# Electronic Supplementary Information for: Caveat when using ADC(2) for studying the photochemistry of carbonyl-containing molecules

Emanuele Marsili, Antonio Prlj,<sup>a)</sup> and Basile F. E. Curchod<sup>b)</sup> Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK

### CONTENTS

I. Computational Details	2
II. Additional information on formaldehyde	4
A. Contributing configurations along the LIIC	4
B. SCS-ADC(2) vs ADC(2), and the influence of the basis set	5
C. CC2 and SCS-CC2 vs SCS-ADC(2)	6
D. Influence of the vertical shift on XMS-CASPT2 profile	7
III. Comparing XMS-CASPT2(2/2) with XMS-CASPT2(4/3) for all molecules	8
IV. LIIC for thymine	10
References	11

<sup>&</sup>lt;sup>a)</sup>Electronic mail: antonio.prlj@durham.ac.uk

<sup>&</sup>lt;sup>b)</sup>Electronic mail: basile.f.curchod@durham.ac.uk

#### I. COMPUTATIONAL DETAILS

The following electronic-structure methods were used in this work: MP2 (Møller-Plesset perturbation theory up to second-order)<sup>1</sup>; (strict) ADC(2) (Algebraic Diagrammatic Construction up to second-order)<sup>2-4</sup> and its Spin-Component Scaled variant (SCS-ADC(2)), CC2 (Coupled-Cluster up to the second-order)<sup>2,5</sup> and SCS-CC2<sup>6</sup>, DFT (Density Functional Theory)<sup>7,8</sup> and LR-TDDFT (Linear-Response Time-Dependent DFT)<sup>9,10</sup>, SA-CASSCF (State-Averaged Complete Active Space Self-Consistent Field)<sup>11</sup>, XMS-CASPT2 (extended Multi-State Complete Active Space second-order perturbation theory)<sup>12,13</sup> in its Single-State, Single-Reference (SS-SR, used if not stated otherwise) and Multi-State, Multi-Reference (MS-MR) versions<sup>14,15</sup>, MR-CI (Multi Reference Configuration Interaction)<sup>16</sup> including single and double excitations MR-CISD. The calculations were performed with Gaussian09<sup>17</sup> (DFT and LR-TDDFT), Turbomole 7.3<sup>18</sup> (MP2, ADC(2), SCS-ADC(2), CC2 and SCS-CC2), BAGEL 1.2<sup>19</sup> (SA-CASSCF, SS-SR-XMS-CASPT2), and MOLPRO 2012.1<sup>20,21</sup> (SA-CASSCF, MS-MR-XMS-CASPT2, and MR-CISD) program packages.

The PBE0 exchange-correlation functional was used for all DFT and LR-TDDFT calculations<sup>22,23</sup>, within the Tamm-Dancoff approximation. MP2, ADC(2), SCS-ADC(2), CC2, and SCS-CC2 were performed with frozen core and the Resolution of the Identity (RI)<sup>24</sup>. The standard scaling factors were used for SCS-ADC(2) and SCS-CC2. BAGEL calculations were performed using Density Fitting (DF) and frozen core. DF and frozen core approximations were not utilized in MOLPRO calculations. All XMS-CASPT2 calculations employed a real vertical shift of 0.5 Hartree unless otherwise stated (see Fig. S5 for a test of this value). The Karlsruhe basis sets def2-SVP and def2-TZVP were employed<sup>25–27</sup> – a def2-SVP basis set should be assumed if not stated otherwise.

For each molecule studied in this work, a linear interpolation in internal coordinates pathway was calculated between the Franck-Condon geometry (minimum on the S<sub>0</sub> potential energy surface, optimized at SCS-MP2/def2-SVP level of theory) and the S<sub>1</sub>/S<sub>0</sub> crossing points (SCS-MP2/def2-SVP for S<sub>0</sub> and SCS-ADC(2)/def2-SVP for S<sub>1</sub>). The minimum-energy crossing points close to the Franck-Condon region were located with ClOpt<sup>28</sup>. We note that while the ClOpt code in principle returns minimum-energy conical intersections, we prefer to coin the geometries obtained in this work 'crossing points' (CPs) given that ADC(2) does not describe adequately the branching space of S<sub>0</sub>/S<sub>1</sub> conical intersections<sup>29</sup>.

