Supporting Information for "Time-dependent ab initio molecular-orbital decomposition for high-harmonic generation spectroscopy"

Marco Marchetta [a],[†] Chiara Morassut,[‡,†] Julien Toulouse,[‡,¶] Emanuele Coccia,[*,†] and Eleonora Luppi[*,‡]

†*Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Trieste 34127, Italy*

‡*Laboratoire de Chimie Théorique, Sorbonne Université, CNRS, Paris, F-75005, France*

¶*Institut Universitaire de France, F-75005 Paris, France*

E-mail: ecoccia@units.it; eleonora.luppi@sorbonne-universite.fr

[a]M.M. and C.M. contributed equally to this paper.

1 CO_2

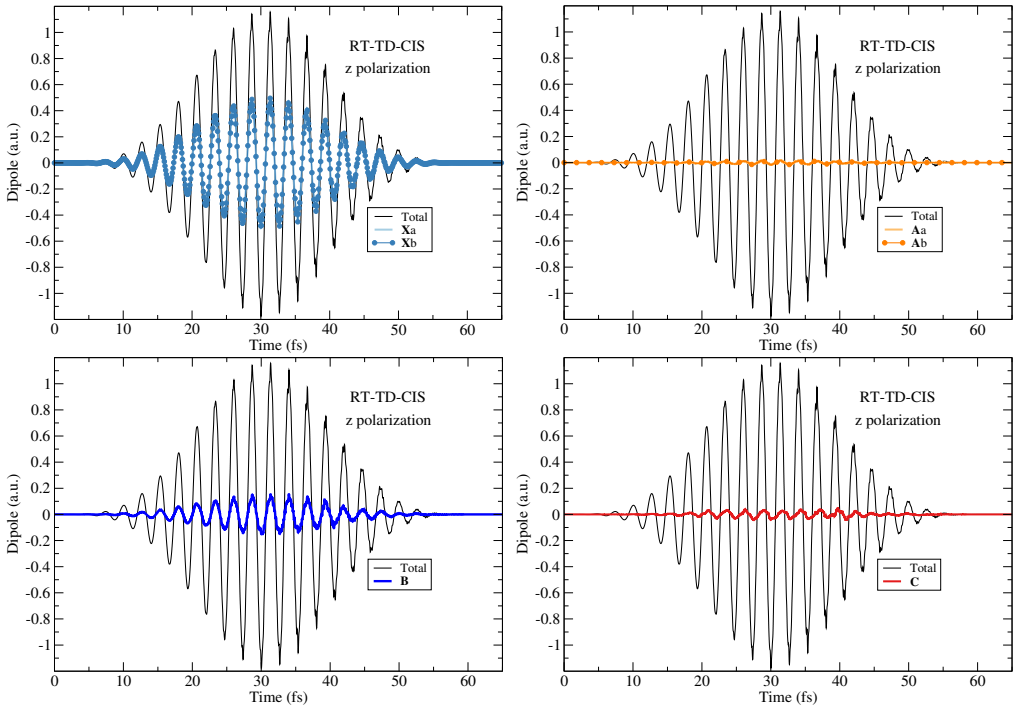

Figure S1: MO decomposition of the time-dependent dipole moment for CO_2, with laser-pulse polarization along the z axis, at the RT-TD-CIS level of theory.

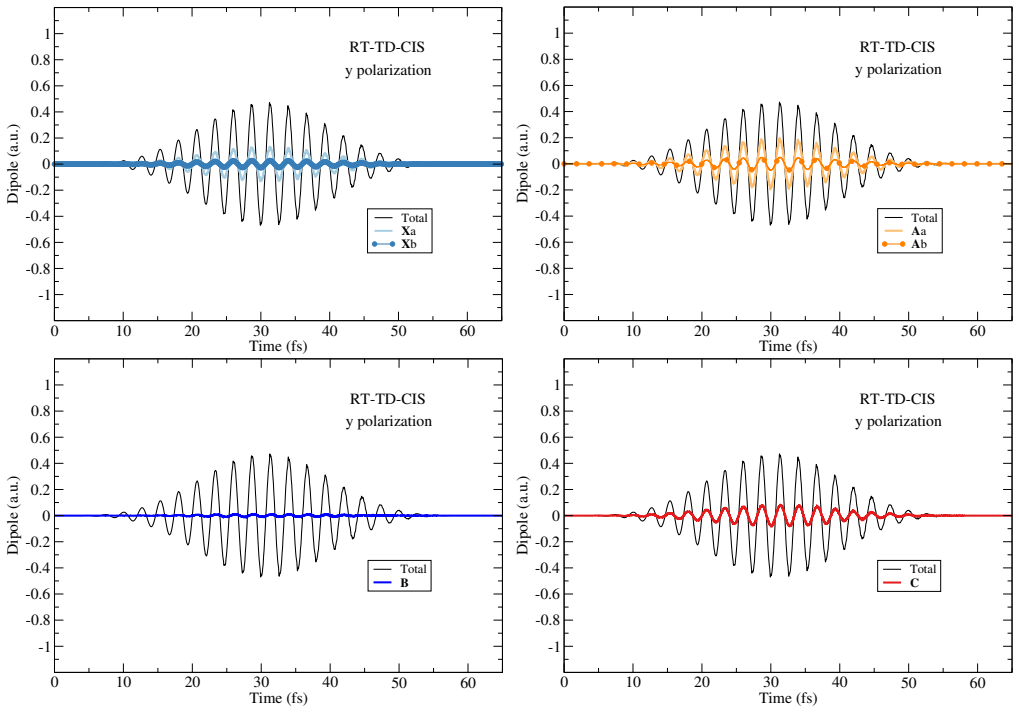

Figure S2: MO decomposition of the time-dependent dipole moment for CO_2, with laser-pulse polarization along the y axis, at the RT-TD-CIS level of theory.

