undertaken at various levels of theory including time dependent density functional theory (TD-B3LYP), complete active space, second order perturbation theory (CASPT2) and the completely renormalized equation-of-motion coupled cluster theory with single, double and iterative triples correction (CR-EOMCCSD(T)).

2. Experimental and theoretical methods

2.1. Experimental setup

The experimental setup incorporates a magnetic bottle photoelectron spectrometer and a Ti:sapphire laser system operating with a central wavelength of 800 nm that were used as described before [21]. Pump and probe pulses were 200 and 267 nm, generated analogously to Ref. [22] at intensities of 0.25 and 4.5 μ J/ pulse, respectively. The cross correlation was 160 ± 10 fs as measured using non-resonant [1 + 1′] ionization of nitric oxide. The pump and probe beams were combined on a dichroic mirror and focused into the interaction region of the spectrometer using a concave aluminum coated mirror (f = 50 cm). For the liquid samples (NBE and BA, Sigma–Aldrich, purities 99% and used without further purification), a molecular beam was generated by flowing approximately 100 Torr of helium through a glass bubbler before expanding the resultant mixture through a 200 μ m nozzle in the experimental chamber. Solid samples (2-, 3-, 4-NBA, Sigma–Aldrich, purities 98%) were placed in a modified glass bubbler where the outlet arm was joined directly to a glass capillary nozzle. Heating tape was used to gently warm the entire assembly to a temperature close to the melting point of the particular sample under study. Approximately 100 Torr of helium was again used as a carrier gas. Time invariant one-color pump-alone and probe-alone signals were subtracted from the pump-probe data prior to the extraction of decay time constants using a global fitting routine that is described in more detail later.

2.2. Theoretical methods

Molecular geometries of the S₀ and T₁ electronic states of all molecules under investigation were optimized with density functional theory (DFT) at the B3LYP/6-31G(2df,p) level of theory while time-dependent TD-B3LYP/6-31G(2df,p) was used for the S₁ state, applying the tight convergence criterion for all computations. Harmonic vibrational frequencies were used to ensure that the optimized geometries were located at a proper stationary point on the potential energy surface. Minimum energy pathways for each state (S₀, T₁ and S₁) were characterized starting from the transition state structure to the reactant or product channels by intrinsic reaction coordinate calculations at the B3LYP/6-31G(2df,p) level of theory.

In order to increase the accuracy of the energetic description, the S_0 state potential energy surface was calculated with the G4MP2 composite method [23]. The performance of these calculations was checked for the dissociation reactions of NBE to phenyl + NO₂ and to phenoxyl + NO. The calculated heat of reaction values are 307.8 and 86.6 kJ/mol, respectively, and agree within 5 kJ/mol with the values of 302.9 and 84.5 kJ/mol evaluated using the corresponding heat of formation values from Burcat's database [24].

The first vertical ionization potentials were calculated via electron propagator theory using a combination of the outer-valence Green's function method (OVGF) with the extended cc-pVQZ basis set. No breakdown of the orbital picture of ionization is expected (Koopmans' description is qualitatively valid) since the calculated pole strengths were always above 0.89 [25]. The maximum absolute deviation between the calculated and measured ionization potentials is 0.14 eV, therefore, the experimental vertical ionization potentials of 2- and 3-NBA are expected to be within 0.14 eV of the calculated values.

In 2-, 3- and 4-NBA, the experimental vertical excitation energies to the first singlet electronic excited state (S1) were also compared to the computed values. These calculations were performed with three different methods: (i) equation-of-motion coupled cluster singles and doubles (EOM-CCSD), (ii) the more expensive completely renormalized equation-of-motion coupled cluster with singles, doubles, and perturbative triples (CR-EOMCCSD(T) [26-28]) as implemented in the GAMESS software [29] combined with the cc-pVDZ basis set, and (iii) TD-B3LYP/6-31G(2df,p), using the same combination of functional and basis set applied for the ground state S₀. While EOM-CCSD underestimates the experimental vertical excitation energy values [3] (the maximum absolute deviation is 0.28 eV for 3-NBA), the TD-DFT functional shows an overestimation (the maximum absolute deviation is 0.42 eV for 2-NBA). However, these values may be compared with those from MS-CASPT2/CASSCF calculations, because such treatments have been demonstrated to be one of the most accurate methods to calculate excitation energies [30]. Levva et al. showed [3] that multistate complete active space second-order perturbation theory and complete active space self-consistent field theory MS-CASPT2/ CASSCF(16,12) and MS-CASPT2/CASSCF(12,11) prescriptions of these excitations also have a deviation of 0.40 eV from the experimental vertical excitation energy value. This is comparable with our TD-B3LYP results. Because of the good performance of TD-B3LYP/6-31G(2df,p) for evaluating vertical excitation energies, we applied this method to obtain S₁ excited-state geometries and corresponding adiabatic ionization potentials. The full absorption spectrum up to an energy of 6.2 eV has been calculated using CR-EOMCCSD(T) in order to characterize all the potentially involved states while also giving a reasonable description of the doubly excited character.

