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SUPPORTING INFORMATION

Resolving s-*trans*-dominant ionization dynamics in tiglic aldehyde via VUV-MATI spectroscopy and PES analysis

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Table S1. Optimized geometrical parameters of the s-*trans* conformer of TA in the S_0 and D_0 states, calculated for different density functionals using the cc-pVTZ basis set.

Parameter	B3LYP		CAM-B3LYP		M06-2X		ωB97X-D	
	S_0	**D_0**	**S_0**	**D_0**	**S_0**	**D_0**	**S_0**	**D_0**
	Opt		Opt		Opt		Opt	
Bond length (Å)								
1C-2C	1.476	1.493	1.473 (-0.003)[a]	1.505 (0.012)[a]	1.478 (0.002)	1.514 (0.021)	1.477 (0.001)	1.511 (0.018)
1C-5O	1.210	1.202	1.204 (-0.006)	1.193 (-0.009)	1.204 (-0.006)	1.192 (-0.010)	1.204 (-0.006)	1.192 (-0.010)
1C-6H	1.110	1.105	1.108 (-0.002)	1.193 (0.088)	1.107 (-0.003)	1.192 (0.087)	1.109 (-0.001)	1.192 (0.087)
2C-3C	1.341	1.382	1.333 (-0.008)	1.393 (0.011)	1.335 (-0.006)	1.407 (0.025)	1.336 (-0.005)	1.392 (0.010)
2C-7C	1.499	1.474	1.494 (-0.005)	1.458 (-0.016)	1.496 (-0.003)	1.457 (-0.017)	1.496 (-0.003)	1.461 (-0.013)
3C-4C	1.491	1.463	1.488 (-0.003)	1.454 (-0.009)	1.491 (0.000)	1.455 (-0.008)	1.490 (-0.001)	1.457 (-0.006)
3C-8H	1.087	1.087	1.086 (-0.001)	1.087 (0.000)	1.087 (0.000)	1.088 (0.001)	1.087 (0.000)	1.088 (0.001)
4C-9H	1.087	1.084	1.086 (-0.001)	1.084 (0.000)	1.086 (-0.001)	1.084 (0.000)	1.087 (0.000)	1.084 (0.000)
4C-10H	1.093	1.103	1.092 (-0.001)	1.102 (-0.001)	1.092 (-0.001)	1.103 (0.000)	1.092 (-0.001)	1.102 (-0.001)
4C-11H	1.093	1.096	1.092 (-0.001)	1.095 (-0.001)	1.092 (-0.001)	1.095 (-0.001)	1.092 (-0.001)	1.094 (-0.002)
7C-12H	1.087	1.086	1.086 (-0.001)	1.085 (-0.001)	1.086 (-0.001)	1.084 (-0.002)	1.087 (0.000)	1.085 (-0.001)
7C-13H	1.091	1.098	1.090 (-0.001)	1.099 (0.001)	1.090 (-0.001)	1.101 (0.003)	1.090 (-0.001)	1.099 (0.001)
7C-14H	1.091	1.096	1.090 (-0.001)	1.096 (0.000)	1.090 (-0.001)	1.097 (0.001)	1.090 (-0.001)	1.096 (0.000)
Bond angle (°)								
1C-2C-3C	116.5	115.8	116.5 (0.0)	116.7 (0.9)	116.5 (0.0)	116.9 (1.1)	116.4 (-0.1)	116.6 (0.8)
2C-3C-4C	128.6	126.7	128.3 (-0.3)	126.7 (0.0)	128.0 (-0.6)	126.5 (-0.2)	128.3 (-0.3)	126.5 (-0.2)
2C-1C-5O	124.6	123.2	124.4 (-0.2)	121.1 (-2.1)	124.0 (-0.6)	120.1 (-3.1)	124.4 (-0.2)	121.3 (-1.9)
7C-2C-3C	127.1	128.0	127.3 (0.2)	126.8 (-1.2)	127.7 (0.6)	126.1 (-1.9)	127.3 (0.2)	126.9 (-1.1)
2C-3C-8H	116.4	117.3	116.5 (0.1)	116.8 (-0.5)	116.6 (0.2)	116.4 (-0.9)	116.6 (0.2)	117.0 (-0.3)
2C-7C-12H	112.7	112.6	112.6 (-0.1)	113.9 (1.3)	112.7 (0.0)	114.5 (1.9)	112.7 (0.0)	113.8 (1.2)
2C-7C-13H	110.2	110.4	110.2 (0.0)	109.2 (-1.2)	109.9 (-0.3)	108.1 (-2.3)	110.1 (-0.1)	109.0 (-1.4)
3C-4C-9H	113.2	115.1	113.1 (-0.1)	115.1 (0.0)	112.8 (-0.4)	114.9 (-0.2)	113.1 (-0.1)	115.0 (-0.1)

