Quantitative analysis of aligned molecule photoelectron angular distributions: Supplementary Information

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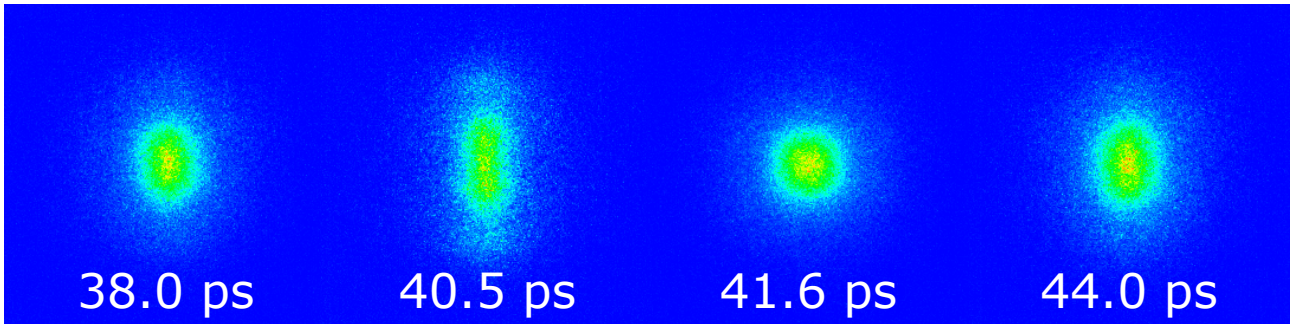

FIG. S1: Coulomb explosion images of O^+ and S^{2+} ions at the specified time delays following the alignment (pump) pulse.

hν / eV	Source	$\tilde{X}$	$\tilde{A}^\dagger$	$\tilde{B}^\dagger$	$\tilde{C}$
20.5	ePolyScat (MEG)	1.00	0.43	0.80	0.80
20.5	ePolyScat (stretched)	1.24	0.71	0.58	0.41
20.5	expt. (eKE / eV)	1.50 ± 0.10 (8.8 - 9.3)	0.44 ± 0.04 (4.9 - 5.8)	0.50 ± 0.10 (4.1 - 4.8)	0.50 ± 0.10 (2.3 - 2.9)
21.2	Carlson 1982	1.22 ± 0.07	0.62 ± 0.10	0.34 ± 0.10	0.51 ± 0.07
23.6	ePolyScat (MEG)	0.85	0.73	0.73	0.82
23.6	ePolyScat (stretched)	1.30	0.89	0.60	0.45
23.6	expt. (eKE / eV)	1.60 ± 0.10 (12.0 - 12.4)	0.76 ± 0.03 (8.1 - 8.7)	0.77 ± 0.09 (7.4 - 8.0)	0.66 ± 0.10 (5.7 - 5.9)
24.0	Carlson 1982	1.30 ± 0.07	1.06 ± 0.10	0.50 ± 0.10	0.61 ± 0.07

TABLE S1: PAD β_2 parameters from photoelectron spectra of unaligned OCS molecules at the stated ionization photon energies. The β_2 values at 20.5 eV and 23.6 eV photon energy are from the current work, while those at 21.2 eV and 24.0 eV photon energy are reproduced from the synchrotron data in Carlson *et al.* 1982. The eKE ranges used for the experimental average β_2 values from this work are presented in parentheses beneath each value. †States are very overlapped so the β_2 values are likely a weighted average of contributions from both channels.

