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Electronic supplementary information (ESI)

Excited electronic states of thiophene: high resolution photoabsorption Fourier transform spectroscopy and *ab initio* calculations

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Table S1

Calculated and experimental geometry of thiophene (Figure 1). Bond lengths in Å, angles in degrees.

Bonds	MP2 [a]	Exp.[b]	Angles	MP2	Exp.[b]
$S - C_2$	1.727	1.714	$C_{2'} - S - C_2$	92.0	92.2
$C_2 - C_3$	1.388	1.370	$S - C_2 - C_3$	111.6	111.5
$C_3 - C_{3'}$	1.426	1.423	$C_2 - C_3 - C_{3'}$	112.4	112.5
$C_2 - H_2$	1.090	1.078	$S - C_2 - H_2$	120.3	119.9
$C_3 - H_3$	1.092	1.081	$C_2 - C_3 - H_3$	123.1	123.2

[a] This work, aug-cc-pVDZ basis (see text for details - without polarization diffuse functions -).

[b] Bak et al.[62]

Table S2

Calculated and measured frequencies (cm^{-1}) of the totally symmetric vibrations in the ground state of thiophene

Vibrational mode	MP2 [a]	Experiment[80]
1	3292	3126
2	3264	3097
3	1457	1410
4	1393	1364
5	1088	1082
6	1069	1036
7	868	840
8	612	609

[a] This work, aug-cc-pVDZ basis (see text for details – without polarization diffuse functions -).

Table S3

Energies Ω (eV), oscillator strengths f (a.u.), and quantum defects δ for $1a_2(\pi_3) \rightarrow nl\gamma\ (^1\Gamma)$ vertical Rydberg excitations of thiophene; dipole moments μ (a.u.) and second electronic moments $< r^2 >$ (a.u.) for the final states calculated at the EOM-CCSD level of theory using aug-cc-pVTZ basis set augmented by further Rydberg functions (see text for details).

Γ	$nl\gamma$	Ω	f	δ [a]	μ	$< x^2 >$	$< y^2 >$	$< z^2 >$
A_1	$3da_2$	7.61	0.056	-0.06	-1.08	-81	-71	-38
	$4da_2$	8.24	0.011	-0.07	-2.36	-161	-146	-147
	$4fa_2$	8.26	0.001	-0.11	0.54	-272	-250	-102
	$5\mathrm{d}a_2$	8.55	0.003	-0.14	-3.48	-336	-332	-313
	$5fa_2$	8.55	0.001	-0.18	2.32	-549	-528	-204
A_2	$3sa_1$	6.19		0.82	0.43	-46	-41	-40
	$3pa_1$	6.89		0.50	-0.49	-44	-38	-73
	$3da_1$	7.20		0.30	-0.80	-49	-38	-48
	$3\tilde{d}\,a_1$	7.24		0.27	1.26	-41	-55	-58
	$4sa_1$	7.76		0.76	1.36	-144	-109	-89
	$4pa_1$	7.98		0.44	-5.14	-97	-83	-236
	$4da_1$	8.06		0.32	3.87	-119	-72	-215
	$4\tilde{d}\,a_1$	8.11		0.22	-1.15	-122	-231	-102
B_1	$3pb_2$	6.94	0.024	0.47	1.57	-41	-63	-43
	$3db_2$	7.63	<0.001	-0.09	-1.42	-46	-84	-68
	$4pb_2$	7.98	0.006	0.45	3.04	-98	-223	-109
	$4db_2$	8.15	<0.001	0.13	-4.46	-65	-167	-142

Table S3 (continued)

Γ	$nl\gamma$	Ω	f	δ [a]	μ	$< x^2 >$	$< y^2 >$	$< z^2 >$
B_2	$3pb_1$	6.93	0.044	0.47	0.06	-76	-36	-39
	$3db_1$	7.65	0.016	-0.11	-0.66	-86	-37	-78
	$4pb_1$	7.99	0.004	0.43	0.14	-243	-94	-94
	$4db_1$	8.21	0.002	0.01	-0.66	-176	-176	-60
	$4fb_1$	8.23	0.001	-0.05	-0.93	-187	-61	-194
	$4\tilde{f}b_1$	8.27	<0.001	-0.16	-0.92	-285	-102	-277
	$5pb_1$	8.41	0.004	0.42	0.81	-658	-222	-234
	$5db_1$	8.52	0.002	-0.01	-0.69	-437	-416	-125
	$5fb_1$	8.54	<0.001	-0.09	0.52	-377	-170	-420
	$5\tilde{f}b_1$	8.56	<0.001	-0.22	-2.96	-508	-206	-469
	$6pb_1$	8.65	0.003	0.27	0.62	-1063	-350	-366

[a] The quantum defects were obtained by using the Rydberg formula $E_n = E_\infty - 13.606/(n-\delta)^2$, where E_∞ is the relevant ionization energy, presently computed at the IP-EOM-CCSD (basis A) level of theory (9.06 eV for the $(1a_2)^{-1}$ $\tilde{X}\,^2A_2$ state).