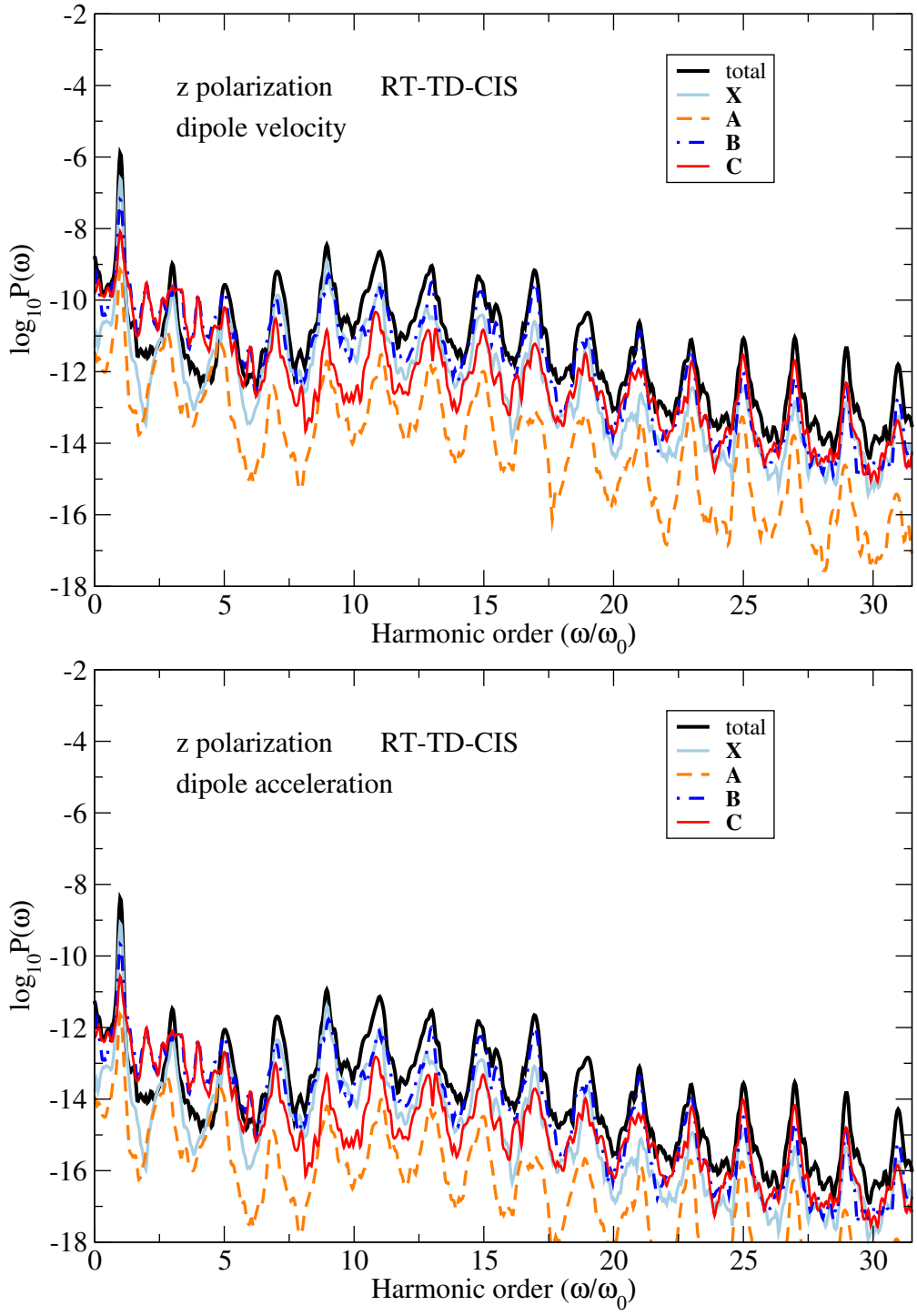

Figure S3: Dipole-velocity (top) and dipole-acceleration (bottom) forms of the HHG spectrum of the CO_2 molecule and its MO decomposition, with laser-pulse polarization along the z axis, at the RT-TD-CIS level of theory. The vertical axis has a different scale with respect to that of Figure 3 in the main text.

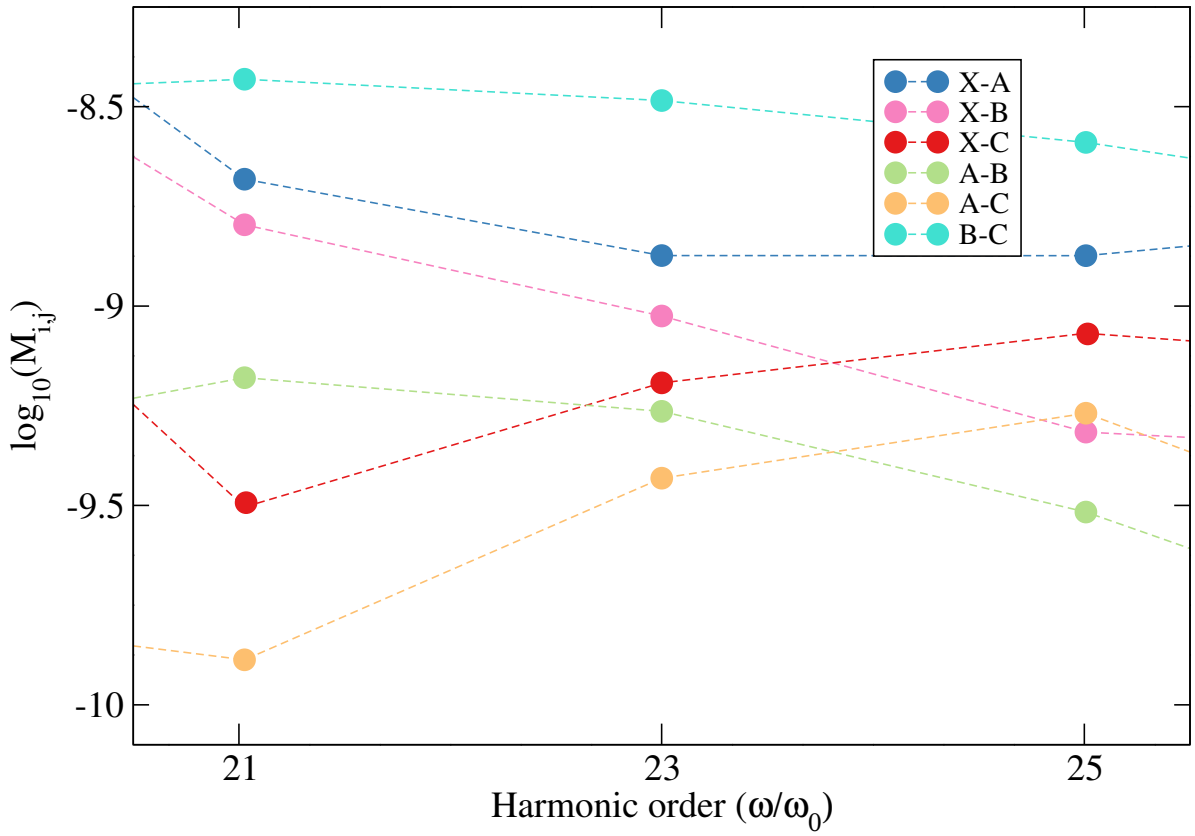

Figure S4: Magnitude of interferences between channels for CO_2 with laser-pulse polarization along the z axis.