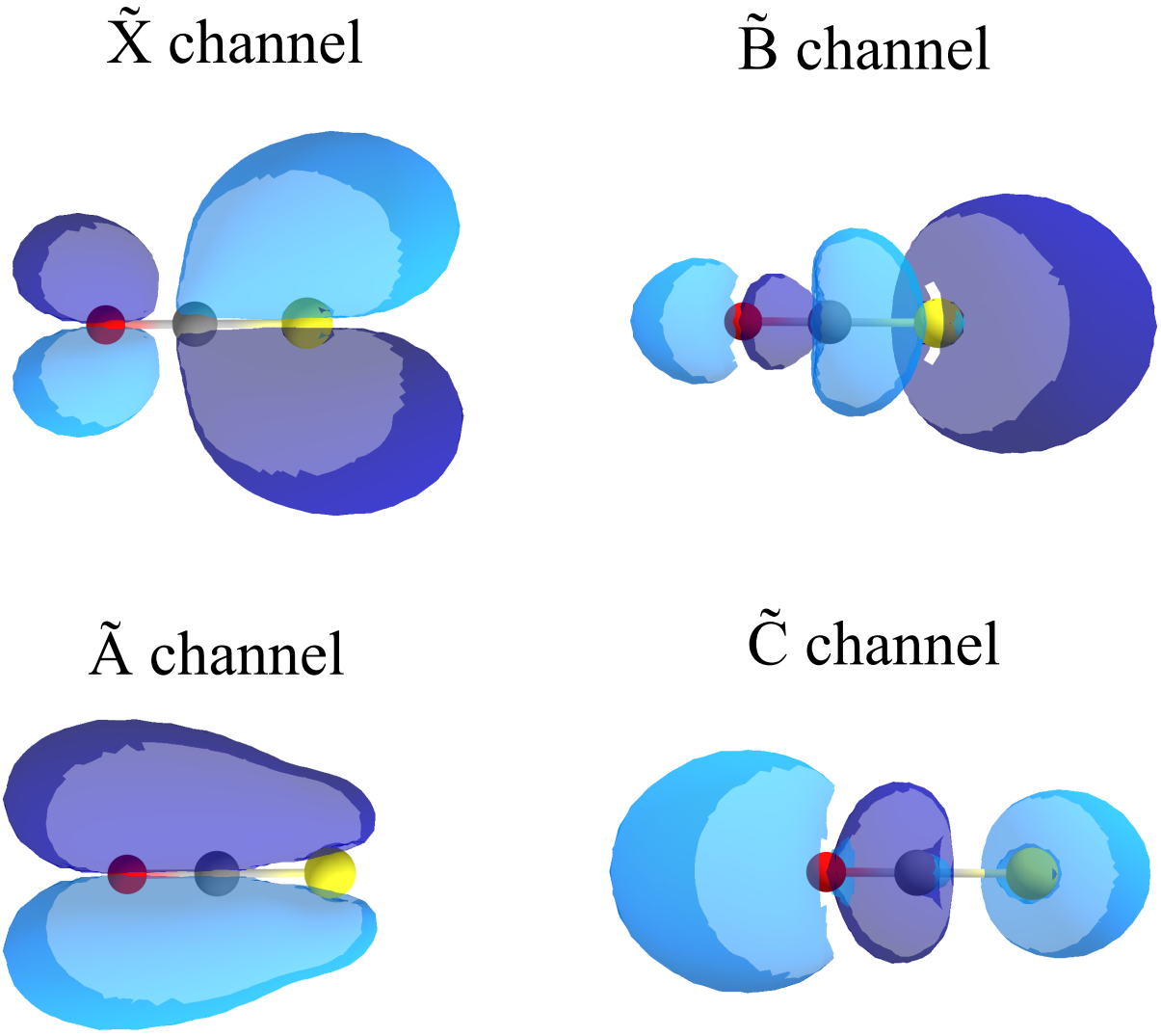

FIG. S2: Transparent 97.5% isosurfaces of the molecular orbitals which are ionized for the first four ionization channels of OCS. Atomic color labels: Red= Oxygen, Gray= Carbon, Yellow = Sulfur.

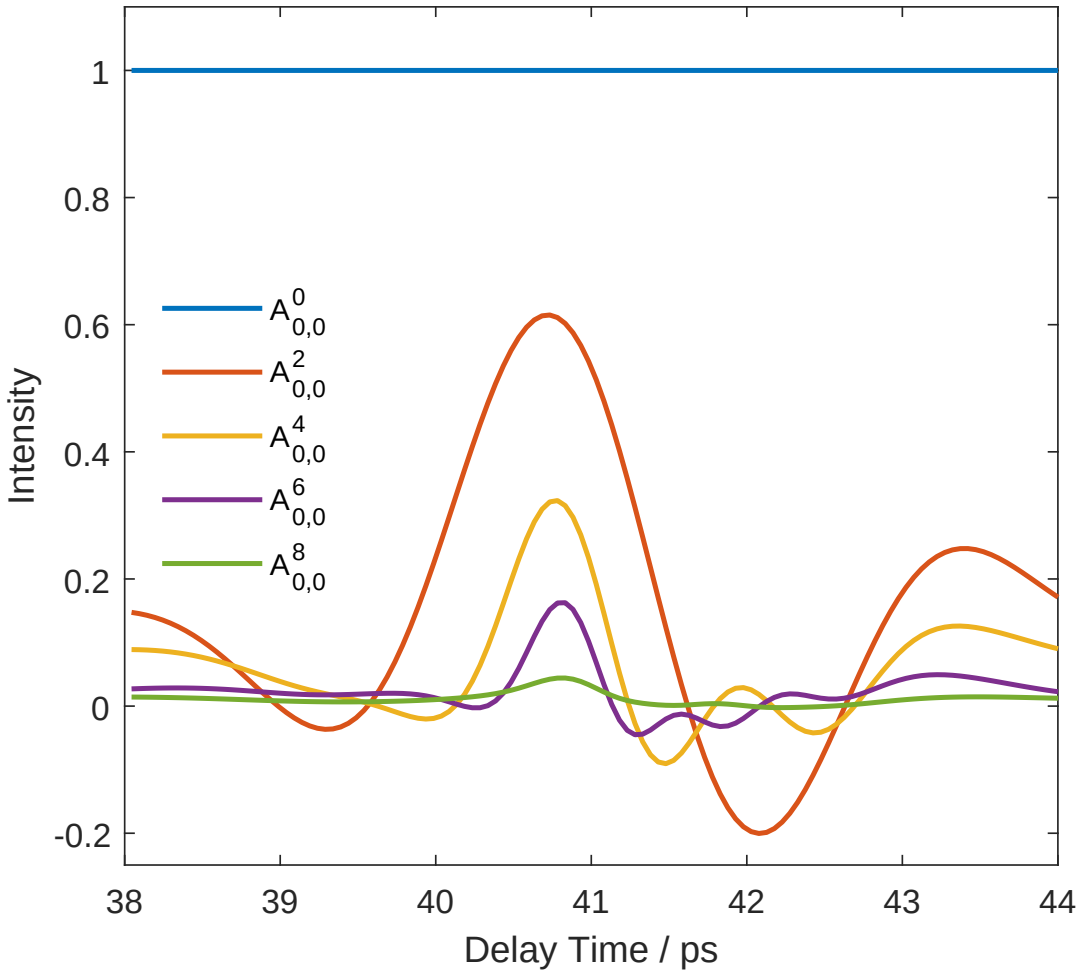

FIG. S3: Experimental $A^K_{Q,S}(t)$ parameters across the rotational revival in the range 38 ps - 44 ps.