3C-4C-10H	110.3	107.3	110.3 (0.0)	107.0 (-0.3)	110.2 (-0.1)	106.8 (-0.5)	110.1 (-0.2)	106.7 (-0.6)
Dihedral angle (°)								
1C-2C-3C-4C	180.0	164.2	180.0 (0.0)	161.8 (-2.4)	180.0 (0.0)	164.0 (-0.2)	180.0 (0.0)	160.8 (-3.4)
5O-1C-2C-3C	180.0	166.8	180.0 (0.0)	165.1 (-1.7)	180.0 (0.0)	165.7 (-1.1)	180.0 (0.0)	164.0 (-2.8)
1C-2C-7C-12H	180.0	164.8	180.0 (0.0)	165.1 (0.3)	180.0 (0.0)	169.2 (4.4)	180.0 (0.0)	166.8 (2.0)
1C-2C-7C-13H	-58.4	-75.3	-58.4 (0.0)	-74.5 (0.8)	-58.3 (0.1)	-69.5 (5.8)	-58.4 (0.0)	-72.7 (2.6)
2C-3C-4C-10H	-121.5	-120.5	-121.4 (0.1)	-118.2 (2.3)	-121.3 (0.2)	-115.2 (5.3)	-121.4 (0.1)	-116.9 (3.6)
2C-3C-4C-11H	121.5	127.1	121.4 (-0.1)	130.0 (2.9)	121.3 (-0.2)	132.9 (5.8)	121.4 (-0.1)	130.9 (3.8)

[a] Values in parentheses indicate deviations from the B3LYP/cc-pVTZ reference geometry.