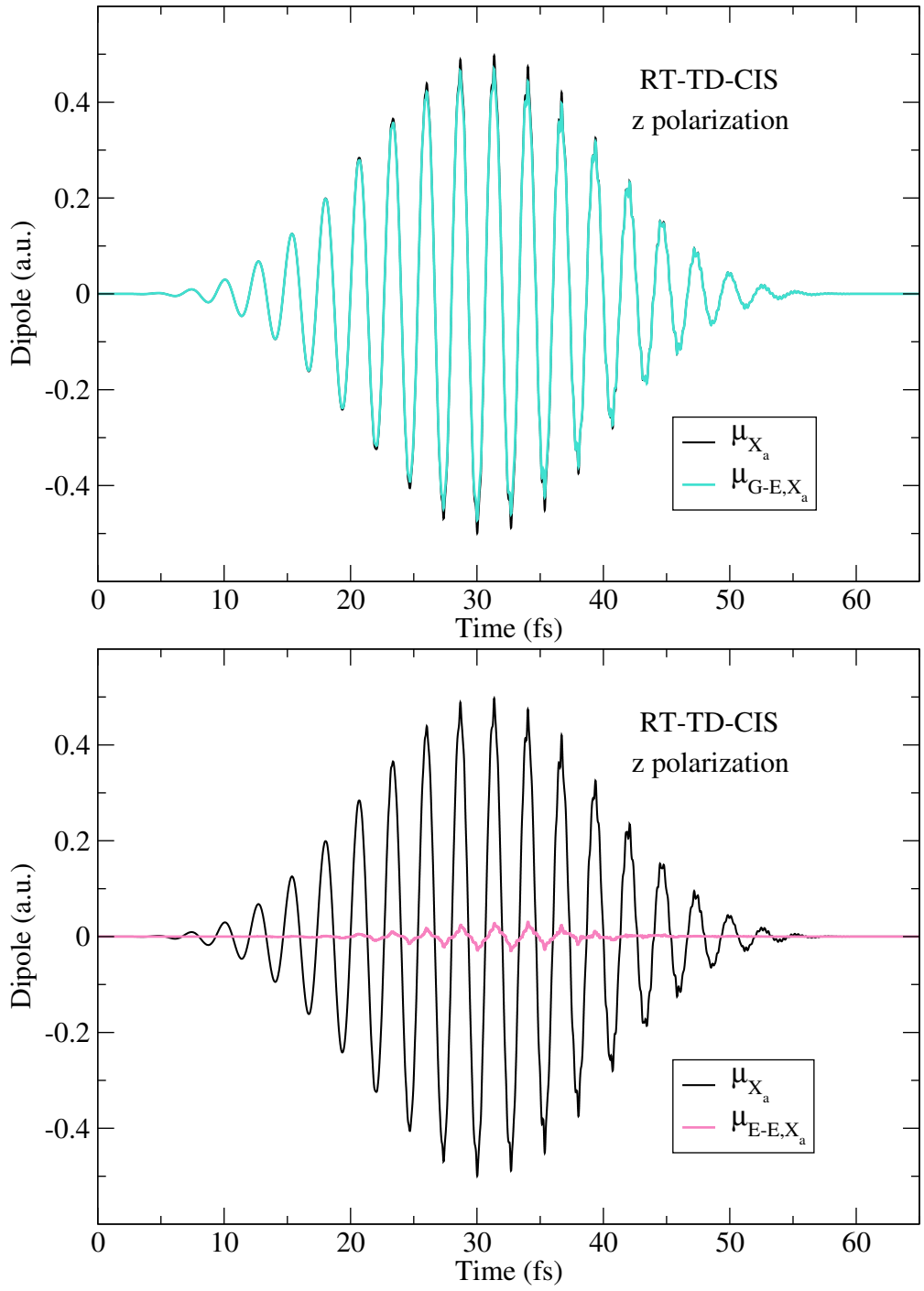

Figure S5: Ground-excited (G-E, top) and excited-excited (E-E, bottom) contributions to the time-dependent dipole moment for the $\mathbf{X}_a$ channel of CO_2, with laser-pulse polarization along the z axis, at the RT-TD-CIS level of theory.

Table S1: Ionization energies (eV) for the various channels of CO_2 at the LC-ωPBE level.

	Exp.[a]			LC-ωPBE
$1^2\Pi_g$ **X**	13.8	$1\pi_g$	HOMO	13.5
$1^2\Pi_u$ **A**	17.3	$1\sigma_u$	HOMO-1	17.7
$1^2\Sigma_u^+$ **B**	18.1	$1\pi_u$	HOMO-2	17.9
$1^2\Sigma_g^+$ **C**	19.4	$1\sigma_g$	HOMO-3	19.0

[a] Ref.[1]

Table S2: Difference between the ionization energies (eV) for the channels of CO_2 at the LC-ωPBE level.