Table S4

Energies Ω (eV), oscillator strengths f (a.u.), and quantum defects δ for $3b_1(\pi_2) \rightarrow nl\gamma$ ($^1\Gamma$) vertical Rydberg excitations of thiophene; dipole moments μ (a.u.) and second electronic moments $< r^2 >$ (a.u.) for the final states calculated at the EOM-CCSD level of theory using aug-cc-pVTZ basis set augmented by further Rydberg functions (see text for details).

Γ	$nl\gamma$	Ω	f	δ [a]	μ	$< x^2 >$	$< y^2 >$	$< z^2 >$
A_1	$3pb_1$	7.23	0.080	0.48	0.05	-74	-37	-37
	$3db_1$	7.97	0.013	-0.12	0.37	-95	-41	-86
	$4pb_1$	8.31	<0.001	0.41	0.43	-253	-108	-105
	$4db_1$	8.52	0.001	-0.01	-0.11	-190	-67	-179
	$4fb_1$	8.52	0.001	-0.01	-0.60	-194	-203	-85
	$4\tilde{f}b_1$	8.58	<0.001	-0.15	0.00	-301	-127	-275
	$5pb_1$	8.72	0.001	0.42	-0.41	-658	-215	-248
	$5db_1$	8.83	0.001	-0.02	-0.70	-475	-318	-203
	$5fb_1$	8.83	0.001	-0.04	-0.23	-378	-243	-407
	$5\tilde{f}b_1$	8.84	0.001	-0.09	-1.60	-350	-379	-291
A_2	$3pb_2$	7.32		0.42	1.26	-45	-75	-38
	$3db_2$	7.91		-0.06	-1.95	-49	-83	-79
	$4pb_2$	8.32		0.39	2.29	-173	-243	-126
	$4db_2$	8.46		0.14	-2.87	-63	-168	-149
	$4fb_2$	8.52		0.01	-1.34	-234	-154	-117
	$4\tilde{f}b_2$	8.55		-0.06	-4.09	-419	-146	-350

Table S4 (continued)

Γ	$nl\gamma$	Ω	f	δ [a]	μ	$< x^2 >$	$< y^2 >$	$< z^2 >$
B_1	$3sa_1$	6.53	<0.001	0.81	0.04	-47	-40	-40
	$3sa_1$	7.15	0.025	0.52	0.13	-43	-40	-72
	$3da_1$	7.52	<0.001	0.29	0.03	-46	-31	-60
	$3\tilde{d}\,a_1$	7.61	<0.001	0.22	0.17	-45	-76	-41
	$b_1/4sa_1$ [b]	8.08	<0.001		0.74	-95	-60	-43
	$4sa_1/b_1$ [b]	8.09	0.003	0.74	-0.51	-92	-74	-95
	$4pa_1$	8.29	0.007	0.46	-1.10	-98	-104	-248
	$4da_1$	8.40	<0.001	0.26	0.25	-133	-87	-195
	$4\tilde{d}\,a_1$	8.43	0.002	0.20	-3.79	-109	-299	-110
	$4fa_1$	8.47	<0.001	0.12	6.45	-78	-194	-180
	$4\tilde{f}\,a_1$	8.51	0.010	0.02	-0.58	-233	-121	-153
	$5sa_1$	8.62	<0.001	0.75	0.98	-415	-319	-246
	$5pa_1$	8.71	0.002	0.46	-8.02	-219	-196	-642
B_2	$3da_2$	7.95	0.002	-0.09	0.29	-97	-82	-42
	$4da_2$	8.54	0.001	-0.06	-2.33	-210	-148	-213
	$4fa_2$	8.57	<0.001	-0.12	1.44	-332	-262	-183
	$5da_2$	8.85	<0.001	-0.11	0.55	-360	-343	-348
	$5fa_2$	8.86	<0.001	-0.17	-2.51	-561	-532	-217

[a] The quantum defects were obtained by using the Rydberg formula $E_n = E_\infty - 13.606/(n-\delta)^2$, where E_∞ is the relevant ionization energy, presently computed at the IP-EOM-CCSD (basis A) level of theory (9.37 eV for the $(3b_1)^{-1}$ $\tilde{A}\ {}^2B_1$ state).