The standard notation XMS(k)-CASPT2(n/m) was used to indicate the details of the chosen active spaces and state-averaging protocol, with n electrons in m active orbitals while k states are considered. The reference XMS-CASPT2 energies for each molecule (using a SVP basis set) were obtained at the following level of theory: XMS(2)-CASPT2(6/5) for formaldehyde, XMS(2)-CASPT2(6/5) for acrolein, XMS(3)-CASPT2(6/5) for pyrone, XMS(4)-CASPT2(12/9) for 2-HPP, and XMS(3)-CASPT2(8/6)/def2-SVP for oxalyl-fluoride. The natural orbitals for these reference calculations are presented in Fig. S1. The reduced 4/3 active spaces were constructed by keeping only the n,  $\pi$ , and  $\pi^*$  orbitals localized on the carbonyl moiety (and a state-averaging over the two lowest electronic states).

Trajectory surface hopping dynamics employed Tully's fewest switches algorithm<sup>30</sup> and were performed with Newton-X version  $2.0^{31,32}$  using the Turbomole interface and the ADC(2) implementation discussed in Ref 33. The initial conditions were randomly selected

from a Wigner distribution for uncoupled harmonic oscillators, generated from a ground-state optimized geometry and corresponding vibrational frequencies obtained at SCS-MP2/def2-SVP level of theory. The excited-state dynamics were initiated in a  $n\pi^*$  state for all molecules and employed a time step of 0.5 fs. Trajectories were stopped whenever they reach a region of configuration space where the S<sub>1</sub>/S<sub>0</sub> energy gap was smaller than 0.01 eV. The default parameters of Newton-X were employed for all dynamics.



FIG. S1. SA-CASSCF natural orbitals (isovalue of 0.1) employed for the reference XMS-CASPT2 calculation (see text). Top to bottom: formaldehyde, acrolein, pyrone, 2-HPP, and oxalyl fluoride.

#### II. ADDITIONAL INFORMATION ON FORMALDEHYDE



#### A. Contributing configurations along the LIIC

FIG. S2. Contributing configurations to the MS-MR-XMS(2)-CASPT2(4/3)/SVP wavefunctions along the formaldehyde LIIC pathway: closed shell (CS) configuration, singly-excited configurations  $n\pi^*$  and  $\pi\pi^*$ , and doubly-excited configuration obtained from the promotion of a *n* and a  $\pi$  electron to the  $\pi^*$  orbital  $(n + \pi \rightarrow \pi^*)$ . These configurations are plotted along the LIIC for the groundstate (upper panel) and first excited-state (lower panel) wavefunctions. The %T<sub>2</sub>, computed at the SCS-ADC(2)/SVP level of theory, is shown for S<sub>1</sub> with an orange dotted line.

Figure S2 shows the different contributions to the ground- and first excited-state wavefunctions based on MS-MR-XMS(2)-CASPT2(4/3), along the LIIC pathway of formaldehyde. Close to the FC region, the S<sub>0</sub> state is mostly characterized by a closed-shell (CS) configuration. Moving along the LIIC, one observes that the singly-excited configuration,  $\pi\pi^*$ , gains more importance. The increased weight of this configuration is in line with the dramatic increase of the D<sub>1</sub> diagnostic reported in the main text (Fig. 3). The S<sub>1</sub> state mostly preserves a dominant  $n\pi^*$  configuration. We note a small increase in the doublyexcited configuration when progressing along the LIIC (in line with the increase in %T<sub>2</sub> for SCS-ADC(2)).





FIG. S3. Comparison between SCS-ADC(2)/SVP (black), SCS-ADC(2)/TZVP (grey) and ADC(2)/SVP (blue) for the LIIC of formaldehyde (solid line for  $S_0$  and dashed line for  $S_1$ ). The D<sub>1</sub> diagnostic is given by a dotted orange line (SCS-MP2) or a red line (MP2).

Figure S3 offers a confirmation that the spurious  $S_1/S_0$  crossing observed in the main text is also present when employing a larger basis set (TZVP) or standard ADC(2).