	ΔExp.	ΔLC-ωPBE
X-**A**	3.5	4.2
X-**B**	4.3	4.4
X-**C**	5.6	5.5
A-**B**	0.8	0.2
A-**C**	2.1	1.3
B-**C**	1.3	1.1

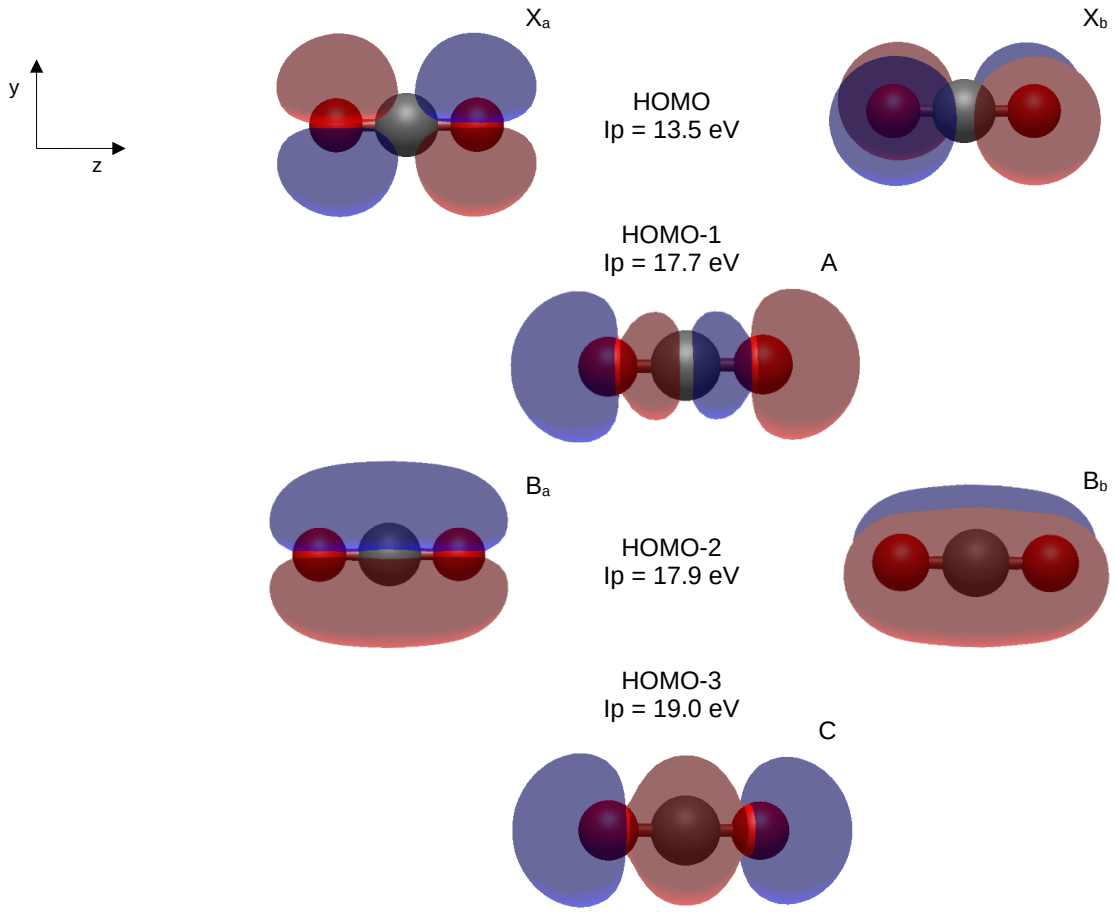

Figure S6: Ionization channels and corresponding MOs of CO_2 at the LC-ωPBE level.

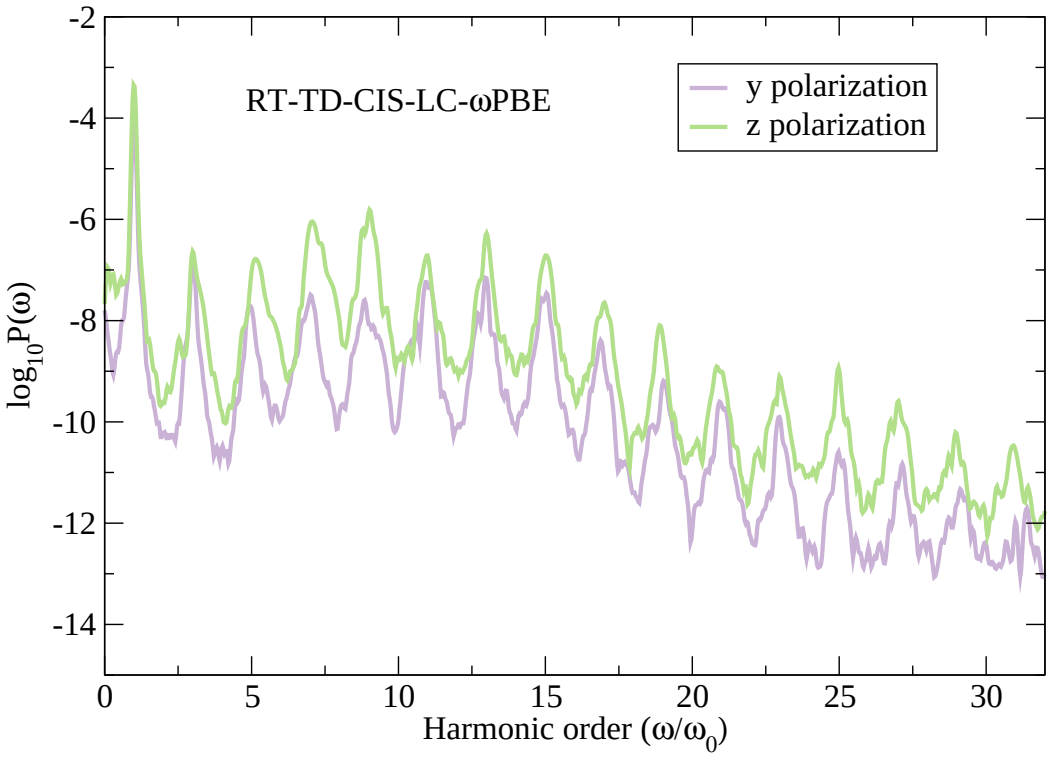

Figure S7: Total HHG spectra for CO_2 with laser-pulse polarization along the y axis (light purple line) and along the z axis (light green line), at the RT-TD-CIS-LC-ωPBE level of theory.