[b] Mixing of configurations $11a_1$-b_1 and $3b_1$-$4sa_1$.

Table S5

Energies Ω (eV) and oscillator strengths f (a.u.) for vertical valence-type excitations of thiophene; dipole moments μ (a.u.) and second electronic moments $< r^2 >$ (a.u.) for the final states calculated at the EOM-CCSD level of theory using aug-cc-pVTZ basis set augmented by further Rydberg functions (see text for details).

State	Leading configuration	Ω	f	μ	$< x^2 >$	$< y^2 >$	$< z^2 >$
1^1A_1 [a]				-0.21	-30	-24	-26
$^1A_1$	$3b_1(\pi_2) \rightarrow 4b_1(\pi_4^*)$	5.78	0.081	-0.14	-31	-25	-27
$^1A_1$	$1a_2(\pi_3) \rightarrow 2a_2(\pi_5^*)$	7.74	0.232	1.09	-55	-43	-38
$^1B_2$	$1a_2(\pi_3) \rightarrow 4b_1(\pi_4^*)$	6.13	0.084	-0.30	-32	-23	-29
$^1B_2$	$3b_1(\pi_2) \rightarrow 2a_2(\pi_5^*)$	7.78	0.111	0.80	-46	-32	-40
$^1B_1$	$1a_2(\pi_3) \rightarrow 8b_2(\sigma^*)$	6.33	0.013	-2.48	-33	-37	-35
$^1A_2$	$3b_1(\pi_2) \rightarrow 8b_2(\sigma^*)$	6.37		-1.99	-31	-32	-32

[a] Electronic ground state (only dipole moments and second electronic moments are shown).

Table S6

Energies Ω (eV) and oscillator strengths *f* (a.u.) for vertical excitations of thiophene computed using various equation-of-motion (linear response) coupled cluster models.

Excitations		Vertical excitation energies, Ω						CCSD oscillator strengths		
		CCSD[a]	CC3[a]	CCSD[b]	CCSDR(3)[b]	CCSD[c]	CCSDR(3)[c]	f^{a}	f^{b}	f^{c}
$^1A_1$	$1a_2 \rightarrow 3da_2$	7.61				7.53	7.50	0.056		0.013
	$1a_2(\pi_3) \rightarrow 2a_2(\pi_5^*)$	7.74				7.81	7.71	0.232		0.294
	$3b_1(\pi_2) \rightarrow 4b_1(\pi_4^*)$	5.78	5.64	5.78	5.69	5.78	5.70	0.081	0.076	0.082
	$3b_1 \rightarrow 3pb_1$	7.23	7.17			7.11	7.10	0.080		0.041
	$3b_1 \rightarrow 3db_1$	7.97				7.83	7.81	0.013		0.017
$^1B_2$	$1a_2(\pi_3) \rightarrow 4b_1(\pi_4^*)$	6.13	5.97	6.13	6.01	6.23	6.10	0.084	0.077	0.080
	$1a_2 \rightarrow 3pb_1$	6.93				6.84	6.81	0.044		0.032
	$1a_2 \rightarrow 3db_1$	7.65				7.56	7.54	0.016		0.002
	$3b_1(\pi_2) \rightarrow 2a_2(\pi_5^*)$	7.78				7.96	7.85	0.111		
	$3b_1 \rightarrow 3da_2$	7.95				7.81	7.80	0.002		
$^1A_2$	$1a_2 \rightarrow 3sa_1$	6.19	6.12	6.19	6.15	6.10	6.05			
	$1a_2 \rightarrow 3pa_1$	6.89				6.78	6.74			
	$1a_2 \rightarrow 3da_1$	7.20				7.18	7.14			
	$1a_2 \rightarrow 3\tilde{d}a_1$	7.24				7.23	7.19			

Table S6 (continued)