Finally, conical intersections (CoIns) between the ground and the lowest lying excited state were optimized using state averaged SA-3-(9,10) CASSCF/cc-pVDZ as implemented in the Firefly software package [31].

3. Results and discussion

3.1. Theoretical results

Computational results are summarized in Tables 1–3, Fig. 2 and supporting information. The tables summarize the static properties of the molecules and the good agreement with experimental values shows that the theoretical methods are well suited for calculating the critical points on the potential energy surfaces. These critical points are shown in Fig. 2 while the explicit values of all indicated species are summarized in supporting information.

Table 3 shows the lowest excited state energies, calculated at the CR-EOMCCSD(T)/cc-pVDZ level of theory. Here, we observe that the energies of the excited states are only slightly affected by the aldehyde group, especially for the states belonging to the A" manifold which have oscillator strengths on the order of 10^{-5} . As a trend, the excited state energies of NBE and 3-NBA seem to be higher than those for 2-, and 4-NBA which can be explained by the ground state stabilizing mesomeric effect for meta substitutions governed by the NO₂ group (as discussed in most undergraduate-level texts on organic chemistry). The main differences between NBE and the NBA molecules is the presence of a low lying $n\pi^*$ state which is localized on the aldehyde function. Energetic differences between similar states are larger for the A' manifold, especially for the bright 5A' state which might be predominantly excited at 200 nm in 2-, and 3-NBA, but not necessarily in 4-NBA. Levva et al. conducted a more detailed analysis of the absorption spectra of the NBA-molecules which agree with the values calculated in this study [3]. Of note is the charge transfer state (3A') which has a reasonable oscillator strength and is the state that is excited at lower photon energies (see Table 3).

3.2. Experimental results and data analysis

Time-resolved photoelectron spectra of 2-NBA and NBE upon excitation at 200 nm and subsequent ionization with a 267 nm probe are shown in Fig. 3 while the spectra of BA, 3- and 4-NBA can be found in supporting information (Figs. S5–S7). The features of 3- and 4-NBA are very similar to the signals of 2-NBA and NBE, while the spectral signature of BA is significantly different. This leads to the conclusion that the nitrobenzaldehyde dynamics are mainly driven by the presence of the NO₂ group and not of the aldehyde group. The strongest signal of the NO₂ containing molecules is seen at low electron kinetic energies and originates from one photon resonant pump-one photon probe [1,1']. The total absorbed energy for such a [1,1'] process is 6.2 eV + 4.65 eV =10.85 eV. A distinct energy cut-off, apparent as a sudden drop in photoelectron signal, is observed at 0.6 eV for 2-,3-, and 4-NBA, while cut-offs of 0.9 and 1.1 eV were found for NBE and BA, respectively. These values agree with what would be expected based on the vertical ionization potentials (VIPs) of the molecules, which have been experimentally determined to be 9.92 eV for NBE [32,33], 9.71 eV for BA, [34] and 10.27 eV for 4-NBA [34] $(E_{[1,1']} = E_{pump} + E_{probe}$ - VIP). The adiabatic ionization potentials are about 0.1 eV lower. No experimental ionization potentials for 2- and 3-NBA have previously been reported. However, calculations at the OVGF/cc-pVQZ//B3-LYP/6-31G(2df,p) level of theory show almost identical vertical ionization potentials for 2-, 3-, and 4-NBA (10.46, 10.43, and 10.45 eV, respectively; see Table 2) in agreement with the maximum [1,1'] photoelectron kinetic energy cut-offs in our experiments. At higher electron kinetic energies (extending beyond the [1,1'] cutoffs), the very weakly observed bands result from two-photon [1,2'] probe ionization and appear slightly shifted in time by about 20-30 fs in 2- and 3-NBA while the spectra for 4-NBA and NBE exhibit no such shift.