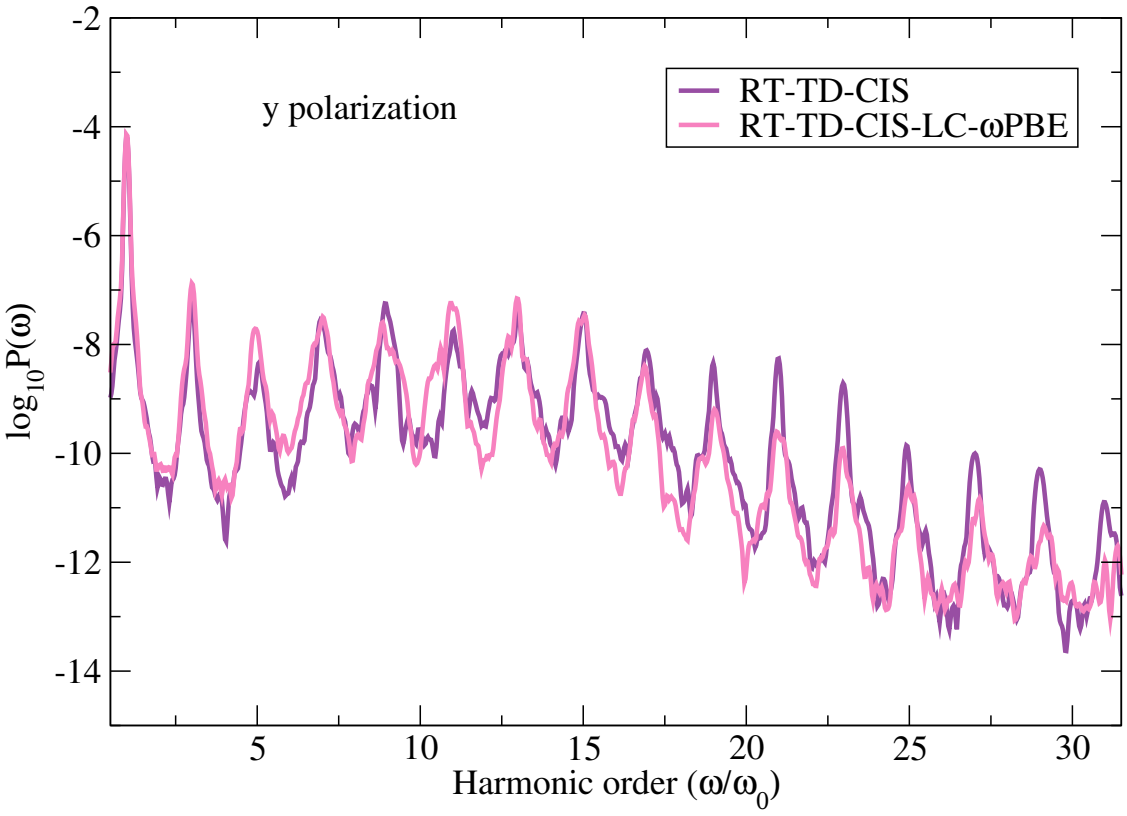

Figure S8: Comparison between the total HHG spectra for CO_2 at the RT-TD-CIS and RT-TD-CIS-LC-ωPBE levels of theory, with laser-pulse polarization along the y axis.

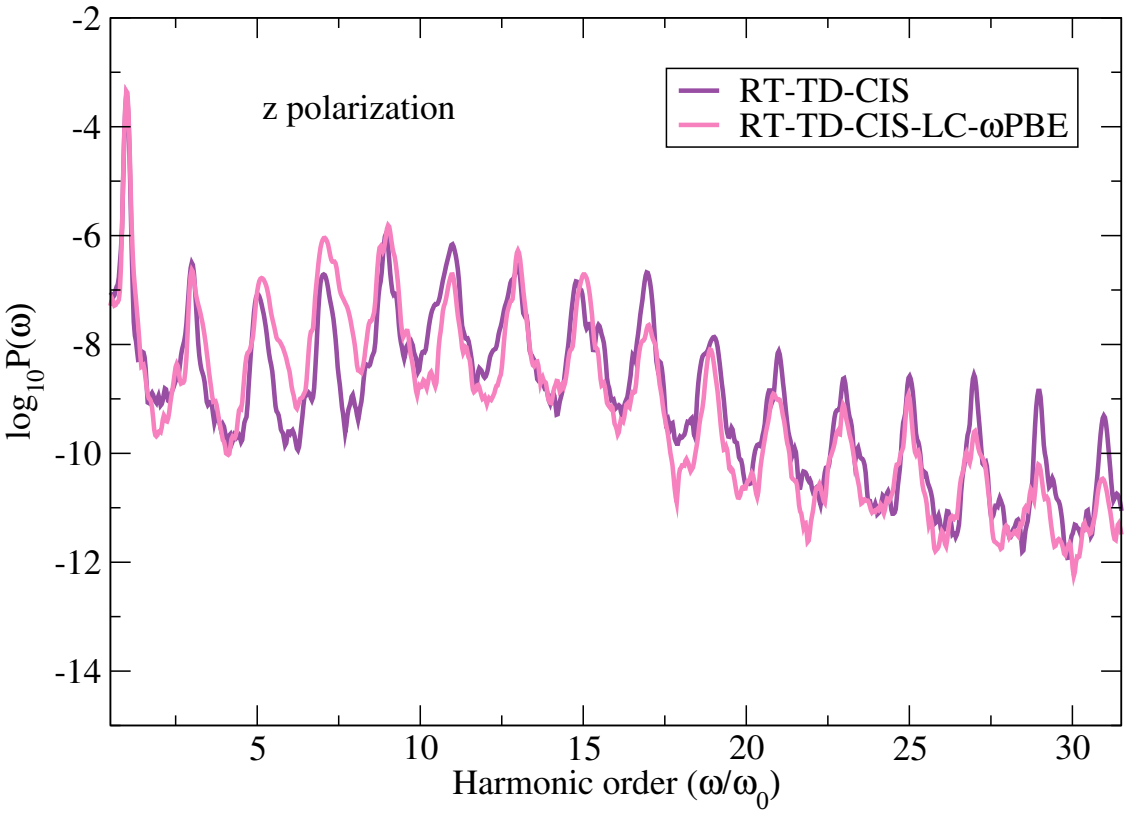

Figure S9: Comparison between the total HHG spectra for CO_2 at the RT-TD-CIS and RT-TD-CIS-LC-ωPBE levels of theory, with laser-pulse polarization along the z axis.

