# Influence of Alkoxy Groups on the Photoinduced Dynamics of Organic Molecules Exemplified on Alkyl Vinyl Ethers

O. Schalk,<sup>1</sup>\* M. Stenrup,<sup>2,3</sup> T. Geng,<sup>1</sup> R. Lindh,<sup>2,3</sup> R. D. Thomas,<sup>1</sup> R. Feifel,<sup>4</sup> T. Hansson<sup>1</sup>

<sup>1</sup>Department of Chemical Physics, AlbaNova University Centre, Stockholm University, Roslagstullsbacken 21, 106 91 Stockholm, Sweden

<sup>2</sup>Department of Chemistry – Ångström, The Theoretical Chemistry Programme, Uppsala University, P.O. Box 518, 751 20 Uppsala, Sweden

<sup>3</sup>Uppsala Center for Computational Chemistry – UC<sub>3</sub>, Uppsala University, P.O. Box 518, 751 20 Uppsala, Sweden

<sup>4</sup> Department of Physics, University of Gothenburg, Origovägen 6B, 412 96 Gothenburg, Sweden

\*electronic address: oliver.schalk@fysik.su.se

# Abstract

A series of different alkyl vinyl ethers is investigated in order to decipher the possible reaction channels upon photoexcitation to the  $\pi$ 3s-Rydberg and the  $\pi\pi^*$ -valence state at 200 nm using time-resolved photoelectron spectroscopy and on-the-fly time-dependent density functional theory dynamics simulations. The results indicate two possible relaxation pathways: (1) a radiationless decay through the  $\pi\pi^*$ -state back to the ground state via torsion of the C=C double bond, in accordance with the dynamics found in ethylene; and (2) a fast dissociation of the C-O bond between the alkyl and the vinoxy group in the  $\pi\sigma^*$ -state. The latter state can be accessed only after excitation to the  $\pi$ 3s-Rydberg state (quantum yield of ~50 % according to the dynamics simulations). Additionally, the excited state barrier leading to formation of a vinyl radical was found to be too high to be crossed. These results indicate that the dynamics of ethers crucially depend on the excitation wavelength and that the  $\pi\sigma^*$ -state constitutes an important competitive reaction channel that leads to dissociation of the molecules.

## I. INTRODUCTION

The dynamics of unsaturated hydrocarbons upon photoexcitation in the ultraviolet/visible (UV/Vis) spectral region has been the subject of many theoretical and experimental studies (see refs 1-5 and references cited therein). While each molecule is unique, certain rules have been found to understand and predict the outcome of these photo-induced processes: Most successful have been the ideas of Woodward and Hoffman<sup>6</sup> and their rules to predict the outcome of chemical reactions are subject of many textbooks on organic chemistry. However, the Woodward-Hofmann rules only cover a certain range of organic molecules. These rules have been refined first by van der Lugt and Oosterhoff<sup>7</sup> and later by other authors.<sup>8</sup> In another approach, it has been shown that the dynamics in polyenes can often be understood by the dynamics of the ethylene molecule<sup>4,9-11</sup> which acts as a dynamophore, which is defined as "that part of the molecule where the dynamics of a molecule is approximately localized".<sup>9,12</sup> This means that the excited state dynamics often follows the dynamical patterns that are observed for ethylene, i.e. twist of the C=C-double bond and then either pyramidalization at one of the CH<sub>2</sub>-groups or hydrogen transfer to form HC-CH<sub>3</sub>.<sup>4,13</sup> A consequence of the double bond twist is cis-trans isomerization, which has been observed in larger chain polyenes and biomolecules, see e.g. ref 14. In ring-shaped molecules, the CH2-twist manifests either through ring puckering or, most often, ring opening reactions.<sup>9,15</sup>

While the photo-induced dynamics of polyenes are reasonably well understood, most organic molecules are more complex as they possess functional groups including heteroatoms such as nitrogen, oxygen or sulfur. These functional groups make the interpretation of femtosecond time-resolved experimental studies of excited state dynamics more complicated because different functional groups can influence the reaction pathways in different ways. For example, the lone pair orbital of oxygen is in the same energetic region as the  $\pi$ -orbitals of a C=C-double bond and the dynamics of oxygen containing molecules can be influenced by  $n\pi^*$ -states which can act as doorway states for intersystem crossing.<sup>16</sup> Another example is the antibonding  $n\sigma^*$ - and  $\pi\sigma^*$ -states in molecules containing HN-, OH or OCH<sub>3</sub>-groups which can lead to direct dissociation of the molecules.

In order to understand the influence of the different functional groups, a bottom-up approach is followed, in which one group at a time is focused on before subsequently increasing the complexity of the molecules. With this approach, it is expected that knowledge of the functionality of the different groups and the way how they influence the photo-induced dynamics of molecules will be able to provide crucial information to not only understand the

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function of biomolecules but also to tailor functional materials used in light sensitive devices with respect to quantum yields in the desired channel, the absorption cross section, or other properties that might be important in functional materials such as molecular photo-switches.