For further analysis, each spectrum $S(E, \Delta t = t - t_0)$ was fitted with a global fitting routine based on a Levenberg-Marquardt algorithm according to [35]

$$S(E,\Delta t) = \sum_{i} A_{i}(E) \cdot P_{i}(\Delta t) \otimes g(\Delta t),$$
(5)

where $P_i(\Delta t)$ is the time dependent population expressed in terms of exponential functions $\exp\{-\Delta t/\tau_i\}$, $g(\Delta t)$ is the experimentally determined Gaussian cross-correlation function and t_0 is the independently measured time zero of the experiment. The A_i are called decay associated spectra (DAS) and represent the amplitudes that belong to the exponential functions i at a specific photoelectron

Table 1

Vertical excitation energy (VEE) of the lowest lying excited state and time constants extracted from a global fitting routine. The excitation wavelength λ_{pu} was 200 nm unless indicated differently. Estimated errors of the time constants are 20 %. (a) Ratios of the decay associated spectra as defined in Eq. (5). A₁ relates to τ_1 , A₂ relates to τ_2 , and A₃ relates to the constant offset. For comparison, A₁ is set to 1000.

Molecule	VEE/eV experiment	VEE/eV TD-B3LYP	τ_1/fs	τ_2/ps	Integral $A_1:A_2:A_3^a$
NBE	3.54 [44]	3.84	40	0.48	1000:27:2.0
BA	3.34 [45]		100	6	
2-NBA	3.73 [3]	3.52	60	0.52	1000:51:14
3-NBA	3.72 [3]	3.63	20	1.48	1000:24:3.8
4-NBA					
λ_{pu} =200 nm	3.76 [3]	3.34	70	1.64	1000:36:4.6
λ_{pu} =267 nm			-	1.82	-:4:1

Table 2

Calculated (VIP_{theo}) and experimental (VIP_{exp}) vertical ionization potentials of nitrobenzene (NBE), benzaldehyde (BA), 2-, 3- and 4-nitrobenzaldehyde (2-NBA, 3-NBA and 4-NBA). Calculations are carried out at the OVGF/cc-pVQZ//B3LYP/6-31G (2df,p) level of theory (associated deviations from experimental values are given in parenthesis).

Species VIP _{th}		_{eo} /eV	VIP _{exp} /eV
	cis	trans	
NBE	10.06 (+0.14)		9.92
BA	9.60(-0.11)		9.71
2-NBA	10.46	10.33	
3-NBA	10.43	10.52	
4-NBA	10.45 (+0.08)		10.37

kinetic energy *E*. In addition, large amplitude molecular motions tend to shift time-resolved photoelectron spectra towards lower electron kinetic energies. Along the reaction pathway, the molecule transfers potential to kinetic energy while the ionization potential typically increases. As a consequence, less energy is available for the photoelectron. This can be considered by artificially changing time zero as a function of the electron's kinetic energy $(t_0 = t_0(E))$ as is detailed in references [36,37].

Experimental data for each molecule could be fitted satisfactorily with two exponentially decaying functions, which we label using their respective time constants τ_1 and τ_2 , and a constant offset that did not change within the maximum time delay of the experiments (250 ps). The numerical values of the time constants can be found in Table 1 and the respective DAS are shown in Fig. 4. Although NBA and NBE are known to also absorb light at 267 nm we saw no meaningful probe-pump signal evolving to negative delay times following excitation with 267 nm pump pulses. The exception was 4-NBA which has the largest absorption cross section of all four molecules at this wavelength [4]. The photoelectron spectra of BA showed significant pump contribution from both 200 and 267 nm and were clearly distinct from the other spectra (see SI), so it was concluded that the dynamics in NBA are predominantly shaped by the nitro-group. Given this observation, we therefore restrict the subsequent discussion to consideration of just NBE, 2-, 3-, and 4-NBA.