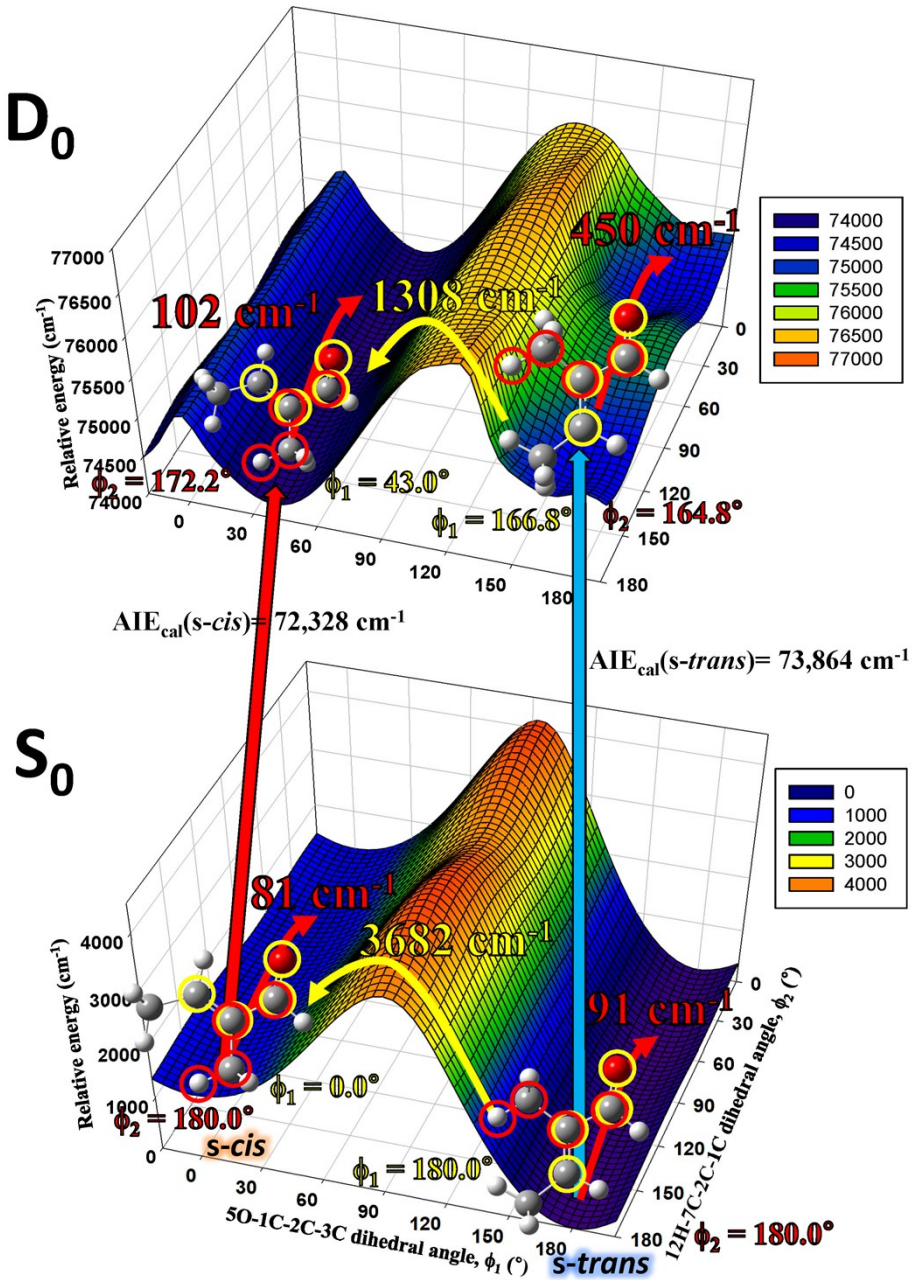

Fig. S1. 2D-PES diagrams for the s-*cis*/s-*trans* interconversion of TA in the S_0 (bottom) and D_0 (top) states, calculated at the B3LYP/cc-pVTZ level of theory. In the S_0 state, the s-*trans* conformer is more stable than the s-*cis* conformer by ~1140 cm^{-1}, with an interconversion barrier of ~3530 cm^{-1}, indicating that TA exists almost exclusively as the s-*trans* conformer under jet-cooled conditions, in excellent agreement with CAM-B3LYP/cc-pVTZ results. In the D_0 state, the relative stability is reversed by ~1540 cm^{-1}, and both conformers adopt slightly nonplanar geometries.