In this work, the alkoxy-groups in alkyl-vinyl ethers is the focus. From the perspective of the dynamics, these molecules might be considered as ethylene molecules where one hydrogen atom is replaced by an alkoxy group. The most prominent species of this group is methyl vinyl ether (CH<sub>2</sub>=CH-O-CH<sub>3</sub>). While vinyl ethers have many industrial applications such as polymerization (e.g. poly methyl vinyl ethers), its photoreactions are only sparsely investigated. Often, methyl vinyl ether (MVE) is used as a precursor for studies on the vinoxy radical (CH<sub>2</sub>=CHO) which is a crucial intermediate in combustion<sup>17</sup> and photochemical smog cycles.<sup>18</sup> In these experiments, an excimer laser is used at 193 nm to dissociate MVE. At this wavelength, MVE is excited primarily to its lowest lying  $\pi\pi^*$ -state (absorption maximum at 188 nm). The quantum yields of this reaction were investigated by Morton et al. in crossed laser molecular beam experiments.<sup>19</sup> They found two different reaction channels, the major one leading to ground state CH<sub>3</sub> and vinoxy in the excited state ( $\tilde{A}^2 A$ ) while a second channel leads to ground state vinoxy (~X<sup>2</sup>A''). Both channels potentially lead to further fragmentation of the vinoxy radical. Investigating the spatial product distribution of the CH<sub>3</sub>fragments showed almost no anisotropy which led to the conclusion that the dissociation process at 193 nm needs more time than the rotational reorientation of the molecule. This is in agreement with ground state dissociation, where a dissociation constant of 2.7 x  $10^{11}$  exp(-43800 cal mol<sup>-1</sup>/RT) s<sup>-1</sup> was found (for the similar ethyl vinyl ether).<sup>20</sup> To our knowledge, there are no further studies investigating the relaxation pathways of photoexcited alkyl vinyl ethers, although several questions remain unresolved, for example the time scale of the excited state dynamics, the reaction mechanism, and if there exists an excited state C-O bond cleavage. Finally, the present investigation aims at answering the questions on whether the excited state dynamics can be described by the ethylene dynamophore and how the methoxy group modifies this dynamics. In this study, time-resolved photoelectron spectroscopy (TRPES) is used as a tool to follow the dynamics of different vinyl ethers with varying alkoxy groups, namely ethyl vinyl ether (EVE), propyl vinyl ether (PVE) and 2-propanol vinyl ether (2PrVE, see inset of Figure 1 for a sketch of the molecules) and complement the experimental investigations with on-the-fly dynamics simulations on MVE, which is computationally less demanding than for the other molecules. Possible differences in the photoelectron spectra of the different molecules are supposed to show a trend that can be interpolated to the theoretical

results of MVE.

# **II. METHODS**

## **A. Experimental methods**

Ethyl vinyl ether, propyl vinyl ether, and 2-propanol vinyl ether were purchased from Sigma-Aldrich with a purity of 99% and used without further purifications.

Absorption spectra were taken in a 1 cm quartz cuvette (Hellma) under saturated vapor pressure using a Cary 5e photospectrometer (Varian). The electron spectrometer used for the time-resolved studies is of the magnetic bottle type and was originally developed for multiparticle coincidence experiments. A detailed description of it can be found in refs 21 and 22. Pump and probe wavelengths were 200 and 267/400 nm, respectively, produced by frequency doubling and subsequent mixing processes of the fundamental of a Ti:Sapphire regenerative amplifier (Coherent Legend USP-HE) with an output energy of 4 mJ/pulse at a repetition rate of 1 kHz and a center wavelength of 800 nm. The beams were gently focused into the electron spectrometer by f/150 for the pump and f/125 for the probe pulse. The cross-correlation between the pulses was measured in situ to be  $140 \pm 10$  fs for both the 200 + 267 nm and the 200 + 400 nm experiments utilizing the non-resonant ionization signal of xenon. The spectral bandwidth of the pump and probe pulses were around  $200 \text{ cm}^{-1}$  and the used laser intensities were 100 nJ, 700 nJ and 2 µJ for the 200, 267 and 400 nm pulses, respectively. Perpendicular to the incoming laser pulses, the sample gas was introduced into the interaction region of the magnetic bottle spectrometer by an effusive needle. The time delay between the pump- and the probe pulses was controlled by a motorized translation stage. At each delay, the measured pump-probe signal was corrected by subtracting the background signals due to the pump and probe laser pulses alone.

## **B.** Computational methods

The excited state dynamics of MVE was simulated by solving Newton's equations for an ensemble of 200 trajectories in the  $S_1$  electronic state. The forces guiding each trajectory were calculated on-the-fly,<sup>23</sup> i.e. evaluated directly as needed in the simulations, using the method of time-dependent density functional theory (TD-DFT) together with the CAM-B3LYP functional and 6-31+G\* basis set. Initial positions and momenta were sampled from a ground state Wigner distribution (constructed from the  $S_0$  vibrational ground state in the harmonic

approximation) and then projected onto the S<sub>1</sub> state. The integration time step was 0.5 fs and the maximum simulation time was 200 fs. The dynamics simulations were performed with the NEWTON-X program<sup>24</sup> interfaced with the GAUSSIAN 09 program.<sup>25</sup>

Complementary static calculations, including the determination of equilibrium geometries, energy barriers, and vertical excitation energies were performed at the same DFT level as indicated above.

# **III. RESULTS**

## A. UV-Vis absorption

The gas phase absorption spectrum of MVE is well known.<sup>26,27</sup> The lowest lying  $\pi\pi^*$ -state peaks at 188 nm. On the red wing of the spectrum, structures originating from the  $\pi$ 3s-Rydberg state can be observed. Hence, at an excitation wavelength of 200 nm one would expect to excite to a superposition of the  $\pi\pi^*$ - and the  $\pi$ 3s-Rydberg state in this molecule.