3.3. Discussion

The DAS for τ_1 and τ_2 of NBE, 2-, 3-, and 4-NBA, as well as the time zero shift of NBE, 2-, and 3-NBA (in 4-NBA, the dynamics in the probe direction destroys the time zero structure), show a good agreement with respect to each other, indicating similar dynamics operating in all cases. Moreover, the fitted time constants are in agreement with those obtained from solution phase dynamical studies: The first time constant τ_1 and the shift of the band at higher electron energies can be explained by an ultrafast decay from a high lying ${}^{1}\pi\pi^{*}$ charge transfer state [3] (which is directly excited by the 200 nm pump pulse) to the S_1 state, which possesses $n\pi^*$ character (see Table 3) [1]. This electronic relaxation was proposed for NBE in reference [19] and was theoretically confirmed in reference [38]. The pump process transfers about 3.5 eV excess energy to the internal vibrational modes. This agrees with the amplitude onset observed in the τ_2 DAS at about 2.5 eV (see Fig. 4). This is roughly 3.5 eV below the [1,2'] energy cut-off (see Table 1 for the vertical excitation energies of the molecules).

The second time constant τ_2 , which is ~500 fs for NBE and 2-NBA, and ~1.5 ps for 2-NBA and 3-NBA is in surprisingly good agreement with liquid phase transient absorption data. In these experiments, a time constant of 400 fs for ketene formation from 2-NBA in acetonitrile and intersystem crossing rates of 1.4 and 1.8 ps for 3- and 4-NBA were measured [1]. In addition, the value of τ_2 is basically identical for excitation at 200 and 267 nm in 4-NBA (see Table 1). These similarities lead us to conclude that ISC is the primary initial decay pathway in 3- and 4-NBA while other processes (such as NO₂ elimination) play only a minor role. We may also infer that the acetonitrile solvent does not exhibit any significant influence on the course of the excited state dynamics.

Following ISC from the S_1 state, subsequent processes within the triplet manifold (and also potentially on the hot S_0 ground state) are weakly observed in our photoelectron data on the long ps-timescale (see Fig. 3) but are not specific enough to obtain

Table 3

Excitation energies of nitrobenzene (NBE) and (cis-)2-, (trans-)3- and 4-nitrobenzaldehyde (2-NBA, 3-NBA and 4-NBA) below 6.2 eV using CR-EOMCCSD(T)/cc-pVDZ. (a) The doubly excited state did not converge for 4-NBA. (b) The charge transfer state did not converge for 4-NBA.

State NBE	2-NBA	3-NBA	4-NBA	Character
1A″	3.18	3.533	3.440	$n\pi^*$ (n:CHO)
2A″ 3.512	3.481	3.517	3.469	$n\pi^*$ (n:NO ₂)
3A″ 4.049	3.978	4.032	3.984	$n\pi^*$ (n:NO ₂)
4A″	5.308	5.382	a	$\mathrm{n}\pi^*$ doubly exc.
2A' 4.448	4.138	4.252	4.187	$\pi\pi^*$ doubly exc.
3A′ 5.435	5.103	5.483	b	$\pi\pi^*$ CT
4A′ 5.827	5.647	5.766	5.698	$\pi\pi^{*}$ (π :NO ₂)
5A' 6.900	6.010	5.863	5.154	$\pi\pi^*$



Fig. 2. Energy levels for minimum energy geometries of different states along the reaction path of nitrobenzene (NBE), 2-nitrobenzaldehyde (2-NBA) and 4-nitrobenzaldehyde (4-NBA). Abbreviations of the species are explained in Fig. 1. Green color indicates the ground state, red color the first excited state, and black color the lowest lying triplet state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

information about the further fate of the molecules. We might still conclude, however, that NO_2 elimination is unfavorable in the triplet states of the nitrobenzenes due to a reduction of the energy barriers leading to NO-cleavage (see Fig. 2). This barrier is also reduced in the nitrobenzaldehydes (relative to NBE), suggesting that NO_2 is not formed in the excited state of these molecules.

In 2-NBA and NBE, alternative relaxation channels which may out-compete ISC are known to exist. In 2-NBA, the excited state hydrogen transfer channel leading to 2-nitroso benzoic acid (2NsoBA), as discussed in the Introduction [1–9], seems to be prevalent also in the gas phase. Unfortunately, little can be said about the quantum yield of the return to the 2-NBA ground state or about the formation of the ketene, as was done in reference [9]. Under the assumption of ISC quantum yields close to unity for 3- and 4-NBA and similar ISC rates for 2-, 3-, and 4-NBA, the triplet yield in 2-NBA can be estimated to be about 20%, which is about three times higher than the value in the liquid phase (0.08) [9]. However, the energy gap between the S₁ and the T₁ state is significantly larger in 2-NBA as compared to 3-, and 4-NBA (see Fig. 2 and Table S1 in the supporting information) which generally reduces the ISC rate. Thus, the rate could be below the value in the liquid phase.