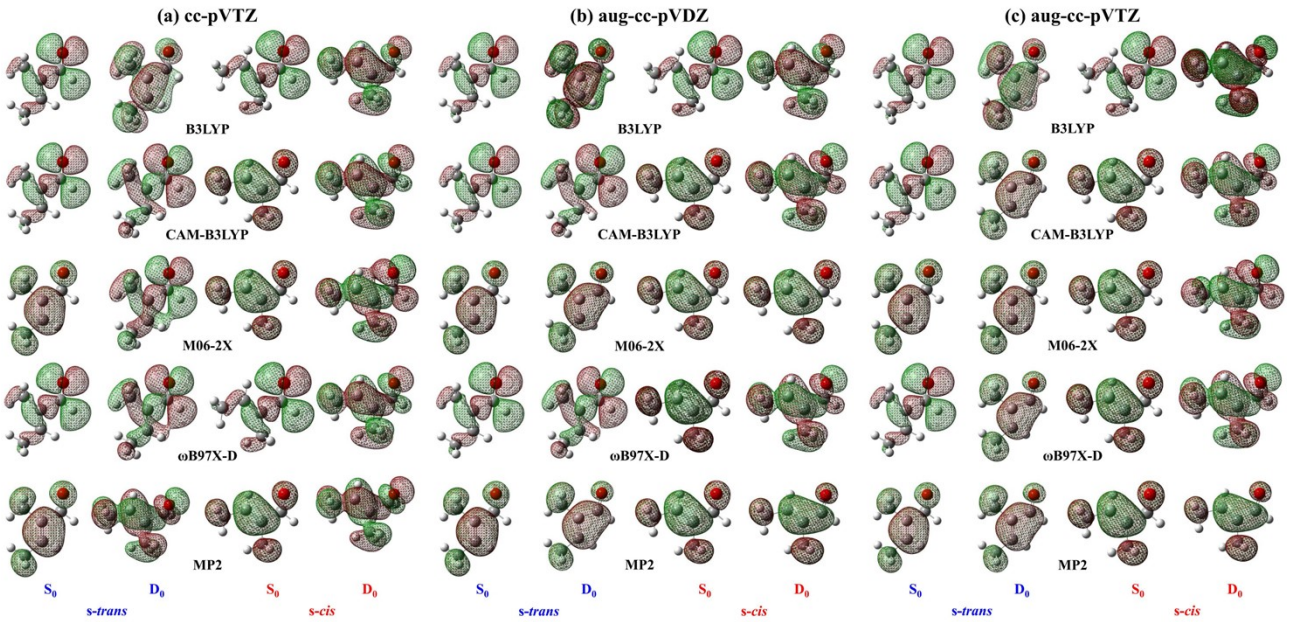

Fig. S2. HOMOs of the s-*trans* and s-*cis* conformers of TA in the S_0 and D_0 states, optimized at the B3LYP, CAM-B3LYP, M06-2X, ωB97X-D, and MP2 levels of theory using the (a) cc-pVTZ, (b) aug-cc-pVDZ, and (c) aug-cc-pVTZ basis sets. All orbitals were analyzed within the NBO framework, which transforms canonical orbitals into natural bond orbitals to provide a detailed description of electron-density distribution. At the MP2 level, optimization of the D_0 state yields a single conformer with the cc-pVTZ basis set but produces two conformers when larger basis sets are employed.