The spectra of EVE, PVE and 2PrVE are so far not reported in literature. Therefore, their absorption spectra down to 190 nm are presented in Figure 1. These spectra are almost identical and agree well with the absorption spectrum of MVE. This finding is confirmed by our electronic structure calculations which show that the lowest lying excited states, i.e. the  $\pi$ 3s-,  $\pi\pi^*$ - and an additional  $\pi$ 3p-state appear at almost the same energies for the different molecules (see Table 1). Hence, we assume that essentially the same states are observed in the molecules under investigation. The superimposed structure on the spectra originates from a C=C vibrational progression in the  $\pi$ 3s-Rydberg state. At 200 nm, two vibrational quanta are put into the C=C stretching mode in MVE.<sup>26</sup>

## **B.** Molecular dynamics simulations

Of the 200 trajectories started in the S1 state (vertically the  $\pi$ 3s Rydberg state, see Table 1) of MVE, 54% underwent C-O bond cleavage to form the vinoxy + methyl radical pair, while 44% were subject to twist and pyramidalization at the C=C bond. In the analysis, trajectories were assigned to the former reaction path if the C-O bond distance was stretched beyond 2.0 Å, and to the latter if the O-C=C-H dihedral angle was increased beyond 60 degrees. The corresponding characteristic times, taken as averages over each subset of trajectories, were

found to be 29 and 44 fs, respectively. We note (i) that the value of 2.0 Å corresponds to that distance where the energy gap between the excited and ionic state is too large to allow ionization with one probe photon in the 200 + 267 nm experiments, and that the characteristic time represents, in that case, the observation window; and (ii) that, in the case of the O-C=C-H twist, the characteristic time does not coincide with the excited state lifetime such that the molecules will likely stay in the observation window for an extended period. An additional group of trajectories was found to exhibit cleavage at one of the C-H bonds. However, this group makes up only 2% of the total number of trajectories and is not considered further in the following discussion.

From an electronic structure point of view, the observed methyl cleavage should be associated with a change in character of the S<sub>1</sub> state from  $\pi$ 3s to  $\pi\sigma^*$ . Similarly, the C=C bond twisting should be associated with a change in character from  $\pi$ 3s to  $\pi\pi^*$ . By carrying out a transition state search on the S<sub>1</sub> potential energy surface, the corresponding energy barriers with respect to the S<sub>1</sub> state minimum were determined to be 0.07 and 0.02 eV, respectively (see Table 1). As a comparison, the analogous barrier for methoxy cleavage seems to be significantly higher, upper limit 1 eV, as estimated from a one-dimensional cut through the S<sub>1</sub> potential energy surface (C-O distance varied, remaining coordinates fixed). This explains why the methoxy radical channel is not observed in the dynamics simulations.

In Figure 2, we show the distance between the methyl carbon and the oxygen atom as a function of propagation time for the channel that experiences C-O bond cleavage (cf. Figure 2a) and the ethylene dynamics channel (cf. Figure 2b). From the analysis of the data, it is concluded that accessing the C-O dissociation channel is a hit-or-miss reaction: either the dynamics proceeds within one vibrational period of the C-O stretch vibration or the dynamics takes place along the ethylene-twist coordinate. To obtain more information, the C-O distance at the start of the trajectories for the two relaxation channels is plotted in Figure 3. Here, it is observed that the fitted C-O distance distribution for the C-O dissociation channel is similar to the first excited state of a harmonic oscillator function, while the fitted distribution for the ethylene channel is closer to a ground state vibrational function (see the fitted curves in Figure 3). With that interpretation, the C-O bond cleavage occurs if enough initial energy is placed into the C-O bond in the electronically excited state to overcome the barrier to the  $\pi\sigma^*$ -state. Otherwise, the molecule is forced to take the ethylene channel in the  $\pi\pi^*$ -state.

In contrast to the CO-dissociation, the ethylene twist coordinate is known to be Franck-Condon inactive and forms a saddle point on the  $\pi\pi^*$ -state.<sup>4,13,15,28</sup> Therefore, the twist

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channel cannot be accessed directly upon photoexcitation, which slows down the reaction by several tens of fs. No distinct initial distribution is observed for the two different channels, and the excited state lifetime is roughly a factor of 2 larger than for the CO-dissociation (depending on how the excited state life time is defined for the CO-dissociation).

It is noted that the present simulations do not take into account any non-adiabatic coupling to the  $S_0$  state. Thus, even though both the C-O bond cleavage and the C=C twisting were found to be accompanied by an intersection of the  $S_0$  and  $S_1$  potential energy surfaces, the calculated trajectories always stayed in the upper state. In fact, when the energy difference between the  $S_0$  and  $S_1$  states became too small, the trajectories were usually terminated due to numerical instabilities in the TD-DFT approach. Hence, the present dynamics results are only representative for the initial dynamics in the  $S_1$  state, before an intersection with the  $S_0$  state is reached.

## C. Time-resolved photoelectron spectroscopy

Time-resolved photoelectron spectra of EVE, PVE and 2PrVE upon excitation at 200 nm (6.2 eV) and ionization at 267 nm (4.65 eV) are shown in Figure 4 a-c. The vertical ionization potential of EVE is 8.83 eV.<sup>29</sup> Therefore, it is expected that the energy cut-off for experiments with one photon pump and one photon probe [1,1'] lies at electron kinetic energies in the range of 10.85 eV - 8.83 eV = 2.02 eV. Considering that the excitation to the  $\pi$ 3s-Rydberg state at 200 nm supplies the molecule with two extra vibrational quanta in the C=C-stretch coordinate with a combined energy of 1890 cm<sup>-1</sup> (0.23 eV),<sup>26</sup> the dominant peak in the photoelectron spectrum at 1.77 eV can be assigned to ionization from that Rydberg state. Although s-Rydberg states often show large Rydberg-valence mixing,<sup>28</sup> an earlier timeresolved photoelectron study on 1,3-butadiene showed that the Rydberg peaks are still spectrally narrow.<sup>30</sup> The stretch of the photoelectron band toward kinetic energies above 2 eV can be explained by the difference between the vertical and adiabatic ionization potentials of about 0.2 eV as found in MVE and PME.<sup>29</sup> This indicates an excitation to the  $\pi\pi^*$ -state because ionization from the Rydberg state can not produce electrons with energies that reach the adiabatic threshold. Some electrons have kinetic energies that exceed the limit of ionization to the adiabatic minimum. These electrons originate from two photon ionization processes. However, this contribution is weak in the data presented and is not considered further.