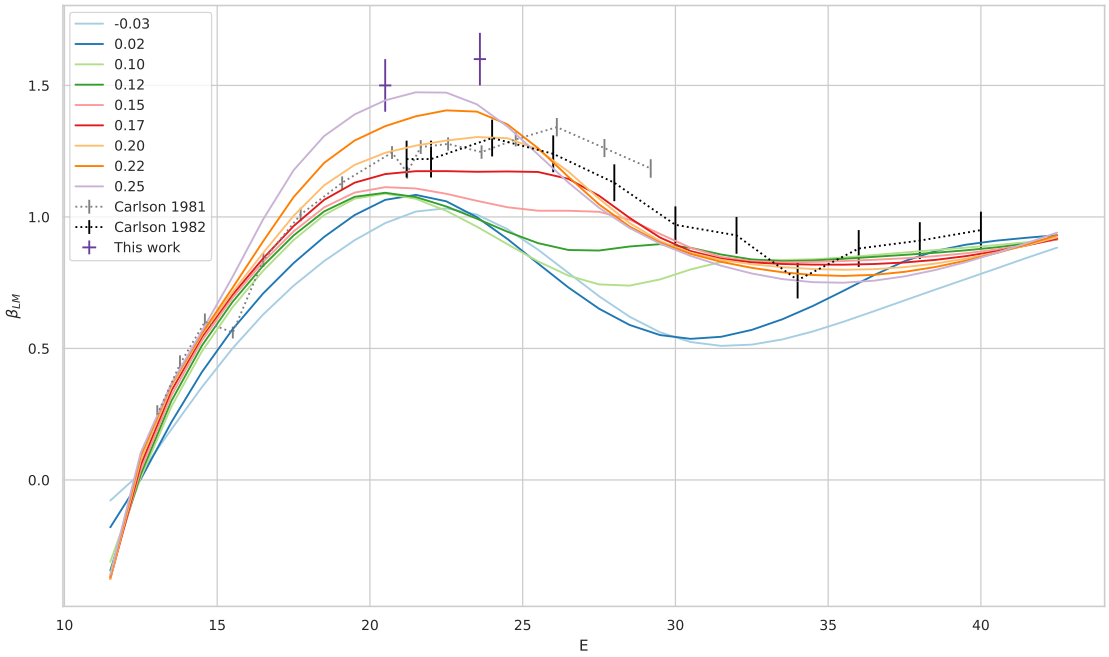

FIG. S4: Experimental β_2 parameters for Carlson *et al.* 1981 and 1982, plotted against ePolyScat calculated β_2 parameters for the $\tilde{\text{X}}$- ionization channel of randomly oriented OCS molecules as a function of electron kinetic energy for several displacements away from the (HF/cc-pVDZ) minimum energy geometry the ground state of OCS. The displacements correspond to a symmetric stretch of both bonds by the given fraction.

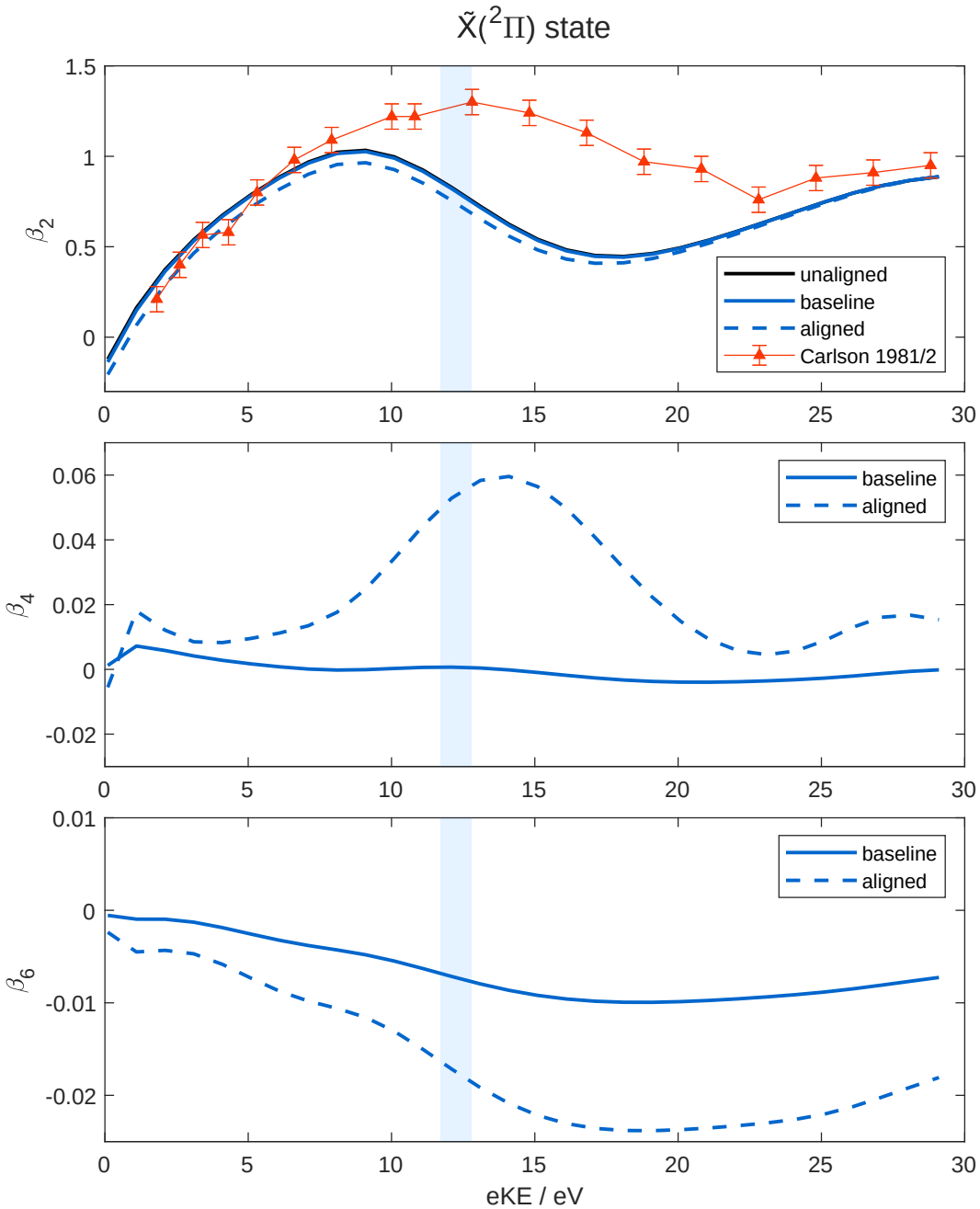

FIG. S5: Calculated β_n parameters for the first ionization channel of OCS molecules as a function of electron kinetic energy. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