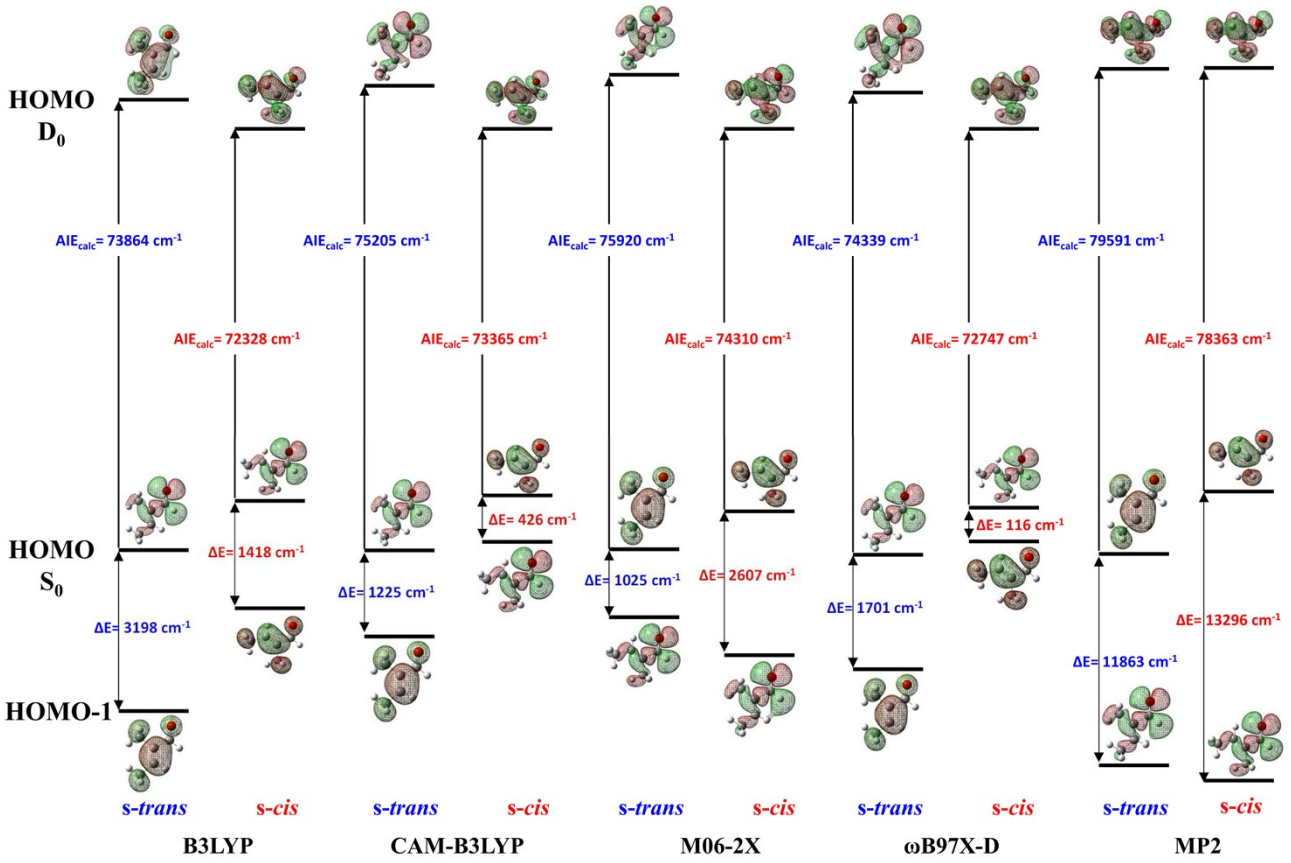

Fig. S3. Energetic diagrams of the s-*trans* and s-*cis* conformers of TA obtained from quantum chemical calculations (B3LYP, CAM-B3LYP, M06-2X, and ωB97X-D) and ab initio MP2 calculations using the cc-pVTZ basis set. The HOMO and HOMO–1 of the neutral and HOMO of the cation are shown, and the ΔE values between HOMO and HOMO–1 are indicated. AIE_{calc} corresponds to the transition to the D_0 cationic state upon the removal of an electron from the HOMO. All values include zero-point energy corrections.