#### C. CC2 and SCS-CC2 vs SCS-ADC(2)

Comparing the LIIC pathway for formaldehyde computed with CC2/SVP and SCS-CC2/SVP to the one obtained with SCS-ADC(2)/SVP (Fig. S4), it appears that CC2 and SCS-CC2 do not predict the same unphysical crossing between S<sub>0</sub> and S<sub>1</sub>( $n\pi^*$ ), despite a rather high D<sub>1</sub> diagnostic. This observation does not come as a complete surprise as numerous reports have shown that CC2 is capable, thanks to its formalism, of describing the branching space of S<sub>1</sub>/S<sub>0</sub> rather accurately<sup>29</sup>, in stark contrast with ADC(2).



FIG. S4. Electronic energies along the LIIC pathway for formaldehyde as obtained with SCS-ADC(2)/SVP (black), CC2/SVP (grey). and SCS-CC2/SVP (blue). A solid line is used for  $S_0$  and dashed line for  $S_1$ . The  $D_1$  diagnostic is given by a dotted orange line (SCS-CC2) or a red line (CC2).

#### D. Influence of the vertical shift on XMS-CASPT2 profile

Figure S5 shows the LIIC for formaldehyde as computed with XMS(2)-CASPT2(6/5)/SVP using two shifts, 0.1 and 0.5 Hartree. Both curves are in close agreement.



FIG. S5. Electronic energies along the LIIC pathway for formal dehyde as obtained with XMS(2)-CASPT2(6/5)/SVP using a 0.1 Ha (light blue) or 0.5 Ha (blue) shift. A solid line is used for  $S_0$  and dashed line for  $S_1$ . The C=O bond length is given by an orange dotted line.

## III. COMPARING XMS-CASPT2(2/2) WITH XMS-CASPT2(4/3) FOR ALL MOLECULES

Figure S6 reproduces the comparison (proposed in the main text for formaldehyde) between XMS-CASPT2(2/2) and XMS-CASPT2(4/3) for all the molecules discussed in this work. The XMS-CASPT2(2/2) calculations only incorporate the carbonyl *n* and  $\pi^*$  orbitals in the active space, while the XMS-CASPT2(4/3) ones include in addition its  $\pi$  orbital (all natural orbitals are given in Fig. S1 above). As observed for the case of formaldehyde, the (2/2) active space leads to an artificial crossing between S<sub>1</sub> and S<sub>0</sub> for all molecules (see red lines in Fig. S6), like (SCS-)ADC(2). Upon inclusion of the  $\pi$  orbital on the carbonyl in the active space (XMS-CASPT2(4/3), blue lines in Fig. S6), the artificial crossing is removed and the LIICs obtained are in line with their corresponding XMS-CASPT2 reference calculations.



FIG. S6. Electronic energies along along the LIIC pathway for formaldehyde as obtained with XMS-CASPT2(2/2)/SVP (red) and XMS-CASPT2(4/3)/SVP (blue) for: (a) formaldehyde, (b) acrolein, (c) pyrone, (d) 2-HPP, and (e) oxalyl fluoride. We note that for oxalyl fluoride the (4/3) active space does not describe  $S_1$  accurately and a (8/6) active space is used instead. A solid line is used for  $S_0$  and dashed line for  $S_1$ . The C=O bond length is given by an orange dotted line.

#### IV. LIIC FOR THYMINE

Figure S7 presents the LIIC computed for thymine (not discussed in the main text). The profile shows that SCS-ADC(2) also exhibits a fictitious crossing between S<sub>1</sub> ( $n\pi^*$  on one of the C=O) and S<sub>0</sub>, in comparison with the reference provided by XMS(5)-CASPT2(12/9). We also show that XMS(2)-CASPT2(2/2) reproduces the artificial crossing, in line with the other molecules (see Fig. S6 above).



FIG. S7. Electronic energies along the LIIC pathway for thymine as obtained with SCS-ADC(2)/SVP (black), XMS(2)-CASPT2(2/2)/SVP (red) and XMS(5)-CASPT2(12/9)/SVP (blue). A solid line is used for  $S_0$  and dashed line for  $S_1$ . The  $D_1$  diagnostic for the SCS-MP2 ground state is shown with a dotted orange line.