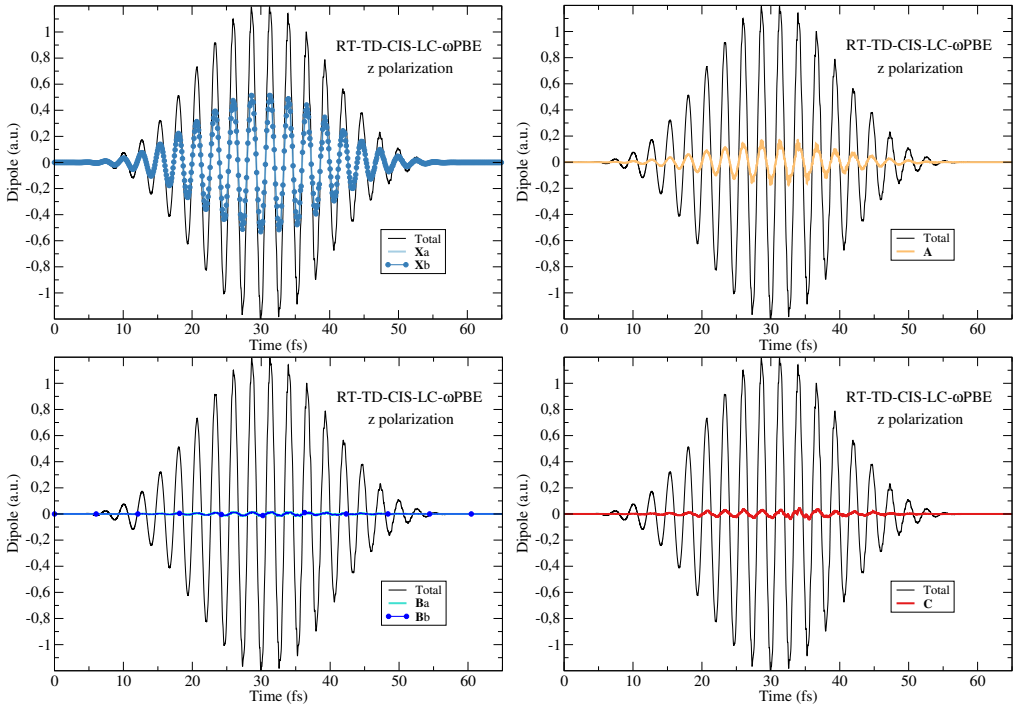

Figure S10: MO decomposition of the time-dependent dipole moment of CO_2, with laser-pulse polarization along the z axis, at the RT-TD-CIS-LC-ωPBE level of theory.

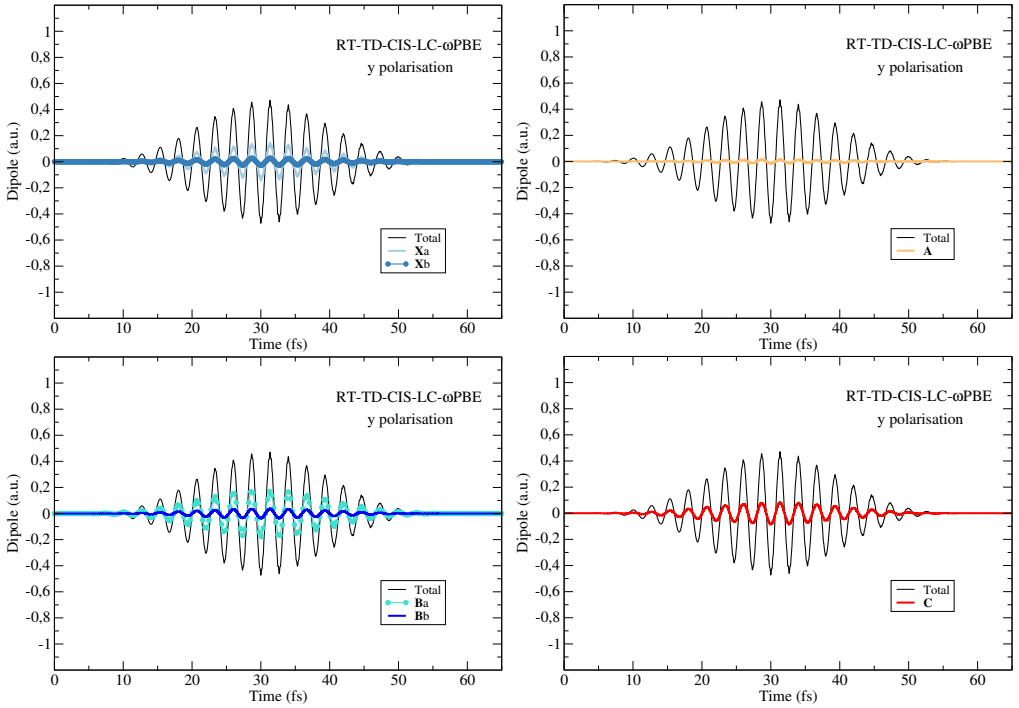

Figure S11: MO decomposition of the time-dependent dipole moment of CO_2, with laser-pulse polarization along the y axis, at the RT-TD-CIS-LC-ωPBE level of theory.

