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Supplementary Information

Analysis of the vibronic structure of *trans*-Stilbene fluorescence and excitation spectra: the S_0 and S_1 P E S along the C_e=C_e and C_e-C_{ph} torsions

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S1. $\Phi_0(\tau,\phi)$ *and* $\Phi_1(\tau,\phi)$ *vibrational eigenfunctions*

A $\Phi_k(\tau,\phi)$ eigenfunction can be expressed as a product of $b_i(\tau)$ and $c_j(\phi)$ functions associated with i and j quanta, namely

$$\Phi_k(\tau,\phi)= \mu_i(\tau) \cdot \nu_j(\phi)= \Lambda_{i,j}(\tau,\phi) \qquad \text{(eq. S1)}$$

The i and j quantum numbers give the number of nodes of $\Lambda_{i,j}$ functions along τ and ϕ coordinates, respectively.

Eigenfunctions and eigenvalues were computed by Meyer numerical procedure[34]. We didn't consider the total angular momentum as this is not giving any additional information on the internal vibrational degrees of freedom that we study here.

We checked the stability of solutions by changing the number of grid points and the angular amplitude. Furthermore, since the vibrational eigenstates of S_0 can be represented as a product of excitations along the τ and ϕ (normal) coordinates, get

$$\Lambda^0_{i,j}(\tau,\phi) = \mu_i(\tau) \cdot \nu_j(\phi)$$

In the same way, the eigenstates of S_1 can be written as

$$\Lambda^1_{i,j}(\tau', \phi') = \mu'_i(\tau') \cdot \nu'_j(\phi') \qquad \text{(eq. S2)}$$

where τ' and ϕ' are the S_1 normal coordinates, which are linear combinations of τ and ϕ S_0 normal coordinates. Thus, a Duschinsky effect[40] is expected for these modes in the S_0 - S_1 transition.

While in S_0 the lower frequency (9 cm^{-1}) mode is based essentially on the (a_u) C_e-C_{ph} torsion and the 59 cm^{-1} mode is based mainly on the a_u C_e=C_e torsion, in S_1 the two lowest frequencies a_u modes, 35 cm^{-1} and 47 cm^{-1}, correspond *qualitatively* to the C_e-C_e and C_e-C_{ph} torsions, respectively. This effect results from the C_e-C_e and C_e-C_{ph} bond orders inversion induced by the S_0-S_1 excitation.

By computing the overlap matrix between the S_0 and S_1 vibrational wavefunctions, we obtain *the S_0-S_1 FC matrix*, which provides the intensity distribution *of the vibronic structure* of fluorescence (along FC matrix lines) and of absorption spectra (along FC matrix columns). The S_0-S_1 FC factors are reported in **Table S4** and in **Table 4** for the a_g (even quantum numbers) and the a_u (odd quantum numbers) wave functions, respectively. They will be used to analyze the vibrational structure of S_0 → S_1 excitation and of the SVL S_1 → S_0 fluorescence spectra that originate from specific S_0 or S_1 vibrational levels (vide infra).

S2. *Assignment of fluorescence excitation spectra from other low vibrational levels of* S_0

Stilbene molecules in *very* cold solutions are *predominantly* in the $36_0\ 37_0$ vibronic level of S_0, and, to a *much lower extent*, in a few low energy $36_i\ 37_j$ vibrational states. Thus, only the $36_0\ 37_1$, $36_0\ 37_2$, $36_0\ 37_3$ and $36_1\ 37_0$ vibrational states may be populated enough at temperatures T ≤ 50K. The fluorescence excitation spectra of Stilbene cold solutions were measured by a number of authors[17-21] and were found to be essentially a super-position of excitation spectra originating from the S_0, $36_0 37_0$ ground level and, with much lower intensity, from the slightly higher S_0, $36_j 37_i$ vibrational levels quoted above. In **Table S5** we show the S_1 vibrational bands energies reported by Zewail[17], Laane[20] and Zwier[19] groups in the 0 - 400 cm^{-1} energy region. Also Tanaka et al.[21] measured stilbene excitation spectra in a low temperature matrix and showed a well structured spectrum, but without giving band intensities. Most vibrational bands are assigned to specific $S_1\ 36^m\ 37^n$ vibrational levels, as shown in **Table S5**. The different temperatures chosen by the above authors[17-21] are reflected in different relative vibrational bands intensities. In conclusion, the presently computed band energies and intensities correlate rather well with most observed features of excitation spectra.