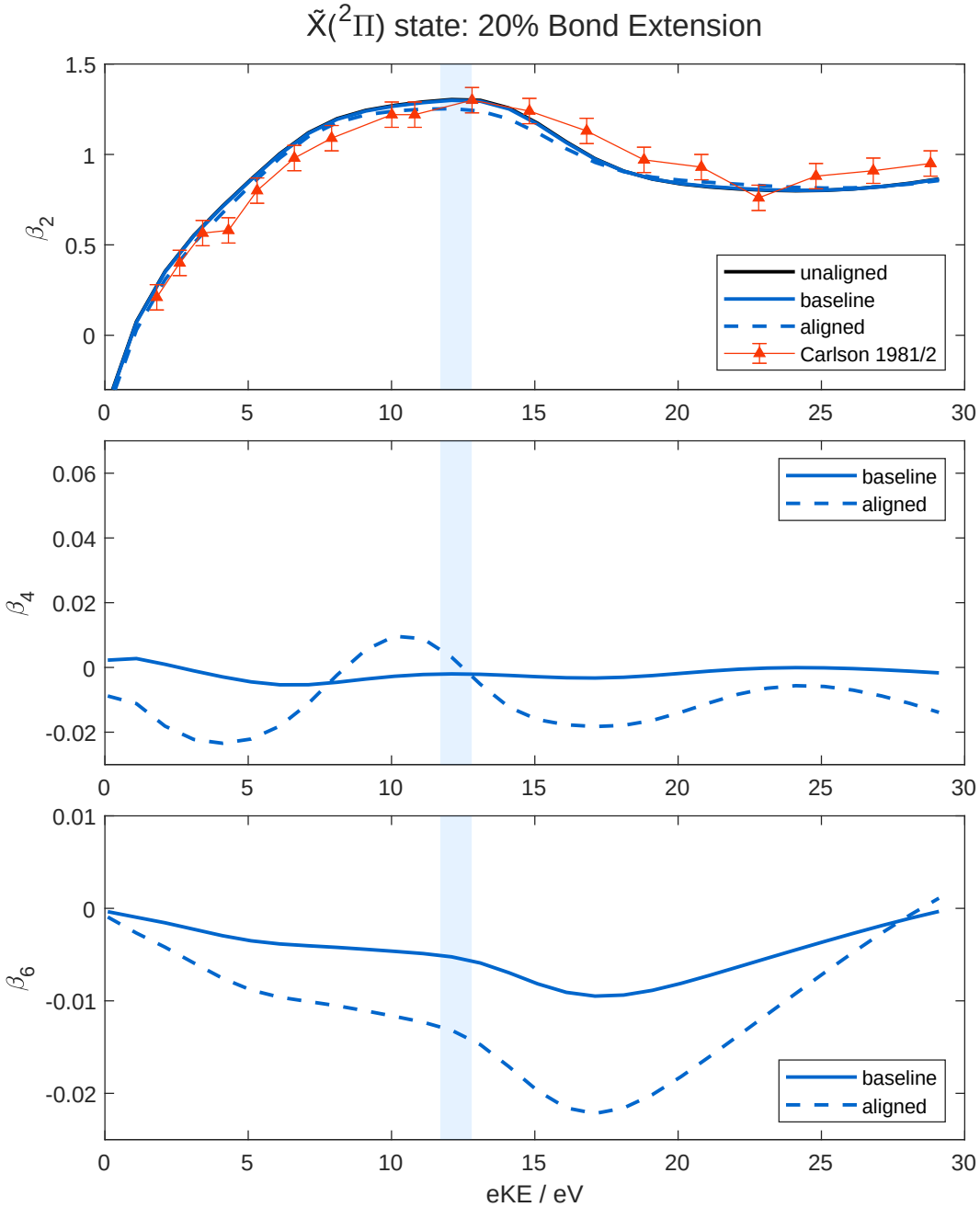

FIG. S6: Calculated β_n parameters for the first ionization channel of OCS molecules with bonds elongated by 20% relative to the ground state equilibrium geometry as a function of electron kinetic energy. This extension corresponds to an increase in bond length from 1.569 Å to 1.854 Å for C−S, and 1.131 Å to 1.386 Å for C−O. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