In NBE, ISC was found to take place within 6 ps upon excitation at 320 nm [39] which is slower than the dynamics we observe. In principle, there are at least two channels besides ISC that are potentially open upon excitation at 200 nm: NO₂ elimination and internal conversion to the ground state [17,19]. NO₂ elimination in the excited state is energetically easily accessible as the unimolecular decomposition into C₅H₆ and excited NO₂ lies ca. 1 eV above the ground state, which agrees with the position of the first excited state of NO₂ [40]. Hence the total required energy for this channel is roughly 4.1 eV (302 nm). This agrees with the experiments of Galloway et al. who found an increase of NO₂ production upon increasing excitation energy ranging from complete absence of NO₂ at 320 nm to a NO₂/NO production ratio of 1.3 ± 0.3 at 280 nm and 5.9 ± 0.3 at 222 nm [18]. In addition, they found through kinetic energy release that at 240 nm, more molecules are produced with less kinetic energy which they explain with the production of excited NO₂. As a consequence, NO₂ production is one channel that is clearly accessed in NBE upon excitation at 200 nm. It is possible that a minor fraction of 3- and 4-NBA also undergoes NO₂ cleavage; however, this channel might potentially be blocked by the presence of the low lying $n\pi^*$ state that is localized at the aldehyde group of the NBA molecules (see Table 3).

Internal conversion between the S₁ state and the ground state has been investigated before in NBE. Upon excitation at 320 nm, Takezaki et al. found that 20% of the molecules take this channel in liquid phase experiments [39,41]. Later, Quenneville et al. found that the geometry of the minimum energy CoIn between the two states exhibits an out of plane bending of the NO₂ group [42]. This geometry lies at an energetically elevated position of about 0.43 eV above the energy minimum of the S_1 state at the SA-2-CAS(10/8)/ cc-pVDZ//SA-2-CAS(16/13)/cc-pVDZ level of theory. A second minimum energy CoIn was found along the ONO bending coordinate at an energy of 0.63 eV above the S₁ minimum [38]. The reduced yield of internal conversion was explained by cooling effects which render the CoIn with the ground state inaccessible. Our experiments take place in the gas phase and excitation at 200 nm offers enough excess energy to circumvent these problems. One possible explanation for the relatively long τ_2 time constant of 3- and 4-NBA as compared to that of NBE (1.48 ps and 1.64 ps vs 0.52 ps) could therefore be an increased barrier towards the CoIn with the ground state.

To determine the potential role of conical intersections in more detail, we performed SA-2-CAS(9/10)/cc-pVDZ calculations on 2and 4-NBA to investigate the influence of the extra aldehyde group on the energetic position of the CoIn. The geometries at the CoIn and at the S_1 minimum energy are shown in Fig. 5. They are similar to the structures found in NBE [42]. The S₁ minimum geometry of 2-NBA shows an NO2 group that is twisted further out of the molecular ring plane relative to 4-NBA, likely due to the interaction with the adjacent aldehyde group. Moreover, the bond distances at the CoIn for the NBA systems seem to be more stretched than those for NBE (128/129 vs. 122 pm for the short NO-bond, 146/147 vs. 138 pm for the long NO-bond and 145/144 vs. 140 pm for the NC bond) which indicates a weakened π system. As a consequence, the difference between the S_1 minimum and the minimum energy CoIn was 0.32 eV for 4-NBA and 0.17 eV for 2-NBA. Both of these values are lower than that for NBE where a value of 0.43 eV was previously reported [38]. Mewes et al. have previously argued that this intersection might not be accessed during the dynamics, and instead suggest a higher-lying intersection located along the ONO



Fig. 3. Time-resolved photoelectron spectra of 2-nitrobenzaldehyde and nitrobenzene upon excitation with 200 nm and probe with 267 nm photons.

bending mode [38]. This barrier is, however, energetically lower in 4-NBA than in NBE. It is also extremely small compared to the excess energy deposited into the molecules following 200 nm excitation. As such, it cannot be the reason for the increased τ_2 lifetime seen in 4-NBA relative to that in NBE.