Photoelectron spectra at a probe wavelength of 400 nm (3.1 eV) are shown in Figure 5 for EVE and PVE. As for the data taken at a probe wavelength of 267 nm, the peak of the Rydberg state is observed at 0.23 eV below the [1,1'] energy cut-off at 0.47 eV. However, due to the higher probe intensity available, a two photon probe signal is observed with the Rydberg peak at 3.34 eV and the energy cut-off at 3.57 eV.

Time constants and their decay associated spectra (DAS) were extracted using a Levenberg-Marquart 2D global fitting scheme,<sup>31</sup> expressed as

$$S(E, \Delta t) = \sum_{i} A_{i}(E) P_{i}(\Delta t) \otimes g(\Delta t)$$
<sup>(1)</sup>

where the  $A_i(E)$  are the DAS of the individual channels which have a time-dependent population  $P_i(\Delta t)$ , expressed in terms of exponential functions, and  $g(\Delta t)$  is the crosscorrelation function measured in a separate experiment (see experimental section). As discussed in previous publications, such a global fitting analysis might suffer from effects of large amplitude motions.<sup>9,11,32</sup> If this is the case, one observes a temporal shift of the spectrum toward smaller photoelectron kinetic energies which is caused by the rise of the vertical ionization potential along the large amplitude deformation coordinates. There are several possibilities to account for such a shift;<sup>32</sup> the most convenient one is to use a 2D global-fitting routine, and artificially varying the "time zero" of the fit as a parameter. Then, "time zero" becomes a variable to describe the ultrafast deformations. Recently, it has been demonstrated that the temporal extent of the shift can be directly correlated to the incubation time of a wavepacket in the excited state, i.e. before population transfer to lower lying states begins.<sup>11</sup> It is noted that fits of time zero are surprisingly robust due to the dispersed nature of the signal, and while exponential time constants typically possess large error bars when they are shorter than the cross correlation, shifts are usually more reliable.<sup>11</sup>

The data taken with a probe wavelength of 267 nm could be fitted with a bi-exponential decay. The shorter time constant was between 10 and 20 fs for all molecules. We note that the actual values should be taken with some caution because they are shorter than the cross correlation and hence are likely to be governed by some comparatively large error bars. Therefore, they are primarily regarded as indicators for the existence of a "fast" process. The longer time constant ranged from  $70 \pm 15$  fs in EVE and  $90 \pm 20$  fs in 2PrVE to  $100 \pm 30$  fs in PVE. The amplitude of the DAS of the longer time constant was  $5 \pm 2$  % of the amplitude of the shorter time constant for photoelectron kinetic energies lower than the Rydberg signal and zero for energies above. The Rydberg signal peaked at 1.77 eV in EVE and PVE and 1.85 eV

in 2PrVE. Time zero shifts are plotted in Figure 6a. The broad band at lower photoelectron kinetic energies shifts on a 20 fs timescale and can be assigned to dynamics either on the  $\pi\pi^*$ or the  $\pi\sigma^*$ -state (see more details in the discussion section). The Rydberg state shows a shift of time zero of  $35 \pm 5$  fs but an individual fit of that energetic region did not reveal any special time dynamics. The photoelectron spectra taken at a probe wavelength of 400 nm could be fitted with the same time constants as the spectra obtained at a probe wavelength of 267 nm. While the [1,1'] regions look identical in both spectra (besides an energy shift of 1.55 eV due to the lower probe photon energy at 400 nm), the dynamics in the [1,2'] region are not a copy of the one photon probe region. Here, the time zero spectrum is shifted by  $60 \pm$ 10 fs instead of the 20 fs at the previous probe wavelength, for both EVE and PVE (see Figure 6b). This shift can be assigned to the ethylene twist dynamics in the  $\pi\pi^*$ -state. As was shown before in butadiene, this twist can be nicely followed with a two photon probe (see refs 12 and 33 for a TRPES spectrum of butadiene) because the wavepacket accumulates doubly excited state character as it progresses  $^{34}$  which yields a good two photon ionization cross section. In ethylene, for example, the singly and the doubly excited valence states are degenerate at a 90 degree twist of the CH<sub>2</sub>-group<sup>4</sup> and the wavepacket receives an increased level of doubly excited character as it moves along the twisting coordinate. At the same time, the  $\pi\sigma^*$ -state is a purely singly excited state and, as a consequence, the two photon probe cross section is reduced. Hence, the data at a probe wavelength of 400 nm evinces that the wavepacket needs about 60 fs to reach the  $\pi\pi^*$ -state but that the dynamics in this state is fast because no long time constant could be extracted.

The differences between the substituted molecules investigated here are minor if any. This can be expected, e.g. from an analysis of the ground state vibrations where the difference of the frequency for the mode localized at the C-O-C stretching coordinate differs by 7 cm<sup>-1</sup> between MVE and PVE. In addition, no effect from adding an OH-group to the alkyl chain is observed.

## **IV. DISCUSSION**

# A. Dynamics of alkyl vinyl ethers and comparison with theoretical results

The results based on absorption spectroscopy, TRPES and on-the-fly trajectory calculations lead to the following picture for the photo-initiated dynamics of alkyl vinyl ethers upon excitation at 200 nm:

(i) Absorption of a 200-nm photon excites the molecules either to the  $\pi$ 3s-Rydberg state or to the lowest lying  $\pi\pi^*$ -state. Absorption to the  $\pi$ 3s-Rydberg state is evidenced by the sharp high intensity band in the photoelectron spectrum between 1.75 and 1.9 eV kinetic energy for the different molecules. The position of the band is 0.23 eV below the [1,1'] energy cut-off and confirms that the Rydberg state is vibrationally excited in agreement with the absorption spectrum.<sup>26</sup> Excitation to the  $\pi\pi^*$ -state can be rationalized by the presence of a significant number of photoelectrons reaching the [1,1'] energy cut-off. The photoelectron spectrum is structureless as can be expected for a valence state with a steep gradient in the Franck-Condon region. Due to their different ionization cross sections, the exact quantum yields for the individual states are not known; however, it is clearly observed that both states are significantly populated.