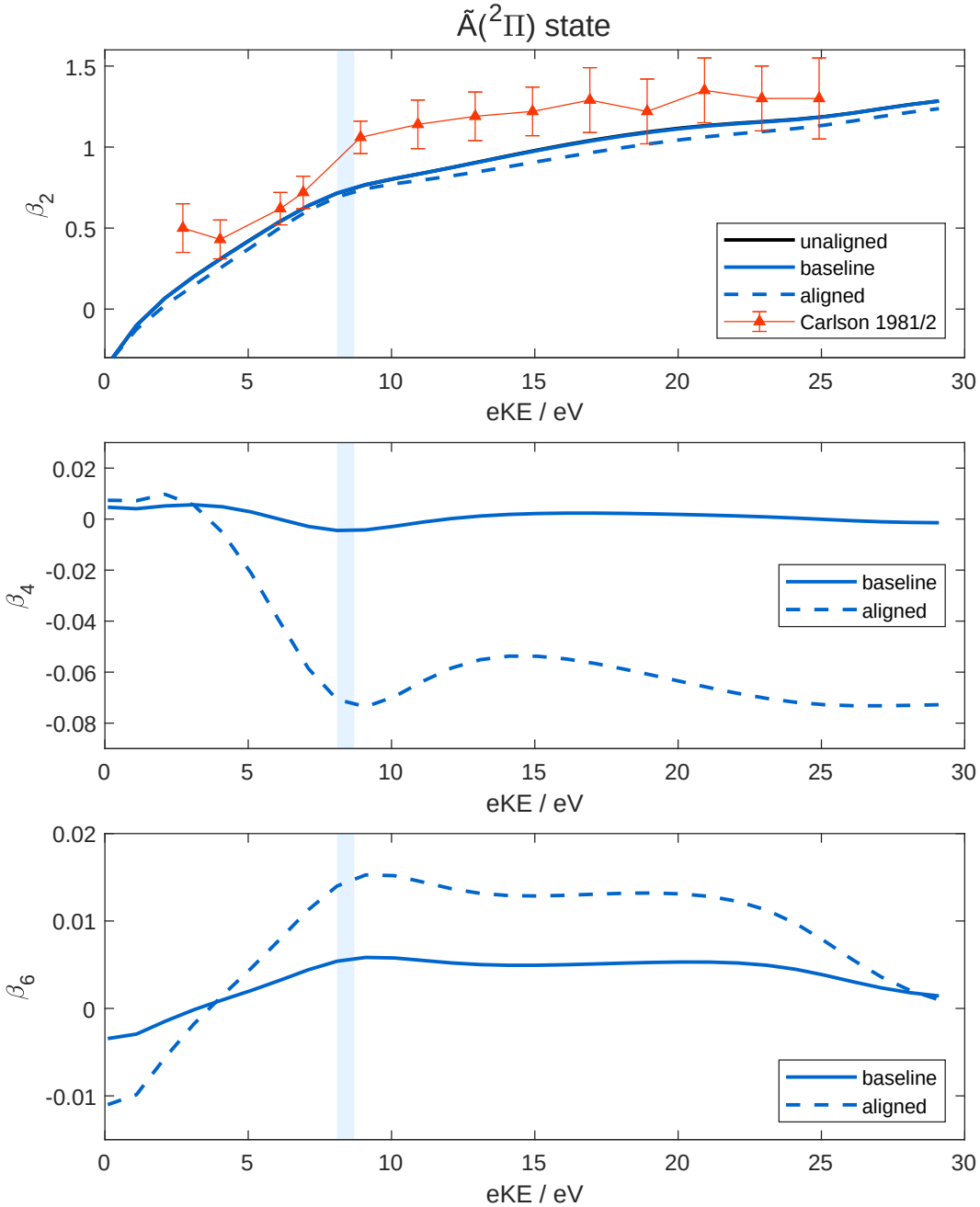

FIG. S7: Calculated β_n parameters for the Ã-state ionization channel of OCS molecules as a function of electron kinetic energy. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

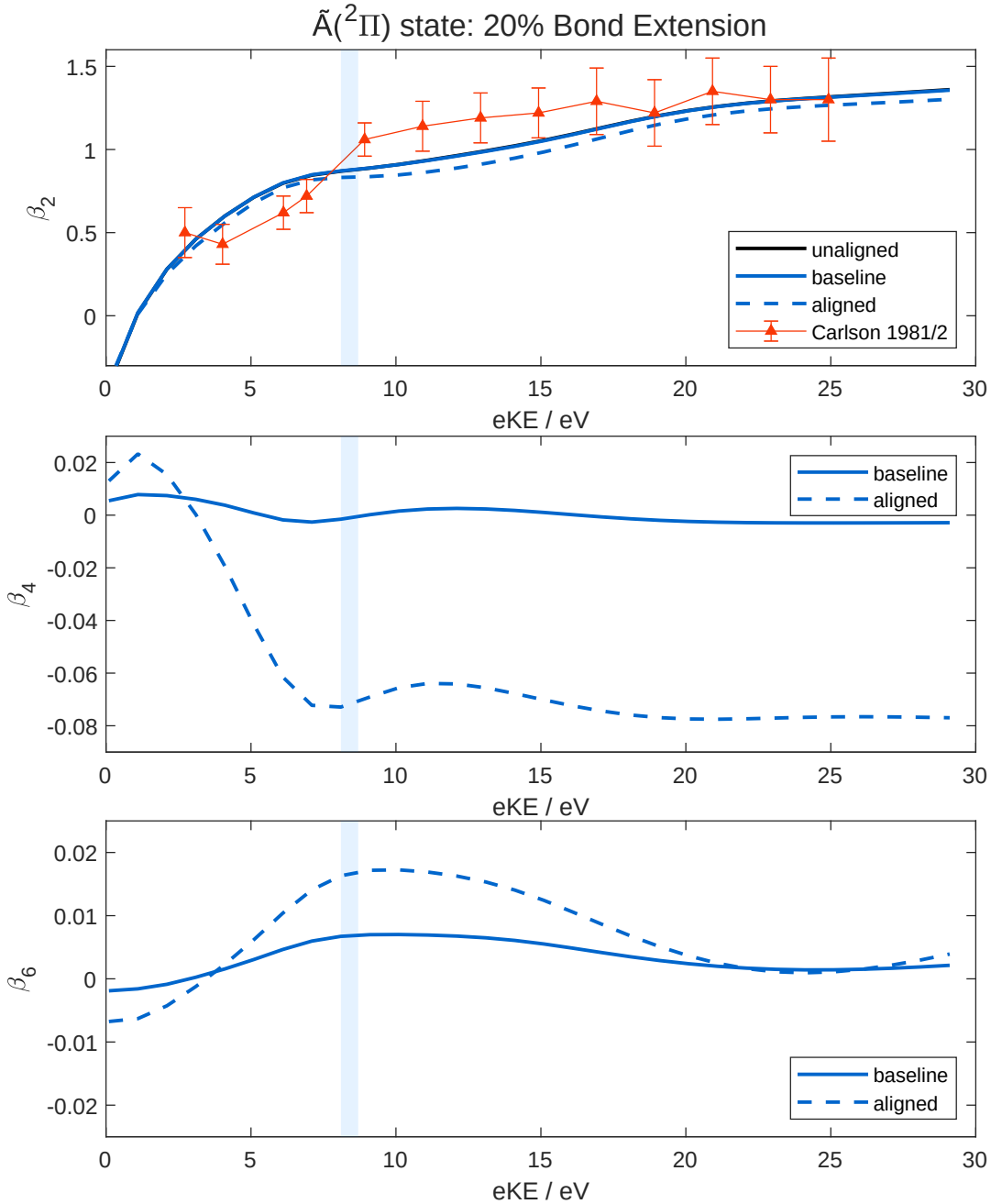

FIG. S8: Calculated β_n parameters for the Ã-state ionization channel of OCS molecules with bonds elongated by 20% relative to the ground state equilibrium geometry as a function of electron kinetic energy. This extension corresponds to an increase in bond length from 1.569 Å to 1.854 Å for C−S, and 1.131 Å to 1.386 Å for C−O. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