The main difference between the electronic structure in NBE versus 3- and 4-NBA is the different character of the lowest lying electronic state in the Franck-Condon region. This state is located on the NO₂ group in NBE, but in the NBAs, it is a charge transfer state, with an excitation from the aldehyde group (n-orbital) to the NO₂ group (see Table 3). It is possible that this state is accessed upon internal conversion from the higher lying, initially excited state. We speculate that the state crossing from the charge transfer

state to the localized $n\pi^*$ state takes enough time to prevent efficient relaxation to the ground state and renders ISC the primary relaxation channel in 3- and 4-NBA. These dynamics are sketched in Fig. 6. In 3- and 4-NBA, the dynamics follow the pathway indicated by the green arrows, while the pathway via the $n\pi^*$ state localized at the NO₂ group (denoted as $n\pi^*(NO_2)$) is energetically unfavorable (red arrows). In NBE, the $n\pi^*$ state localized at the aldehyde function does not exist and the molecules return to the ground state directly via the $n\pi^*(NO_2)$ state and without passing through the triplet manifold. There is no conclusive argument that these paths are taken – especially since optimizations show that the S₁ minimum lies on the localized $n\pi^*(NO_2)$ state – however, this is the only argument that explains our data satisfactorily.



Fig. 4. Decay associated spectra (DAS) and time zero shift for nitrobenzene (NBE) and n-nitrobenzaldehyde (n = 2,3,4). The time constants that belong to the amplitudes are given in Table 1. The DAS associated to τ_1 are normalized to the maximum value and the DAS of τ_2 is given relative to the former.

More information on a reaction path can, in principle, be obtained by running trajectory calculations on a high lying state, which, however, is computationally too demanding at the present time. Table 3 shows the numerous electronic states that need to be considered in such a study. The possibilities of new reaction pathways opening up upon excitation to high lying electronic states were observed recently in pyrrole, where the initially prepared wavepacket transiently populates a Rydberg state which directly influences the quantum yields of the photochemical process [43]. A similar mechanism might also be present in this case, although the photoelectron spectra provide no evidence for this possibility.

4. Conclusions

In conclusion, we observe that the dynamics of nitrobenzene and nitrobenzaldehydes upon excitation at 200 nm show similar time constants to the excited state dynamics after excitation to lower excited states at longer wavelengths. This is intriguing because other channels, notably NO₂ release and direct return to the ground state, are predicted to be open. However, these seem to play only a minor role on the relaxation times. In NBE and 2-NBA, the dominant relaxation channels are NO release on the ground state potential energy surface and rearrangement to 2nitrosobenzoic acid via ketene azenic acid, respectively. We speculate that, in 3- and 4-NBA, the initially prepared wavepacket gets trapped on the S₁ potential energy surface, which is a charge transfer state with an excitation from the aldehyde to the nitro group. This delays internal conversion to the ground state which takes



Fig. 5. Structures of the S₁ minimum and the S₁-S₀ conical intersection of 2 and 4-nitrobenzadehyde calculated at the SA-3-(9,10) CASSCF/cc-pVDZ level of theory. Distances are given in pm. α denotes the O-N-O angle, ϕ is the projection of the C-N axis onto the ONO-plane and τ denotes the torsion of the NO₂ group (in degrees).



Fig. 6. Sketch of the model for the dynamics in NBE, 3-, and 4-NBA. The green arrows indicate the pathway for 3- and 4-NBA while the pathway along the red arrows is energetically unfavorable. In NBE, the $\pi\pi^*$ (CHO) state does not exist and deactivation from the initially excited $\pi\pi^*$ state proceeds directly to the $n\pi^*$ (NO₂) state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

place from a state that is localized at the NO₂ group. Therefore, intersystem crossing to the triplet state is the major relaxation channel. High-level ab initio calculations may reveal the course of the dynamics, but these computations will require a large active space and are currently beyond state-of-the art.

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Appendix A. Supplementary material

Geometry of the minimum ground, S_1 , and S_1 - S_0 conical intersection geometries for 2- and 4-NBA, energies for all minima and transition states along the reaction coordinates depicted in Fig. 2 for the ground, S_1 , and T_1 states of NBE, 2-, 3-, and 4-NBA, time-resolved photoelectron spectra of BA, 3- and 4-NBA. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2017.11.011.

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