(ii) Upon excitation to the  $\pi\pi^*$ -state, the molecules most likely follow the twist and pyramidalization pathway. The absence of a direct dissociation channel from the excited state was already suggested by the lack of anisotropy in the distribution of the CH<sub>3</sub>-fragments seen in the experiments of Morton et al. at a pump wavelength of 193 nm.<sup>19</sup> An initial population of the  $\pi\pi^*$ -state at electron kinetic energies above the Rydberg-peak (1.8-2.2 eV) was observed in the photoelectron spectrum. In that region, no shift in time zero was detected. From the Franck-Condon region, the molecules first elongate along the Franck-Condon active C=C-stretching mode which, however, does not cause a significant change in ionization energy. It is only in a second step that the twisting motion sets in. Typically, the ionization cross section decreases along the twisting mode because of a decreasing Franck-Condon overlap with the ionic state. In that sense, it is likely that the long time constant in the photoelectron spectra of 70-100 fs for the different species is related to the dynamics toward the  $\pi\pi^*$ -state excitation.<sup>34,35</sup>

(iii) Upon excitation to the  $\pi$ 3s-Rydberg state, the molecules have two available reaction pathways: internal conversion to either the  $\pi\pi^*$ - or the  $\pi\sigma^*$ -state. According to the calculations, both channels have approximately equal quantum yields (under the assumption that the extra vibrational energy in the ethylene stretch vibration does not influence the different channels). According to the assignment of the features in the 267 nm probe spectrum originating from excitation to the  $\pi\pi^*$ -state, there are two components of the signals left to explain the dynamics after Rydberg state excitation. Firstly, a strong photoelectron signal is observed that stretches over the whole spectrum with both shift and decay occurring within 20

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fs. This dynamics can be assigned to the  $\pi\sigma^*$ -state, as this state is accessed directly. The calculations show that the gap between the  $\pi\sigma^*$ -state and the ionic state rises for about 4 eV along the C-O stretching coordinate, which is an indication that C-O bond fission occurs (in comparison, the rise of the ionic potential for the ethylene twisting channel in the  $\pi\pi^*$ -state is about 2 eV). The second feature is a shift within the Rydberg state which extends on a longer time scale than required for the dynamics of the  $\pi\sigma^*$ -state. This means that the molecules are staying in the Rydberg state before they convert into the  $\pi\pi^*$ -state from where they reach the ground state via the ethylene conical intersection. The time required for the internal conversion is 60 ± 15 fs according to the data recorded at a probe wavelength of 400 nm.

A summary of the dynamics upon  $\pi$ 3s-Rydberg state excitation is shown in Figure 7. Since the dynamics are localized at the  $\pi$ -system of the molecule and the  $\sigma$ -bond between the alkylcarbon and the oxygen, the size of the alkyl group has only a minor influence on the dynamics. As a consequence, there exists a very good agreement between experimental and theoretical results. The spectral shift and the dynamics found for fragmentation via the  $\pi\sigma^*$ channel are both around 20 fs, the spectral shift of the photoelectron spectrum is reproduced nicely, and the time constants for the twist in the  $\pi\pi^*$ -channel agrees equally well. While the barriers to cross between the Rydberg and the valence states might be plagued by the approximate nature of the TD-DFT approach, this is not evidenced by the experimental results.

## **B.** Dynamics of the ether group and comparison with other work

The dynamics of the ether group strongly depends on how likely it is to populate the  $\pi\sigma^*$ state that leads to dissociation of the alkyl group. Generally, if a  $\pi\pi^*$ -state is populated that leads to fast return to the ground state, the dynamics are likely to follow that route as seen for methyl vinyl ether excited at 193 nm where no dissociation takes place in the excited state.<sup>19</sup> If the molecule is excited to a state which does not directly decay to the ground state, the whole picture might change. In the experiments, it is observed that an excitation to the  $\pi$ 3s-Rydberg state can lead to fast internal conversion to the  $\pi\sigma^*$ -state and from there to vinoxy formation with a significant quantum yield. This example shows the crucial dependence of the reaction mechanism on the excitation wavelength in molecules with dissociative  $\pi\sigma^*$ -states which can make photo-induced dynamics of molecules with ether groups hard to predict. In the dynamophore picture, it can be concluded that localization to the ethylene dynamophore is just one of two possible channels and that – at certain excitation wavelengths - another relaxation path is taken that localizes at the antibonding O-Me bond.

The same picture as for alkyl-vinyl ether also holds for the photo-induced dynamics in aromatic molecules containing an ether group, as for example anisole<sup>36,37,38</sup> (methoxybenzene,  $C_5H_6$ -OCH<sub>3</sub>). Here, the lowest lying state is a  $\pi\pi^*$ -state but, in contrast to ethylene, no fast relaxation channel to the electronic ground state is available. Instead, the barrier to the  $\pi\sigma^*$ -state leading to methyl-fragmentation is relatively low<sup>38</sup> (0.51 eV on the CC2/cc-pVDZ level) and the dissociation dynamics upon excitation at 200 nm was observed to be faster than 100 fs.<sup>38</sup> The methyl dissociation channel also dominates in other phenylethers such as methoxybenzoic acid.<sup>39</sup> Moreover, the wavelength dependence of the accessibility of the Me-dissociation channel has been studied in *p*-methoxyphenol, where two  $\pi\sigma$ \*-states – one promoting dissociation along the O-Me bond and one along the O-H bond – can be populated, depending on which state was excited initially.<sup>40</sup> Here, it was found that O-Me dissociation was observed between 280 and 245 nm while O-H dissociation took place at longer as well as shorter wavelengths. It can be concluded that O-Me dissociation is an important reaction channel in ether molecules but that its accessibility depends both on the state that is excited as well as the dynamics that take place on the  $\pi\pi^*$ -potential energy surfaces of the respective molecules.