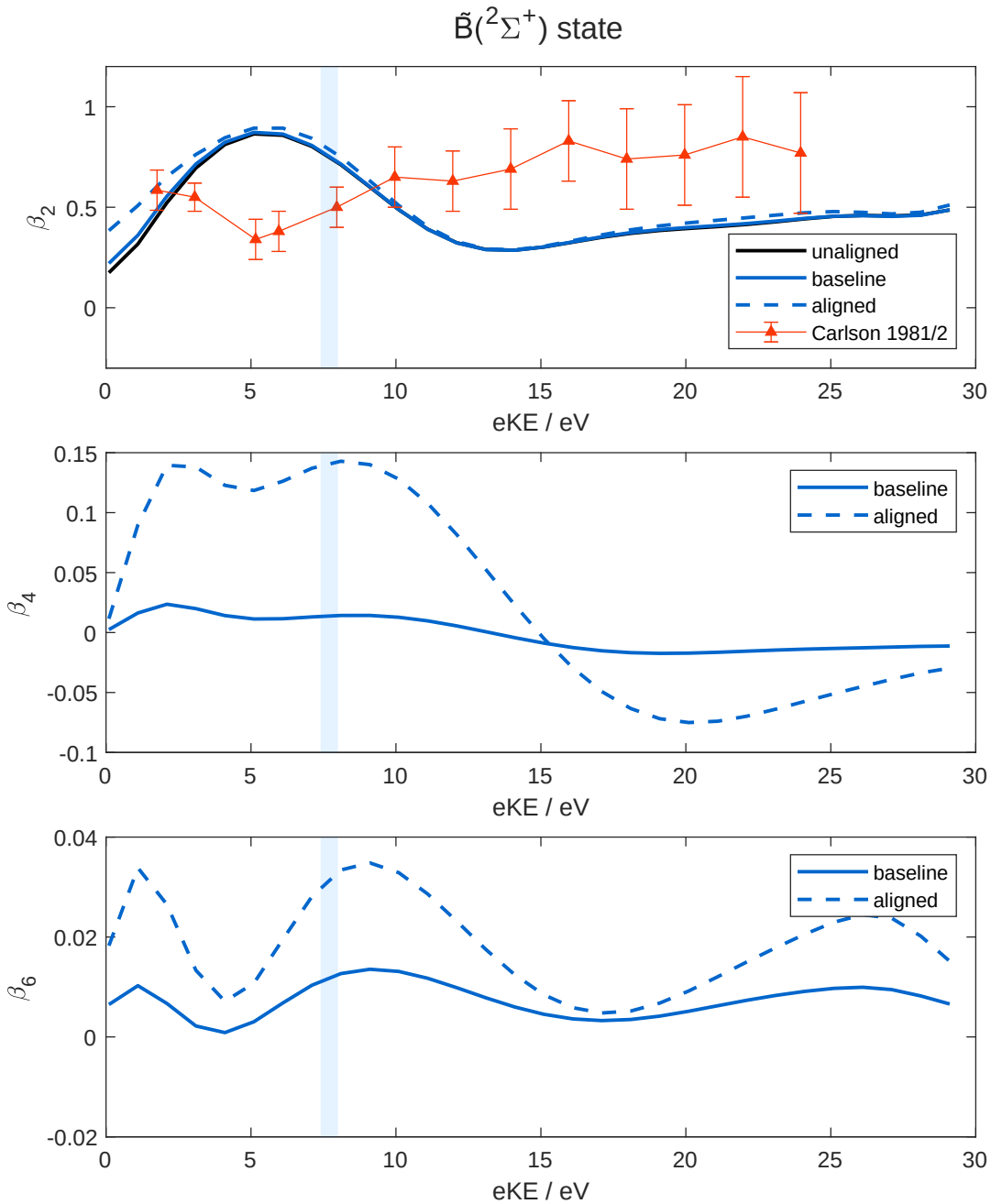

FIG. S9: Calculated β_n parameters for the $\tilde{B}$-state ionization channel of OCS molecules as a function of electron kinetic energy. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