S3. *Fluorescence spectra emitted by the* $S_1(36^0 37^4)$ *vibrations level.*

In **Table 9** we report also the fluorescence spectrum emitted by the $S_1\ 36^0\ 37^4$ vibrational level. The prominent bands are observed at 20, 66 (the strongest), 109, 119 cm^{-1} and in the 147-152 cm^{-1} wavenumbers region[17]. We attribute these bands to the $36^0_0\ 37^4_2$, $36^0_1\ 37^4_1$, $36^0_1\ 37^4_5$, $36^0_0\ 37^4_{10}$ and $36^0_1\ 37^4_7$ vibronic transitions, respectively. The two intense bands at about 147 and 152 cm^{-1} are associated with large FC factors. Also the band at 119 cm^{-1} ($36^0_1\ 37^4_5$) shows an appreciable intensity, in agreement with a relatively large FC factor. In summary, the most intense fluorescence bands emitted by the $36^0\ 37^4$ level are described correctly by this model.

S4. *Fluorescence spectra emitted by odd parity* S_1 *vibrational levels.*

We also consider the fluorescence spectra of $36^1\ 37^0$ and $36^0\ 37^1$ odd vibrational levels of S_1, which were observed by Zewail[17] and Ito[18].

The fluorescence spectrum of the 36^1 37^0 level is summarized in **Table S6**. The strongest band is observed at 49 cm^{-1} below the origin and corresponding to the 36^1_1 37^0_0 transition. It is associated to a large (0.52) FC factor, and it accounts for about half of the total intensity of this fluorescence spectrum. Other prominent bands are the false origin 36^1_0 37^0_1 and the bands at 23, 67 and 115 cm^{-1}, which we assign to the 36^1_0 37^0_3, 36^1_1 37^0_2 and 36^1_2 37^0_1 transitions, respectively. The computed S_0-S_1 Franck-Condon factors shown in Table 15 represent rather accurately the observed intensity distribution of the S_1 36^1_i 37^0_j fluorescence spectrum.

Table S7 summarizes the computed fluorescence spectrum emitted by the $S_1(36^0\ 37^1)$ level and compares it with observed spectra[17, 18]. It is shown that the largest FC factor (0.32) is associated with the origin band (36^0_0 37^1_1)[17, 18], but large FC factors are associated also with the 36^0_0 37^1_3 (22 cm^{-1}) and with the two quasi-degenerate 36^0_1 37^1_0 (49 cm^{-1}) and 36^0_0 37^1_5 (51 cm^{-1}) transitions. The measured[17, 18] fluorescence spectrum shows intense bands for the origin and the vibrational bands at 23, 49, 51 and 67 cm^{-1} above the origin, and thus it agrees nicely with the computed FC factors, as shown in **Table S7**. Furthermore, we tentatively assign the weak bands observed at 115, 140/138 and 165/168 cm^{-1} to the 48^0_2, 48^0_2 37^1_3 and 48^0_2 37^1_5 transitions.

In summary, the computed FC factors appears to mimic correctly the intensity distribution of the fluorescence spectrum[17, 18] emitted by the $S_1(36^0\ 37^1)$ vibronic level.

S5. *Tables*

Table S1. Lowest computed and observed S_0 harmonic vibrational frequencies (cm^{-1}) of a_u and b_g torsional modes of *t*SB.