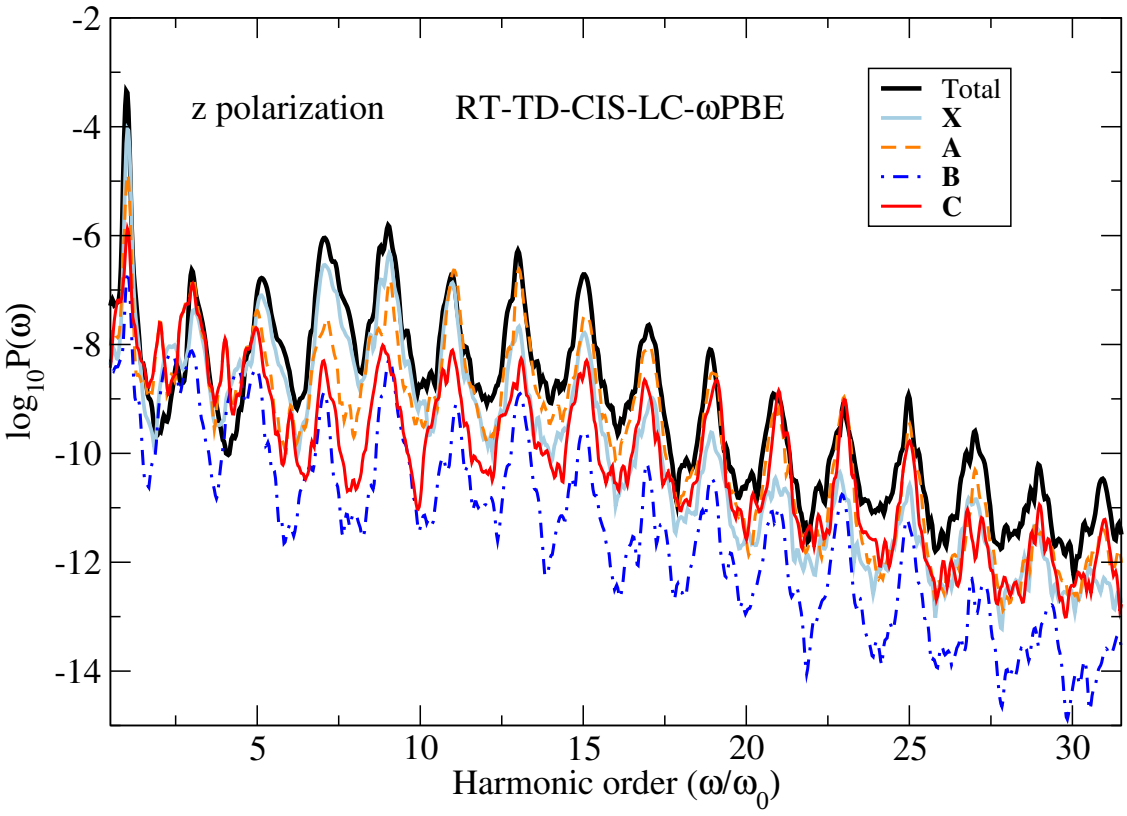

Figure S12: MO decomposition of the HHG spectrum of CO_2, with laser-pulse polarization along the z axis, at the RT-TD-CIS-LC-ωPBE level of theory.

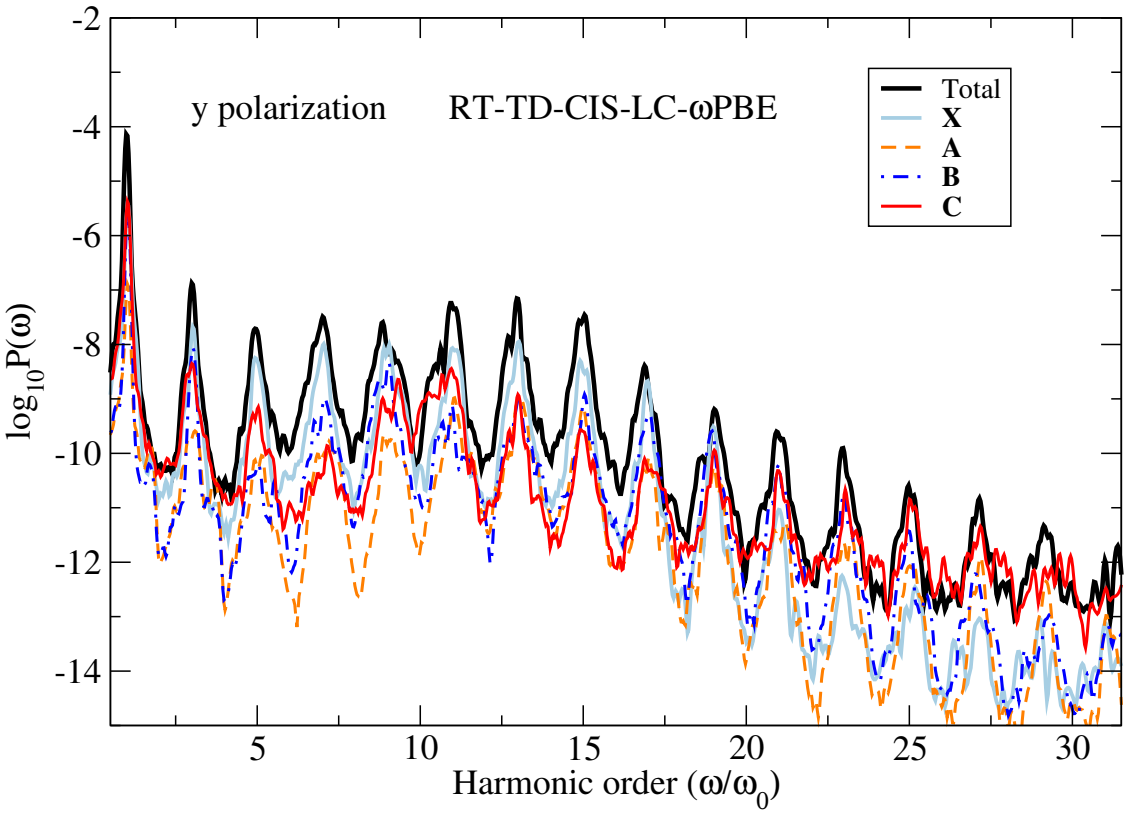

Figure S13: MO decomposition of the HHG spectrum of CO_2, with laser-pulse polarization along the y axis, at the RT-TD-CIS-LC-ωPBE level of theory.