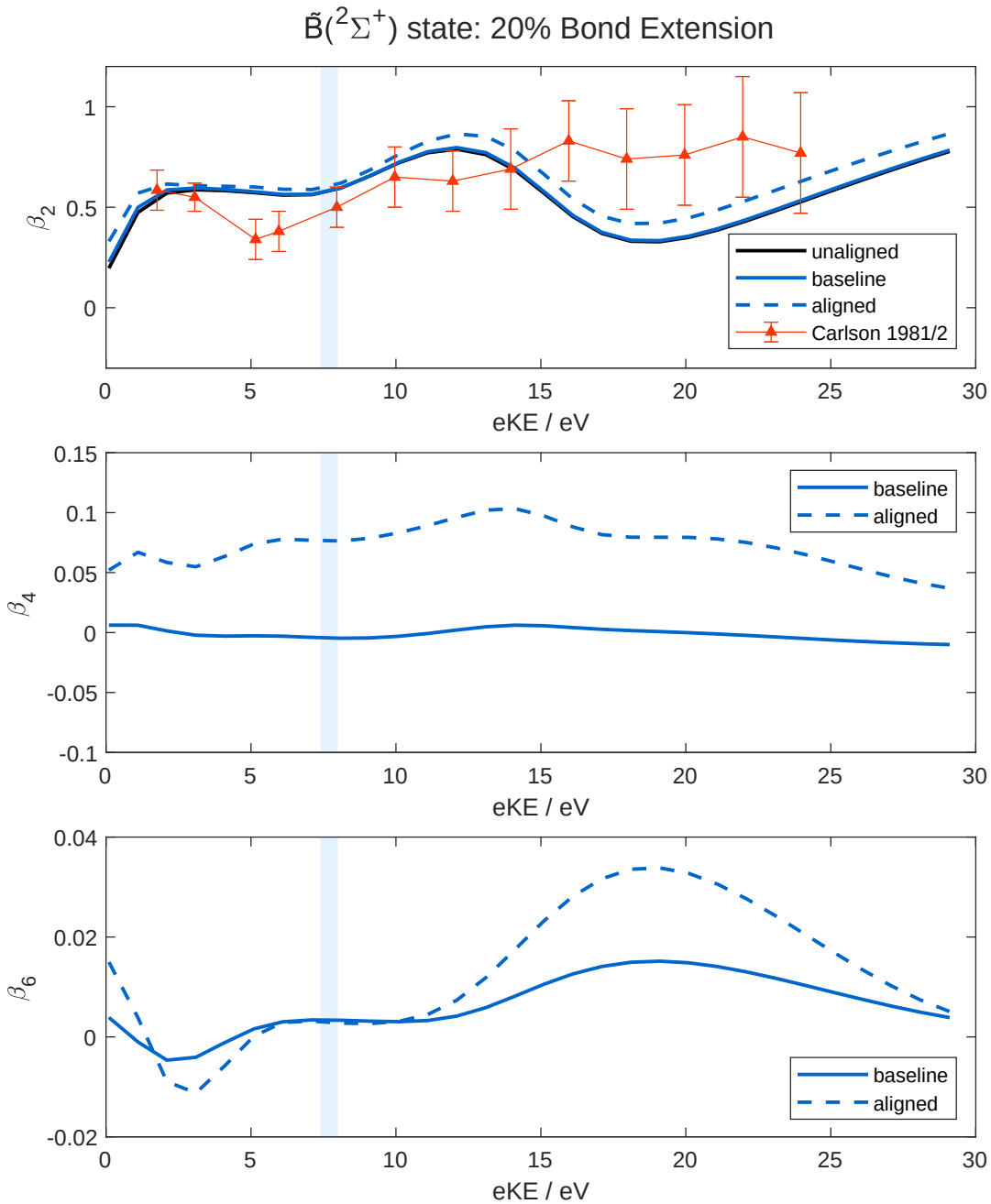

FIG. S10: Calculated β_n parameters for the B̃-state ionization channel of OCS molecules with bonds elongated by 20% relative to the ground state equilibrium geometry as a function of electron kinetic energy. This extension corresponds to an increase in bond length from 1.569 Å to 1.854 Å for C−S, and 1.131 Å to 1.386 Å for C−O. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps).Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