Symm Species	Main Coord	BLYP (a)	; (b)	B3LYP Ref(c)	Anharm. Refs(d)	Observed Frequencies	
a_u							
ν_{35}	flap/ring def.	281	278	283	-	286^a	306
ν_{36}	$(C_e{=}C_e)_{tor}$	58	59	56	-	57^e	60
ν_{37}	$(C_e\text{-}C_{ph})_{tor}$	11	14	5	8	$8^{e,d}$	8^f
b_g							
ν_{47}	$(C_e{=}C_e)_{tor}$	220	213	227	-	227^a	228^g
ν_{48}	$(C_e\text{-}C_{ph})_{tor}$	82	62	86	53	59^f	60^g

a) H. Watanabe, Y. Okamoto, K. Furuya, A. Sakamoto and M. Tasumi, J. Phys. Chem. A106, 3318 (2002); b) F. Negri and G. Orlandi, J. Raman Spectrosc. 29, 501(1998); c) K. Tsumura, K. Furuya, A. Sakamoto and M. Tasumi, J. Raman Spectrosc. 39, 1584 (2008); d) W.-Y. Chiang and J. Laane, J. Chem. Phys. 100, 8755 (1994); e) L.H. Spangler, R. Zee, T.S. Zwier, J. Phys. Chem. **91**, 2782 (1987); f) T. Suzuki, N. Mikami and M. Ito, J. Phys. Chem. 90, 6431 (1986); g) T. Egawa, K. Shinashi, T. Ueda, E. J. Ocola, W.-Y. Chiang, and J. Laane, J. Phys. Chem.A, *118,* 1103 (2014).

Table S2. Lowest computed and observed S_1 harmonic vibrational frequencies (cm^{-1}) of a_u and b_g torsional modes of *t*SB.

		Computed frequencies			Observed frequencies		
Sym Type	Main Coord	TD-DFT[a]	CIS[b]	CAS[c]	d	a	e
a_u							
ν_{35}	flap/ring def.	188	210	248	276	-	-
ν_{36}	$(C_e{=}C_e)_{tor}$	50	48	54	46	48	47.5
ν_{37}	$(C_e\text{-}C_{ph})_{tor}$	24	19	50	34	35	35
b_g							
ν_{47}	$(C_e{=}C_e)_{tor}$	236	274	301	248	248	200
ν_{48}	$(C_e\text{-}C_{ph})_{tor}$	102	118	129	114	114	110

a) K. Tsumura, K. Furuya, A. Sakamoto, M. Tasumi, J. Raman Spectrosc. 39, 1584 (2008); b) H.Watanabe, Y. Okamoto, K. Furuya, A. Sakamoto and M. Tasumi, J. Phys Chem. A 106, 3318 (2002); c) L. Gagliardi, G. Orlandi, V. Molina, P.-A. Malmqvist, B. Roos, J. Phys. Chem. A 101, 3478 (1997); d) T. Urano, H. Hamaguchi, M. Tasumi, K. Yamanouchi, S. Tsuchiya, T. L. Gustafson, J. Chem. Phys. 91, 3884(1989); e) W.-Y. Chiang and J. Laane, J. Chem. Phys. 100, 8755 (1994).

Table S3. Franck-Condon factors for a_g torsion/twist vibrational eigenstates of S_0 and S_1.[a,b,c,d]