2 H_2O

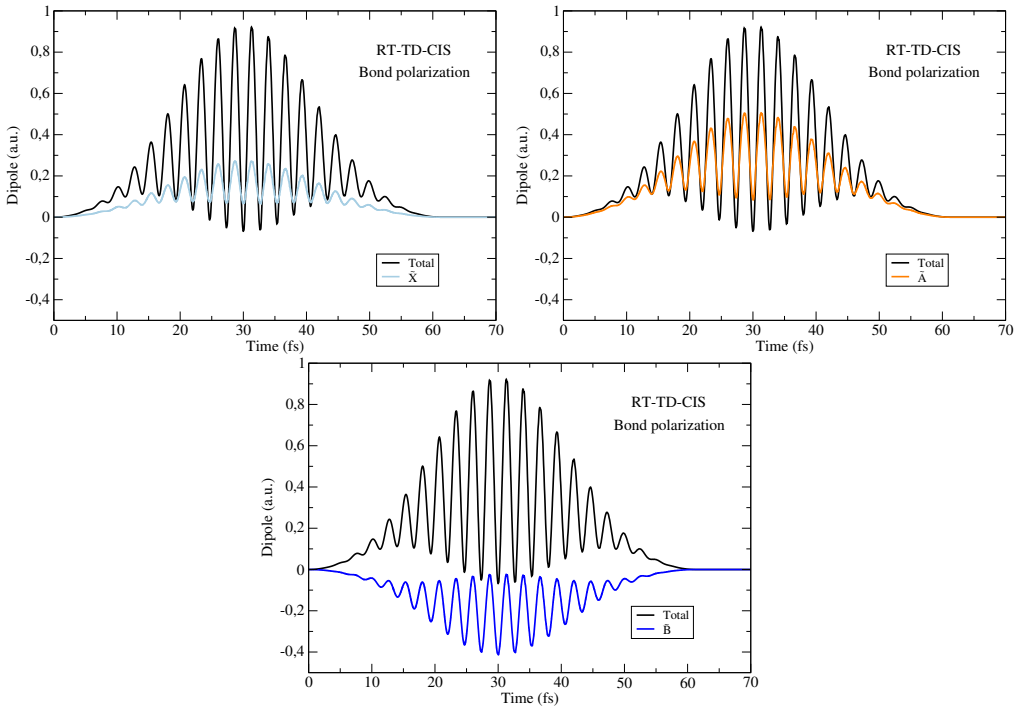

Figure S14: MO decomposition of the time-dependent dipole moment of H_2O, with laser-pulse polarization parallel to a O-H bond, at the RT-TD-CIS level of theory.

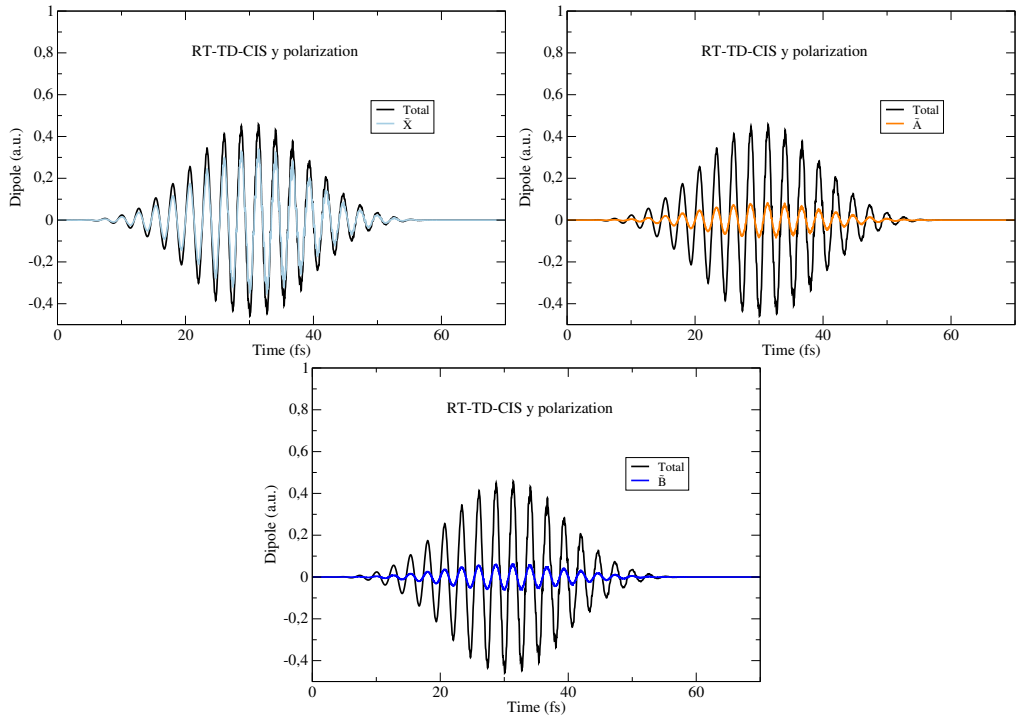

Figure S15: MO decomposition of the time-dependent dipole moment of H_2O, with laser-pulse polarization perpendicular to the molecular plane, at the RT-TD-CIS level of theory.

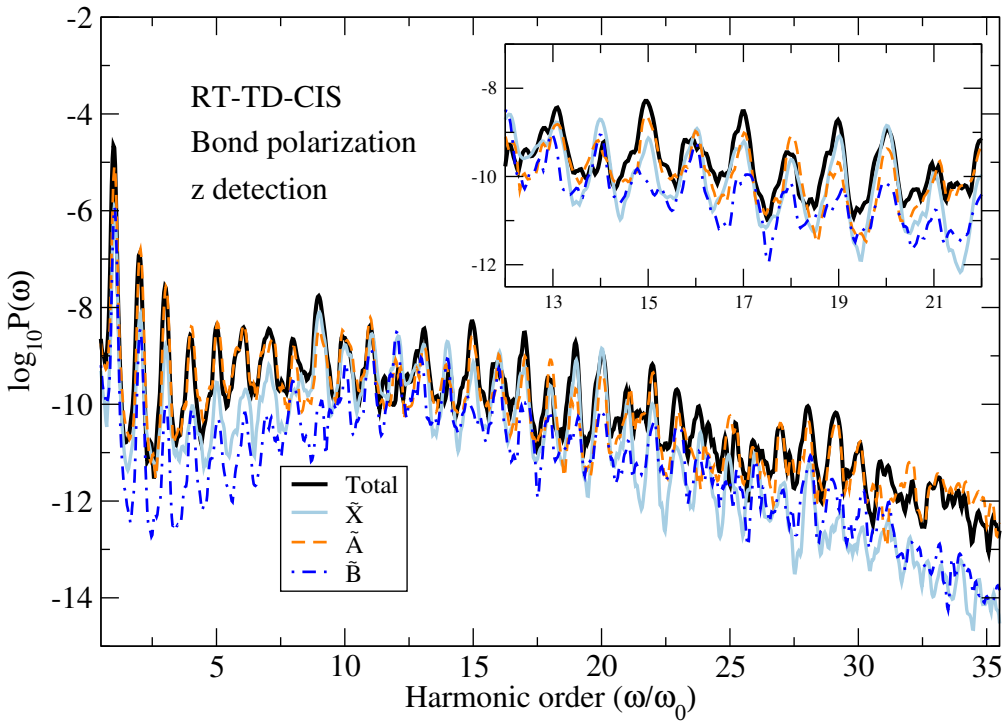

Figure S16: MO decomposition of the HHG spectrum of H_2O with laser-pulse polarization parallel to the O-H bond at the RT-TD-CIS level of theory. The spectra are calculated along the z axis.

References

(1) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. Handbook of HeI Photoelectron Spectra; Scientific Societies Press, Tokyo, 1981.