#### REFERENCES

- <sup>1</sup>C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
- <sup>2</sup>C. Hättig, Advances in Quantum Chemistry **50**, 37 (2005).
- <sup>3</sup>A. B. Trofimov and J. Schirmer, J. Phys. B: At. Mol. Opt. Phys. **28**, 2299 (1995).
- <sup>4</sup>A. Dreuw and M. Wormit, Wiley Interdiscip. Rev. Comput. Mol. Sci. **5**, 82 (2015).
- <sup>5</sup>O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
- <sup>6</sup>A. Hellweg, S. A. Grün, and C. Hättig, Phys. Chem. Chem. Phys. **10**, 4119 (2008).
- <sup>7</sup>W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- <sup>8</sup>R. G. Parr and W. Yang, *Density functional theory of atoms and molecules* (Oxford University Press, 1989).
- <sup>9</sup>E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- <sup>10</sup>M. E. Casida, in *Recent Advances In Density Functional Methods, Part I* (World Scientific, 1995) pp. 155–192.
- <sup>11</sup>T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (John Wiley and Sons, Ltd, Chichester, UK, 2000).
- <sup>12</sup>T. Shiozaki, W. Gyroffy, P. Celani, and H. J. Werner, J. Chem. Phys. **135** (2011), 10.1063/1.3633329.
- <sup>13</sup>J. W. Park and T. Shiozaki, J. Chem. Theory Comput. **13**, 3676 (2017), arXiv:1706.00156.
- <sup>14</sup>B. Vlaisavljevich and T. Shiozaki, J. Chem. Theory Comput. **12**, 3781 (2016).
- <sup>15</sup>L. González, Quantum Chemistry and Dynamics of Excited States: Methods and Applications (Wiley, 2020).
- <sup>16</sup>H. J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
- <sup>17</sup>M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, *et al.*, Inc., Wallingford CT.
- <sup>18</sup>F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, and F. Weigend, Wiley Interdiscip. Rev. Comput. Mol. Sci. 4, 91 (2014).
- <sup>19</sup>T. Shiozaki, Wiley Interdiscip. Rev. Comput. Mol. Sci. **8**, e1331 (2018).
- <sup>20</sup>H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2, 242 (2012).
- <sup>21</sup>H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, *et al.*, See http://www.molpro.net (2012).
- <sup>22</sup>J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
- <sup>23</sup>C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
- <sup>24</sup>F. Weigend, A. Köhn, and C. Hättig, J. Chem. Phys. **116**, 3175 (2002).
- <sup>25</sup>F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7, 3297 (2005).
- <sup>26</sup>F. Weigend, Phys. Chem. Chem. Phys. **8**, 1057 (2006).
- <sup>27</sup>D. Rappoport and F. Furche, J. Chem. Phys. **133**, 134105 (2010).
- <sup>28</sup>B. G. Levine, J. D. Coe, and T. J. Martínez, J. Phys. Chem. B **112**, 405 (2008).
- <sup>29</sup>D. Tuna, D. Lefrancois, Ł. Wolański, S. Gozem, I. Schapiro, T. Andruniów, A. Dreuw, and M. Olivucci, J. Chem. Theory Comput. **11**, 5758 (2015).
- <sup>30</sup>J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
- <sup>31</sup>M. Barbatti, M. Ruckenbauer, F. Plasser, J. Pittner, G. Granucci, M. Persico, and H. Lischka, Wiley Interdiscip. Rev. Comput. Mol. Sci **4**, 26 (2014).

- <sup>32</sup>M. Barbatti, G. Granucci, M. Ruckenbauer, F. Plasser, R. Crespo-Otero, J. Pittner, M. Persico, and H. Lischka, "NEWTON-X: A package for Newtonian dynamics close to the crossing seam." (2016).
- <sup>33</sup>F. Plasser, R. Crespo-Otero, M. Pederzoli, J. Pittner, H. Lischka, and M. Barbatti, J. Chem. Theory Comput. **10**, 1395 (2014).