S_0/S_1	**0.0**[a] $36^0 37^0$	**70**[a] **(70)** $36^2 37^0$	**83**[a] **(83)** $36^1 37^1$	**95**[a] **(95)** $36^0 37^2$	**139**[a] (-)[d] $36^4 37^0$	**152**[a] **(153)** $36^3 37^1$	**165**[a] **(166)** $36^2 37^2$	**178**[a] **(179)** $36^1 37^3$	**191**[a] **(191)** $36^0 37^4$	**234**[a] (-)[d] $36^4 37^2$
0[a] $36_0 37_0$	**0.72**	0.00	**0.11**	**0.08**	0.00	0.00	0.01	0.04	0.01	0.00
20[a] **(19)** $36_0 37_2$	**0.19**	0.03	0.04	*0.07*	0.00	0.01	*0.06*	**0.13**	*0.06*	0.00
46[a] **(45)** $36_0 37_4$	*0.05*	0.03	**0.12**	**0.16**	0.00	0.00	0.00	0.03	0.01	0.01
66[a] **(67)** $36_1 37_1$	0.00	**0.18**	**0.10**	**0.14**	0.00	*0.06*	**0.14**	0.01	**0.09**	0.01
76[a] **(76)** $36_0 37_6$	0.01	0.02	**0.08**	**0.12**	0.00	0.02	0.02	0.02	0.01	0.00
90[a] **(92)** $36_1 37_3$	0.00	**0.12**	*0.06*	**0.13**	0.03	0.01	0.00	0.01	0.00	0.04
108[a]**(108)** $36_0 37_8$	0.00	0.00	0.03	*0.06*	0.00	0.02	*0.05*	*0.07*	*0.06*	0.00
118[a]**(118)** $36_1 37_5$	0.00	**0.14**	0.00	0.03	0.04	0.01	*0.05*	0.01	**0.08**	0.00
119[a]**(118)** $36_2 37_0$	0.01	**0.24**	**0.21**	**0.10**	0.00	**0.23**	0.01	0.01	0.01	*0.06*
138[a]**(139)** $36_2 37_2$	0.00	*0.06*	**0.10**	0.01	**0.09**	0.01	0.01	0.02	0.02	**0.08**
142[a]**(145)** $36_0 37_{10}$	0.00	0.00	0.01	0.03	0.00	0.00	0.02	**0.08**	**0.09**	0.01
152[a] **(-)**[d] $36_1 37_7$	0.00	0.01	0.02	0.02	0.00	0.03	*0.06*	0.01	**0.09**	0.02
161[a] **(-)**[d] $36_2 37_4$	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.02	0.03	0.00

a) First column and first row: computed energies (cm^{-1}) of vibrational states approximated to the nearest integer and, in brackets, the observed energies (from Tabs. 2 and 3); b) *lines* (columns) display *excitation* (emission) band intensities; c) in *bold*, Franck-Condon factors (FC) ≥0.09, in *italic,* 0.05<FC< 0.09; d) bands not observed.

Table S4. Franck-Condon factors between a_u torsion/twist eigenstates of S_0 and S_1[a,b].

S_0 \ S_1	**35 (35)** $36^1 37^0$	**47 (48)** $36^0 37^1$	**105 (104)** 36^3	**118 (118)** $36^2 37^1$	**130 (131)** $36^1 37^2$	**143 (143)** $36^0 37^3$	**173 (-)[d]** $36^5 37^0$	**187 (186)** $36^4 37^1$	**200 (200)** $36^3 37^2$	**213 (213)** $36^2 37^3$
9 (9) $36_0 37_1$	**0.13**	**0.32**	*0.06*	0.03	**0.17**	**0.10**	0.00	0.00	0.00	0.05
32 (31) $36_0 37_3$	**0.09**	**0.23**	0.01	0.01	0.00	0.00	0.00	0.00	0.02	0.05
58 (58) $36_1 37_1$	**0.51**	**0.17**	0.00	**0.15**	0.00	0.07	0.00	0.00	0.03	0.01
60 (60) $36_0 37_5$	0.03	**0.11**	0.01	*0.05*	*0.07*	*0.06*	0.00	0.00	0.00	0.03
78 (76) $36_1 37_2$	**0.12**	*0.07*	*0.07*	0.03	0.01	0.04	0.00	0.02	**0.09**	**0.05**
91 (91) $36_0 37_7$	0.01	0.04	0.01	0.04	**0.09**	**0.10**	0.00	0.01	0.01	0.00
104(103) $36_1 37_4$	0.02	0.02	*0.07*	**0.09**	0.01	**0.11**	0.01	0.00	0.01	0.01
125(126) $36_0 37_9$	0.00	0.01	0.00	0.02	*0.06*	**0.08**	0.00	0.01	0.02	0.03
128(126) $36_2 37_1$	0.01	0.00	**0.18**	0.03	**0.09**	*0.07*	0.01	**0.09**	*0.07*	0.07
134(133) $36_1 37_6$	0.01	0.01	0.03	*0.06*	0.01	**0.09**	0.02	0.04	0.03	0.01
151(150) $36_2 37_3$	0.01	0.00	**0.10**	0.00	**0.11**	*0.05*	*0.05*	0.00	0.00	0.02
179 (-)[d] $36_2 37_5$	0.03	0.01	**0.19**	**0.10**	*0.06*	0.04	0.01	**0.14**	*0.07*	0.00

a) First column and first row: S_0 and S_1 computed energies (cm^{-1}) of vibrational states, and, in brackets, the observed energies from Tabs. S2 and 1; b) *lines* (columns) display *excitation* (emission) band intensities; c) in *bold*, Franck-Condon factors (FC) ≥0.09, in *italic,* 0.05<FC< 0.09); d) bands not observed.