# V. CONCLUSIONS

In conclusion, the reaction pathways of photo-excited alkyl vinyl ethers depend critically on the state they are excited to. In general, two fast and competitive reaction channels exist: The first is the twist and pyramidalization channel known from the dynamics in ethylene which takes place on the  $\pi\pi^*$  potential energy surface; and the second is a formation of a methyl and a vinoxy radical which takes place on the  $\pi\sigma^*$  potential energy surface and is known e.g. from phenylethers. Upon direct excitation to the  $\pi\pi^*$ -state, the ethylene channel is accessed exclusively<sup>19</sup> but excitation to the  $\pi3s$ -Rydberg state opens up both pathways. The dissociation channel of the ether group is, therefore, predicted to play a role in molecules that can be excited to states that do not lead to a fast internal conversion back to the ground state. Therefore, aromatic systems seem to be more susceptible to this channel than non-aromatic polyenes because they often show slow valence state relaxation in their  $\pi\pi^*$ -states. In this work, excitation to a Rydberg state was chosen to highlight a case where the  $\pi\sigma^*$ -state can Page 13 of 38

influence the dynamics also in a polyene-chain. In order to get a more complete picture of the dynamics induced by an ether group, more research is required. This includes cyclic alkyl vinyl ethers such as 2,3-dihydrofuran as well as longer open chained polyenes where the ether group might act as an electron donating group to the  $\pi$ -system. While this does not play a major role for ethylene because the dynamics take place on a single  $\pi\pi$ \*-state, longer polyenes might be affected due to two close-lying valence states which can both take part in the reaction pathway (see e.g. ref. 41).

# Acknowledgement

This work was supported by the Swedish Research Council (VR), the Knut and Alice Wallenberg Foundation, the Göran Gustafsson Foundation, the Wenner-Gren Foundation and the Swedish strategic research programme eSSENCE. In addition, the authors would like to thank the group of Wolfgang Zinth (Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München) for sharing their 2D fitting routine.

# References

- [1] Liu, R. S. H.; Hammond, G. S. Photochemical Reactivity of Polyenes: from Dienes to Rhodopsin, from Microseconds to Femtoseconds. *Photochem. Photobiol. Sci.*, 2003, 2, 835–844.
- [2] Deb, S.; Weber, P. M. The Ultrafast Pathway of Photon-Induced Electrocyclic Ring-Opening Reactions: The Case of 1,3-Cyclohexadiene. *Annu. Rev. Phys. Chem.* 2011, 62, 19-39.
- [3] Schalk, O.; Boguslavskiy, A. E.; Schuurman, M. S.; Broogard, R. Y.; Unterreiner, A. N.;
   Wrona-Piotrowicz, A.; Werstiuk, N. H.; Stolow, A. Substituent Effects on Dynamics at
   Conical Intersections: Cycloheptatrienes. J. Phys. Chem. A 2013, 117, 10239-10247.
- [4] Levine, B. G.; Martínez, T. J. Isomerization Through Conical Intersections. Annu. Rev. Phys. Chem. 2007, 58, 613–634.
- [5] Levine, B. G.; Martinez, T. J. Ab Initio Multiple Spawning Dynamics of Excited Butadiene: Role of Charge Transfer. J. Phys. Chem. A 2009, 113, 12815–12824.
- [6] Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry. *Angew. Chem. Internat. Edit.* 1969, *8*, 781–853.
- [7] van der Lugt, W. T. A. M.; Oosterhoff, L. J. Symmetry control and photoinduced reactions. J. Am. Chem. Soc. 1969, 91, 6042-6049.
- [8] Nenov, A.; Kölle P.; Robb, M. A.; de Vivie-Riedle, R. Beyond the van der Lugt/Oosterhoff Model: When the Conical Intersection Seam and the S1 Minimum Energy Path Do Not Cross. J. Org. Chem. 2010, 75, 123-129.
- [9] Schalk, O.; Boguslavskiy, A. E.; Stolow, A.; Schuurman, M. S. Through-Bond Interactions and the Localization of Excited-State Dynamics. J. Am. Chem. Soc. 2011, 133, 16451-16458.
- [10] Kuhlman, T. S.; Glover, W. J.; Mori, T.; Møller, K. B.; Martínez, T. J. Between Ethylene and Polyenes - the Non-Adiabatic Dynamics of cis-Dienes. *Faraday Discuss.* 2012, 157, 193-212.
- [11] Wolf, T. J. A.; Kuhlman, T. S.; Schalk, O.; Martinez, T. J.; Møller, K. B.; Stolow, A.; Unterreiner, A.-N. Hexamethylcyclopentadiene: A Test Case for the Combination of Time Resolved Photoelectron Spectroscopy and ab initio Multiple Spawning

Simulations, Phys. Chem. Chem. Phys. 2014, 16, 11770-11779.