Excitations		Vertical excitation energies, Ω						CCSD oscillator strengths		
		CCSD[a]	CC3[a]	CCSD[b]	CCSDR(3))[b]	CCSD[c]	CCSDR(3)[c]	f^a	f^b	f^c
	$3b_1(\pi_2) \rightarrow 8b_2(\sigma^*)$	6.37		6.37	6.33	6.31	6.28			
	$3b_1 \rightarrow 3pb_2$	7.32				7.14	7.11			
	$3b_1 \rightarrow 3db_2$	7.91				7.81	7.80			
$^1B_1$	$1a_2(\pi_3) \rightarrow 8b_2(\sigma^*)$	6.33	6.17	6.33	6.23	6.28	6.20	0.013	0.014	0.015
	$1a_2 \rightarrow 3pb_2$	6.94				6.85	6.81	0.024		0.022
	$1a_2 \rightarrow 3db_2$	7.63				7.60	7.55	< 0.001		<0.001
	$3b_1 \rightarrow 3sa_1$	6.53		6.53	6.49	6.40	6.36	< 0.001	< 0.001	0.002
	$3b_1 \rightarrow 3pa_1$	7.15				7.01	6.99	0.025		0.024
	$3b_1 \rightarrow 3da_1$	7.52				7.46	7.43	< 0.001		<0.001
	$3b_1 \rightarrow 3\tilde{d}\,a_1$	7.61				7.52	7.50	< 0.001		<0.001

[a] This work.

[b] Stenrup.[22]

[c] Pastore et al.[39]

Table S7

Vibrational coupling constants κ (eV/bohr), vibrational widths Δ (eV) and adiabatic energy lowering ΔE_{ad} (eV) of Rydberg and valence-type excitations of thiophene derived from the ADC(2) calculations with basis set B (the results for the lowest ionization transitions from Trofimov et al[96] are shown for comparison).

	Excitations	Totally symmetric vibrational modes								Δ	ΔE_{ad}
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8		
$^1A_1$	$1a_2 \to 3a_2$	-0.016	0.006	0.119	-0.057	0.045	0.020	0.031	-0.052	0.36	0.16
	$1a_2(\pi_3) \to 2a_2(\pi_5{}^*)$	0.012	0.008	0.031	-0.057	0.031	-0.069	-0.028	-0.012	0.25	0.08
	$1a_2 \to 4da_2$	-0.016	0.005	0.100	-0.062	0.047	0.016	0.031	-0.053	0.34	0.14
	$3b_1(\pi_2) \to 4b_1(\pi_4{}^*)$	0.034	0.004	0.051	-0.051	0.035	-0.088	-0.105	-0.005	0.38	0.20
	$3b_1 \to 3pb_1$	0.003	0.004	-0.069	-0.004	-0.018	-0.053	-0.027	0.042	0.24	0.08
	$3b_1 \to 3db_1$	0.006	0.003	0.021	-0.033	0.009	-0.059	-0.034	0.008	0.19	0.05
	$3b_1 \to 4pb_1$	-0.001	0.001	-0.066	-0.001	-0.018	-0.057	-0.034	0.037	0.24	0.08
	$3b_1 \to 4db_1$	-0.001	0.001	-0.077	-0.001	-0.018	-0.057	-0.033	0.040	0.26	0.09
$^1B_2$	$1a_2(\pi_3) \to 4b_1(\pi_4{}^*)$	0.018	0.005	0.180	-0.070	0.073	-0.008	-0.044	-0.094	0.55	0.38
	$1a_2 \to 3pb_1$	-0.012	0.006	0.122	-0.058	0.048	0.028	0.040	-0.051	0.38	0.17
	$1a_2 \to 3db_1$	-0.014	0.006	0.123	-0.062	0.054	0.023	0.037	-0.056	0.39	0.19
	$1a_2 \to 4pb_1$	-0.016	0.006	0.118	-0.060	0.048	0.021	0.034	-0.053	0.37	0.17
	$1a_2 \to 4db_1$	-0.004	0.010	0.030	-0.059	0.033	-0.055	0.020	-0.030	0.24	0.07
	$3b_1(\pi_2) \to 2a_2(\pi_5{}^*)$	0.013	0.019	-0.017	-0.059	0.011	-0.095	-0.035	-0.002	0.29	0.10
	$3b_1 \to 3da_2$	0.000	0.003	-0.070	-0.001	-0.024	-0.058	-0.035	0.043	0.26	0.09
	$3b_1 \to 4da_2$	-0.001	0.001	-0.078	0.000	-0.023	-0.058	-0.034	0.042	0.27	0.10

Table S7 (continued)