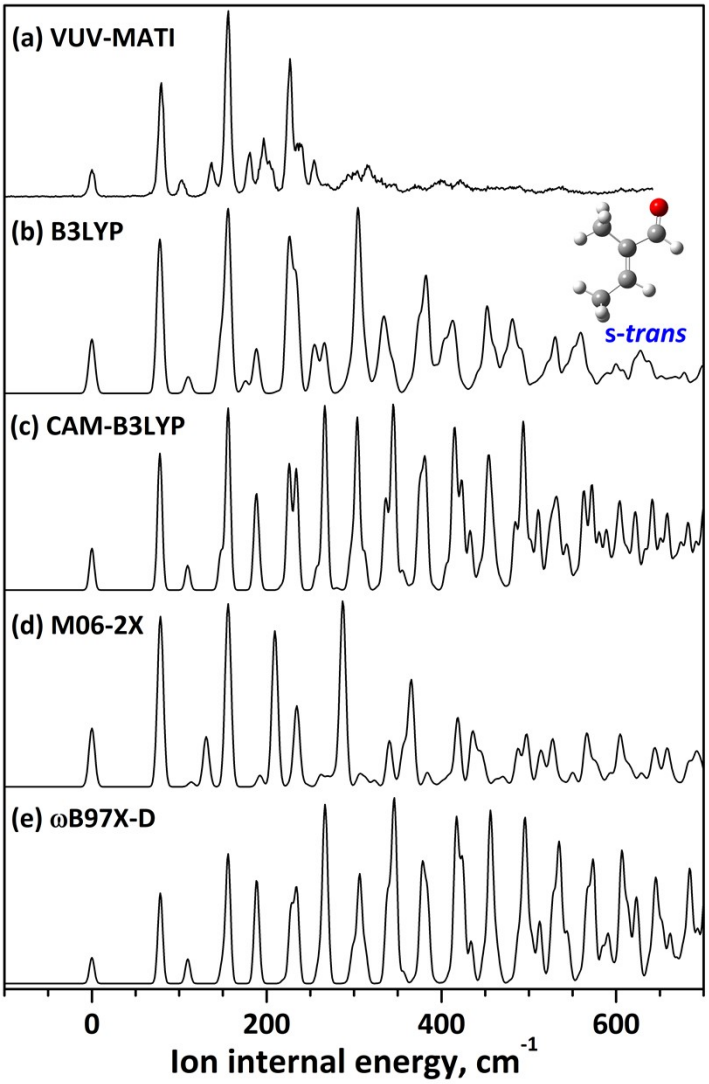

Fig. S4. Comparison of the experimental VUV-MATI spectrum of TA with the FC simulations performed for the s-*trans* conformer at different levels of theory (B3LYP, CAM-B3LYP, M06-2X, and ωB97X-D). The B3LYP/cc-pVTZ calculation provides the best agreement with the observed vibrational progression.

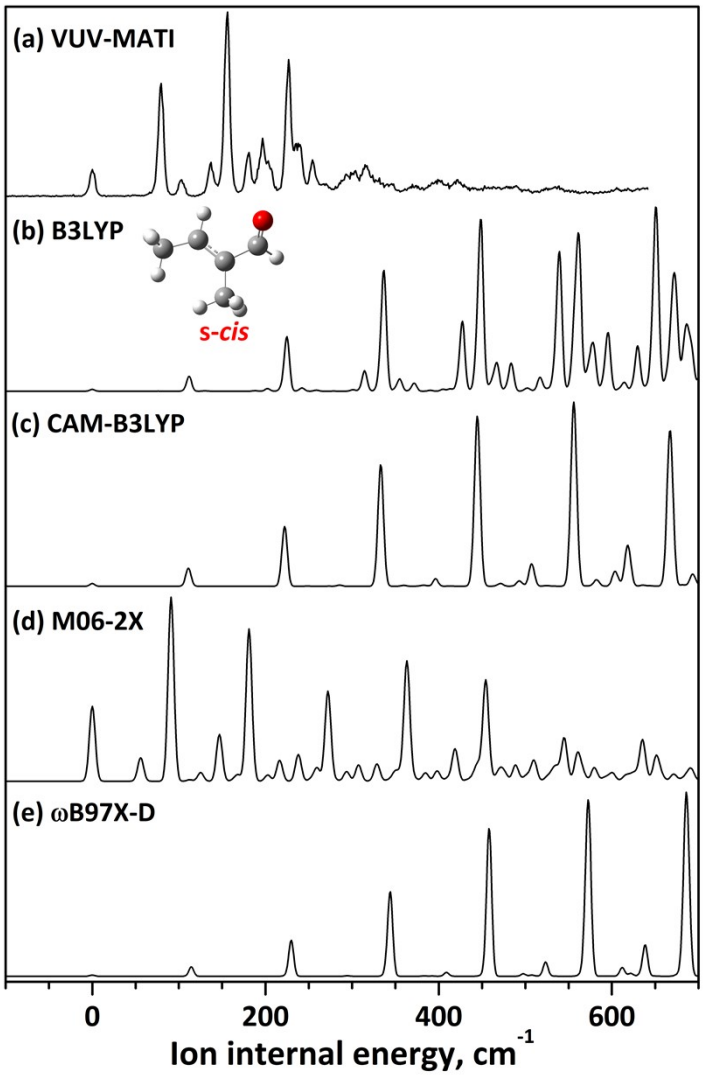

Fig. S5. Comparison of the experimental VUV-MATI spectrum of TA with the FC simulations performed for the s-*cis* conformer at different levels of theory. The simulated spectra do not reproduce either the threshold position or the observed intensity distribution, confirming a negligible s-*cis* contribution under the experimental conditions.