- [12] Schalk, O.; Boguslavskiy, A. E.; Schuurman, M. S.; Stolow, A. The Dynamophore Localization of Excited State Dynamics Studied by Time-Resolved Photoelectron Spectroscopy. *EPJ Web of Conferences* 2013, *41*, 02037.
- [13] Tao, H.; Allison, T. K.; Wright, T. W.; Stooke, A. M.; Khurmi, C.; Van Tillborg, J.; Liu, Y.; Falcone, R. W.; Belkacem, A.; Martinez, T. J. Ultrafast Internal Conversion in Ethylene. I. The Excited State Lifetime. J. Chem. Phys. 2011, 134, 244306(1)-244506(8).
- [14] Schoenlein R. W.; Peteanu L. A.; Mathies R. A.; Shank C. V. The First Step in Vision: Femtosecond Isomerization of Rhodopsin. *Science* 1991, 254, 412-415.
- [15] Mori, T.; Glover, W. J.; Schuurman, M. S.; Martinez, T. J. Role of Rydberg States in the Photochemical Dynamics of Ethylene. J. Phys. Chem A. 2012, 116, 2808-2818.
- [16] El-Sayed, M. A. Spin-Orbit Coupling and the Radiationless Processes in Nitrogen Heterocyclics. J. Chem. Phys. 1963, 38, 2834-2838.
- [17] Carpenter, B. K. Computational Prediction of New Mechanisms for the Reactions of Vinyl and Phenyl Radicals with Molecular Oxygen. J. Am. Chem. Soc. 1993, 115, 9806-9807.
- [18] Barnhard, K. I.; Santiago, A.; He, M.; Asmar, F.; Weiner, B. R. Pressure and Temperature Dependence of the C<sub>2</sub>H<sub>3</sub>O + NO<sub>2</sub> Reaction. *Chem. Phys. Lett.* 1991, *178*, 150-156.
- [19] Morton, M. L.; Szpunar, D. E.; Butler, L. J. Photodissociating Methyl Vinyl Ether to Calibrate O + Etylene Product Branching and to Test Propensity Rules for Product Channel Electronic Accessibility. J. Chem. Phys. 2001, 115, 204-216.
- [20] Shimofuji, K.; Saito, K. O.; Imamura, A. Unimolecular Thermal Decomposition of Ethyl Vinyl Ether and the Consecutive Thermal Reaction of the Intermediary Product Acetaldehyde: Shock Wave Experiment and ab Initio Calculation. J. Phys. Chem. 1991, 95, 155-165.
- [21] Eland, J. H. D.; Vieuxmaire, O.; Kinugawa, T.; Lablanquie, P.; Hall, R. I.; Penent, F. Complete Two-Electron Spectra in Double Photoionization: The Rare Gases Ar, Kr, and Xe. *Phys. Rev. Lett.* 2003, 90, 053003.

- [22] Kłoda, T.; Matsuda, A.; Karlsson, H. O.; Elshakre, M.; Linusson, P.; Eland, J. H. D.;
   Feifel, R.; Hansson, T. Strong-Field Photoionization of O<sub>2</sub> at Intermediate Light Intensity. *Phys. Rev. A* 2010, 82, 033431.
- [23] Barbatti, M. Nonadiabatic Dynamics with Trajectory Surface Hopping Method. WIREs Comput. Mol. Sci. 2011, 1, 620–633.
- [24] Barbatti, M.; Ruckenbauer, M.; Plasser, F.; Pittner, J.; Granucci, G.; Persico, M.; Lischka, H. Newton-X: a Surface-Hopping Program for Nonadiabatic Molecular Dynamics. WIREs Comput. Mol. Sci. 2014, 4, 26-33.
- [25] Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- [26] Planckaert, A. A.; Doucet, J.; Sandorfy, C. Comparative Study of the Vacuum Ultraviolet Absorption and Photoelectron Spectra of Some Simple Ethers and Thioethers. J. Chem. Phys. 1974, 60, 4846-4853.
- [27] Bulliard, C.; Allan, M.; Grimme, S. Electron Energy Loss and Dissociative Electron Attachment Spectroscopy of Methyl Vinyl Ether and Related Compounds. *Int. J. Mass Spect.* 2001, 205, 43–55.
- [28] Wu, G.; Boguslavskiy, A. E.; Schalk, O.; Schuurman, M. S.; Stolow, A. Ultrafast Non-Adiabatic Dynamics of Methyl Substituted Ethylenes: The  $\pi$ -3s Rydberg State. *J. Chem. Phys.* **201**1, *135*, 164309.
- [29] Mölder, U.; Pikver, R.; Koppel, I. I.; Burk, P.; Koppel, I. A. Photoelectron Spectra of Molecules. Part 12. Vinyl, Allyl, and Phenyl Ethers and Sulphides. J. Mol. Struc.:

Theochem. 2002, 579, 205–220.

- [30] Schalk, O.; Boguslavskiy, A. E.; Stolow, A. Two-Photon Excited State Dynamics of Dark Valence, Rydberg, and Superexcited States in 1,3-Butadiene. J. Phys. Chem. Lett 2014, 5, 560-565.
- [31] Schalk, O.; Boguslavskiy, A. E.; Stolow, A. Substituent Effects on Dynamics at Conical Intersections: Cyclopentadienes. J. Phys. Chem. A 2010, 114, 4058-4064.
- [32] Schalk, O.; Schuurman, M. S.; Wu, G.; Lang, P.; Mucke, M.; Feifel, R.; Stolow, A. Internal Conversion versus Intersystem Crossing: What Drives the Gas Phase Dynamics of Cyclic α,β-Enones? J. Phys. Chem. A 2014, 118, 2279–2287.
- [33] Hockett, P.; Ripani, E.; Rytwinski, A.; Stolow, A. Probing Ultrafast Dynamics with Time-Resolved Multidimensional Coincidence Imaging: Butadiene. J. Mod. Opt. 2013, 60, 1409-1425.
- [34] Stert, V.; Lippert, H.; Ritze, H.-H.; Radloff, W. Femtosecond Time-Resolved Dynamics of the Electronically Excited Ethylene Molecule. *Chem. Phys. Lett.* **2004**, *388*, 144-149.
- [35] Kosma, K.; Trushin, S. A.; Fuss, W.; Schmid, W. E. Ultrafast Dynamics and Coherent Oscillations in Ethylene and Ethylene-d<sub>4</sub> Excited at 162nm. J. Phys. Chem. A, 2008, 112, 7514-7529.
- [36] Tseng, C.-M.; Lee, Y. T.; Ni, C.-K. Photodissociation Dynamics of N-Methylindole, N-Methylpyrrole, and Anisole. J. Phys. Chem. A. 2009, 113, 3881–3885.
- [37] Hadden, D. J.; Williams, C. A.; Roberts G. M.; Stavros, V. G. Time-Resolved Velocity Map Imaging of Methyl Elimination from Photoexcited Anisole. *Phys. Chem. Chem. Phys.* 2011, 13, 4494-4499.
- [38] Omidyan, R.; Rezaei, H. Excited State Deactivation Pathways of Neutral/Protonated Anisole and p-Fluoroanisole: a Theoretical Study. Phys. Chem. Chem. Phys. 2014, 16, 11679-11689.
- [39] Ho, Y.-C.; Dyakov, Y. A.; Hsu, W.-H.; Ni, C.-K.; Sun, Y. L.; Hu, W. P. Photodissociation Dynamics of Methoxybenzoic Acid at 193 nm. J. Chem. Phys. 2001, 137, 194309.
- [40] Hadden, D.-J.; Roberts, G. M.; Karsili, T. N. V.; Ashfold, M. N. R.; Stavros, V. G. Competing  ${}^{1}\pi\sigma*$  Mediated Dynamics in Mequinol: O–H *versus* O–CH<sub>3</sub>