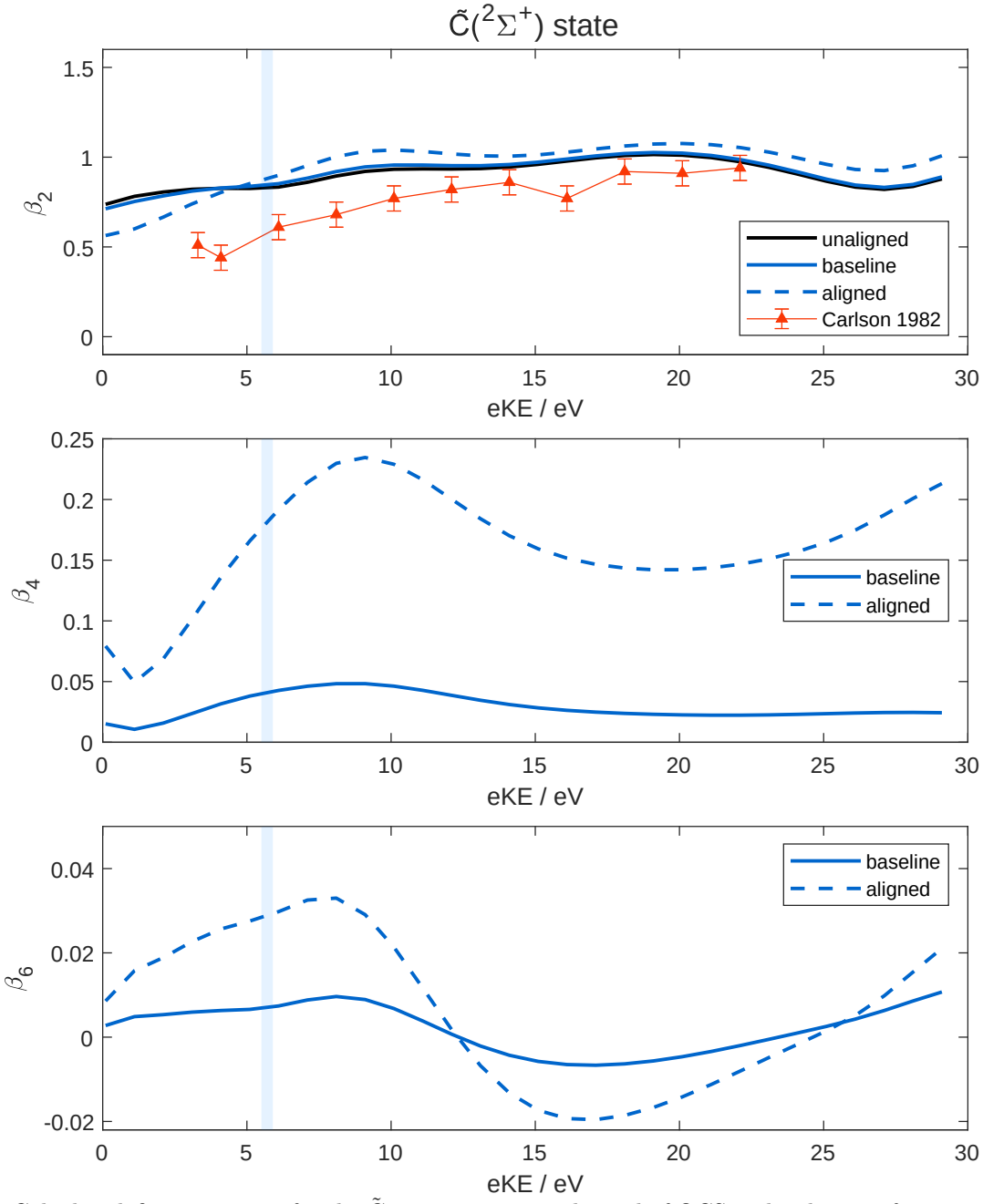

FIG. S11: Calculated β_n parameters for the C̃-state ionization channel of OCS molecules as a function of electron kinetic energy. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.

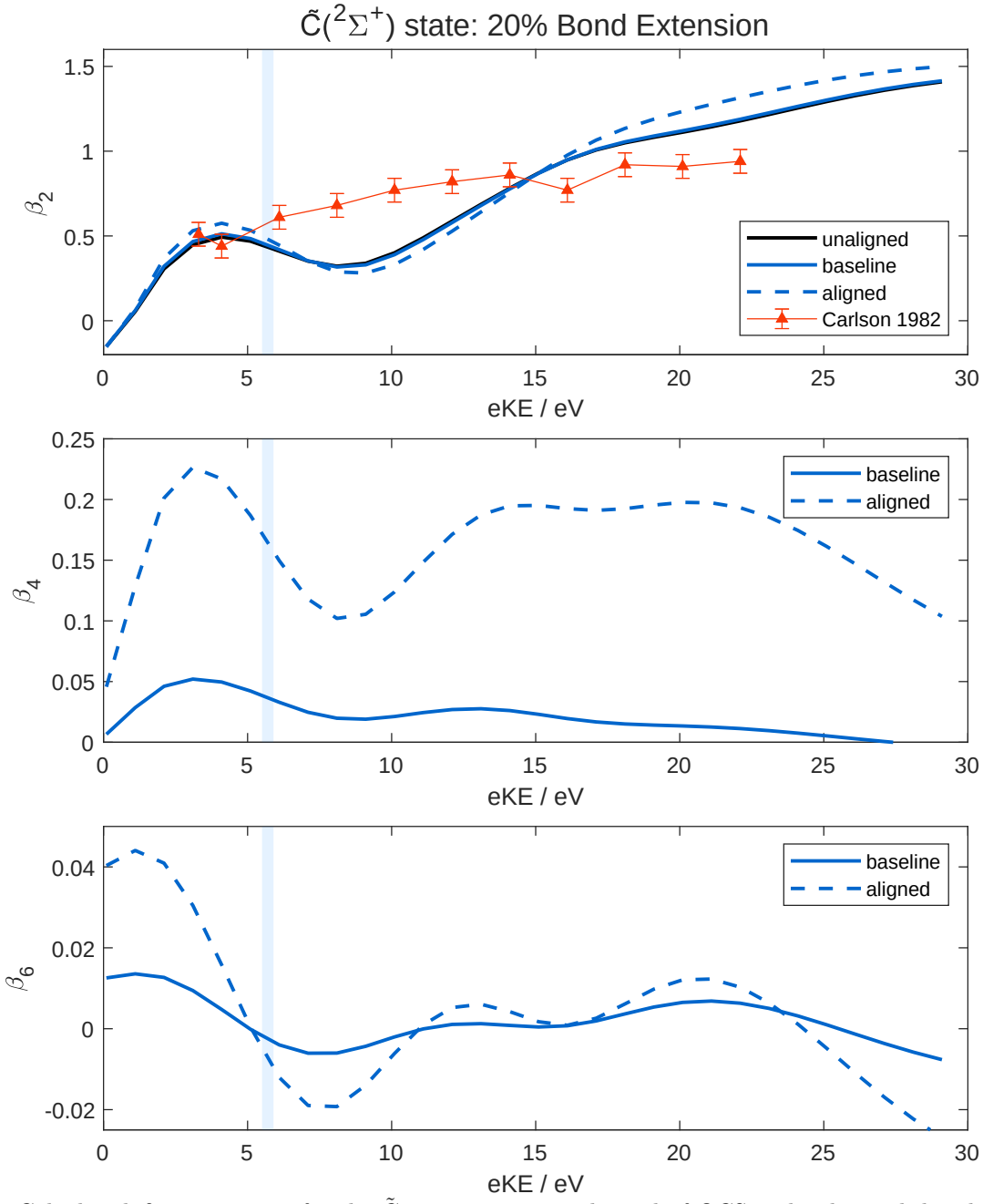

FIG. S12: Calculated β_n parameters for the C̃-state ionization channel of OCS molecules with bonds elongated by 20% relative to the ground state equilibrium geometry as a function of electron kinetic energy. This extension corresponds to an increase in bond length from 1.569 Å to 1.854 Å for C−S, and 1.131 Å to 1.386 Å for C−O. The solid black line represents the β_2 parameters for an unaligned sample of OCS molecules. The solid blue lines represent baseline β_n parameters expected for a sample of OCS molecules after long lived alignment has been induced by the alignment pulse (specifically corresponding delay time 0f 36.8 ps). Please note that the effect of permanent alignment on the β_2 parameters is weak and therefore the differences between the unaligned and baseline values can be negligible. The dashed blue lines represent β_n parameters expected for the aligned sample of OCS molecules at the peak of the first revival following the alignment pulse. The shaded region indicates the eKE range over which the experimental β_n parameters are averaged in the time-resolved data.