	Excitations	Totally symmetric vibrational modes								Δ	ΔE_{ad}
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8		
$^1A_2$	$1a_2 \rightarrow 3sa_1$	-0.025	0.001	0.120	-0.058	0.043	0.027	0.035	-0.051	0.37	0.17
	$1a_2 \rightarrow 3pa_1$	-0.010	0.006	0.064	-0.062	0.055	0.023	0.028	-0.059	0.30	0.12
	$1a_2 \rightarrow 3da_1$	-0.039	0.013	0.117	-0.078	0.034	0.025	-0.011	-0.053	0.38	0.17
	$1a_2 \rightarrow 3\tilde{d}\,a_1$	-0.022	-0.009	0.088	-0.051	0.052	0.021	0.030	-0.049	0.31	0.12
	$1a_2 \rightarrow 4sa_1$	-0.023	0.001	0.120	-0.059	0.049	0.023	0.033	-0.055	0.38	0.17
	$1a_2 \rightarrow 4pa_1$	-0.014	0.006	0.124	-0.063	0.049	0.023	0.027	-0.055	0.38	0.18
	$1a_2 \rightarrow 4da_1$	-0.021	-0.002	0.047	-0.055	0.049	0.011	-0.001	-0.050	0.24	0.08
	$1a_2 \rightarrow 4\tilde{d}\,a_1$	-0.028	0.008	0.112	-0.052	0.037	0.014	-0.010	-0.046	0.33	0.13
	$3b_1(\pi_2) \rightarrow 8b_2(\sigma^*)$	0.001	0.002	-0.047	0.049	0.013	-0.063	-0.092	-0.079	0.36	0.22
	$3b_1 \rightarrow 3pb_2$	-0.012	-0.013	-0.039	-0.004	-0.028	-0.054	-0.035	0.011	0.20	0.05
	$3b_1 \rightarrow 3db_2$	-0.001	0.008	0.031	-0.007	-0.004	-0.042	-0.006	0.001	0.13	0.02
	$3b_1 \rightarrow 4pb_2$	-0.008	0.002	0.058	-0.031	0.008	-0.021	0.011	-0.006	0.32	0.03
$^1B_1$	$1a_2(\pi_3) \rightarrow 8b_2(\sigma^*)$	-0.007	0.009	0.107	-0.034	0.074	0.010	0.007	-0.111	0.41	0.27
	$1a_2 \rightarrow 3pb_2$	-0.024	-0.016	0.103	-0.049	0.037	0.012	0.016	-0.092	0.37	0.20
	$1a_2 \rightarrow 3db_2$	-0.012	0.011	0.064	-0.047	0.062	0.013	0.003	-0.069	0.29	0.13
	$1a_2 \rightarrow 4pb_2$	-0.022	0.002	0.076	-0.057	0.043	0.021	0.025	-0.060	0.30	0.12
	$1a_2 \rightarrow 4db_2$	-0.018	0.011	0.037	-0.048	0.042	0.000	0.016	-0.037	0.20	0.06

Table S7 (continued)

	Excitations	Totally symmetric vibrational modes								Δ	ΔE_{ad}
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8		
	$3b_1 \rightarrow 3sa_1$	-0.008	-0.005	-0.066	0.001	-0.016	-0.049	-0.028	0.032	0.22	0.07
	$3b_1 \rightarrow 3pa_1$	0.003	0.003	-0.072	-0.008	-0.014	-0.050	-0.040	0.033	0.24	0.08
	$3b_1 \rightarrow 3da_1$	-0.021	0.004	-0.028	-0.018	-0.023	-0.052	-0.075	0.020	0.25	0.09
	$3b_1 \rightarrow 3\tilde{d}\,a_1$	-0.019	-0.002	-0.038	0.005	-0.023	-0.054	-0.030	0.045	0.21	0.07
	$3b_1 \rightarrow 4sa_1$	-0.007	-0.002	-0.004	-0.004	-0.006	-0.044	-0.031	0.013	0.13	0.03
	$3b_1 \rightarrow 4pa_1$	0.001	0.002	-0.010	-0.004	-0.021	-0.052	-0.044	0.028	0.18	0.05
	$3b_1 \rightarrow 4da_1$	0.016	-0.020	0.034	0.015	-0.011	-0.060	-0.057	0.042	0.24	0.09
	$3b_1 \rightarrow 4\tilde{d}\,a_1$	-0.016	0.007	-0.059	-0.005	-0.030	-0.057	-0.044	0.044	0.26	0.09
$^2A_2$	$(1a_2)^{-1}$	-0.006	0.008	0.155	-0.077	0.054	0.016	0.026	-0.053	0.45	0.23
$^2B_1$	$(3b_1)^{-1}$	-0.043	0.004	-0.071	0.027	-0.015	-0.067	-0.073	0.042	0.33	0.14