Photodissociation Pathways. Phys. Chem. Chem. Phys. 2012, 14, 13415-13428.

[41] Blanchet, V.; Zgierski, M. Z.; Seideman, T.; Stolow, A. Discerning Vibronicmolecular Dynamics Using Time-Resolved Photoelectron Spectroscopy. *Nature* 1999, 401, 52-54.



**Figure 1.** Gas phase absorption spectra of ethyl vinyl ether (black), propyl vinyl ether (red) and 2-propanol vinyl ether (blue).



Figure 2. Time evolution of the distance between the carbon atom of the methyl group and the oxygen atom of methyl vinyl ether obtained from the dynamics simulations in the S<sub>1</sub> electronic state. Plotted are a) trajectories undergoing C-O cleavage and b) trajectories following the ethylene-twist channel. See text for details.



**Figure 3.** Initial distributions of the distance between the carbon atom of the methyl group and the oxygen atom: a) Total distribution, b) distribution for molecules undergoing CO-dissociation, and c) distribution for molecules following ethylene dynamics. The blue curves are fits to the fundamental and, for panel b, the first excited harmonic oscillator distribution function.

intensity (arb.units)

-0.2

delay times

sd 

0.2

0.4

intensity (arb. units)

-0.2

0 dealy time / ps

intensity (arb. units)

-0.2

delay time 0.2

sd

0.4 1

intensity (arb. units)

0.5 eV (x5)

2.2 eV (x5)

1 eV (x5)

1.8 eV

intensity (arb. units)

0.5 eV (x5)

1 eV(x5)

2.2 eV (x5)

όн

1.8 eV

intensity (arb. units)

0.5 eV (x5)

1 eV (x5)

- 1.8 eV 2.2 eV (x5)

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Figure 4. Time-resolved photoelectron spectra of (a) ethyl vinyl ether, (b) propyl vinyl ether and (c) 2-propanol vinyl ether upon excitation at 200 nm and ionization at 267nm.





**Figure 5.** Time-resolved photoelectron spectra of (a) ethyl vinyl ether and (b) propyl vinyl ether upon excitation at 200 nm and ionization at 400 nm. The peak at 3.4 eV is a replica of the peak at 0.3 eV probed with on additional photon.



Figure 6. a) Time zero shift of the photoelectron spectra pumped at 200 nm and probed at 267 nm. b) Same as a) but for a probe wavelength of 400 nm. The lines are interpolated data to guide the eye.



Figure 7. Schematics of the dynamics initiated in methyl vinyl ether after excitation of the  $\pi$ 3s-Rydberg state.

# Tables

	MVE				EVE	PVE
	S <sub>0</sub> min	$S_1 \min$	S <sub>1</sub> TS, C-O diss	S <sub>1</sub> TS, C=C twist	S <sub>0</sub> min	S <sub>0</sub> min
S <sub>0</sub>	0	0.28	0.53	0.41	0	0
S <sub>1</sub> (π3s)	6.25	6.00	6.07	6.02	6.23	6.23
S <sub>2</sub> (π3p)	6.56	6.40	-	-	6.56	6.55
S <sub>3</sub> (ππ*)	6.96	-	-	-	6.94	6.92

**Table 1.** Electronic state energies (in eV) calculated at the minimum of the ground state andthe  $S_1$  state, as well as at the  $S_1$  transition states (TS) of methyl-, ethyl-, andpropyl vinyl ether using CAM-B3LYP/6-31+G\*.



Graphics for Table of Contents (TOC).



333x251mm (96 x 96 DPI)





372x279mm (96 x 96 DPI)



395x281mm (96 x 96 DPI)



394x282mm (96 x 96 DPI)



Figure 4. Time-resolved photoelectron spectra of (a) ethyl vinyl ether, (b) propyl vinyl ether and (c) 2propanol vinyl ether upon excitation at 200 nm and ionization at 267nm. 395x282mm (96 x 96 DPI)





Figure 5. Time-resolved photoelectron spectra of (a) ethyl vinyl ether and (b) propyl vinyl ether upon excitation at 200 nm and ionization at 400 nm. 395x281mm (96 x 96 DPI)



333x247mm (96 x 96 DPI)



Schematics of the dynamics initiated in methyl vinyl ether after excitation of the n3s-Rydberg state.





167x140mm (96 x 96 DPI)