Table S5. Observed Stilbene vibrational levels in $S_0 \rightarrow S_1$ excitation spectra.

Zewail[1]		Laane[2] 1992		Assignment[1-3,4]	Zwier[3]	
cm^{-1}	Int	cm^{-1}	Int		cm^{-1}	Int
0.0	100	0	100	origin	0.0	100
26.2	2	26	22	$37_1^0\,36_0^1$	26.8	h
38.6	3	39	31	37_1^1	38.7	h
-		70	18	36_0^2	69.6	0.7
83.2	25	83	67	$37_0^1\,36_0^1$	83.6	12
95.1	26	95	77	37_0^2; $37_1^0\,36_0^3$	95.3	15
-		110	6	$37_1^1\,36_0^2$	108.8	h
121.9	2.3	122	26	$37_1^2\,36_0^1$	121.5	h
134.2	2.3	134	26	37_1^3	134.0	h
-		153	10	$37_0^1\,36_0^3$	152.0	0.3
166.0	2.4	166	19	$37_0^2\,36_0^2$	165.5	0.7
178.7	13.2	179	61	$37_0^3\,36_0^1$	178.5	4.2
191.2	9.5	191	45	37_0^4	191.0	2.0
197.6	79	198	100	25_0^1	197.8	63
218.5	1.2	219	19	$37_1^4\,36_0^1$	217	h
224.6	10.5	224	57	$25_0^1\,37_1^0\,36_0^1$	223	h
228.6	6.1	228.1	31	$37_0^2\,36_0^4$	227	1.6
236.7	4.0	236	39	$25_0^1\,37_1^1$	236.0	h
246.4[4]	2.2	247[4]	16	$37_0^3\,36_0^3$; 48_0^2	245[4]	0.5
262.7	2.3	264	24	$37_0^4\,36_0^2$	262	0.6
274.8	4.8	275	39	$37_0^5\,36_0^1$	275	1.5
280.3	30	280	88	$25_0^1\,37_0^1\,36_0^1$	280	9.0
292.4	25	293	85	$25_0^1\,37_0^2$	292	7.4
-		305	20	$25_0^1\,37_0^1\,36_0^2$	305	h
-		315[5]	13	$36_0^2\,48_0^2$	313	0.2
319.5	2.8	320	42	$25_0^1\,37_0^2\,36_1^1$	318	h

1) Table 2 of J. A. Syage, P. M. Felker and A. H. Zewail, J. Chem. Phys. 81, 4685 (1984); 2) Table 3 of W.-Y Chiang and J. Laane, J. Chem. Phys. 100, 8755 (1994); 3) Table 1 of L. H. Spangler, R. van Zee and T. S. Zwier, J. Phys. Chem. 91, 2782 (1987), where h indicates hot bands; 4) Table 1 of this work; 5) a contribute to the 247 and 315 cm^{-1} bands may come from the 48_0^2 band.

Table S6. Fluorescence spectra from the $S_1(36^{1}37^{0})$ vibronic level.

Computed[a]			Observed[b]	
Vibronic transitions	E(cm^{-1})	FC factor	E(cm^{-1})	Int
$36^{1}_{0}\,37^{0}_{1}$	0	0.13	0	24
$36^{1}_{0}\,37^{0}_{3}$	22	0.09	23	18
$36^{1}_{1}\,37^{0}_{0}$	49	0.52	49	100
$36^{1}_{0}\,37^{0}_{5}$	51	0.03		
$36^{1}_{1}\,37^{0}_{2}$	67	0.13	67	25
$36^{1}_{0}\,37^{0}_{7}$	82	0.01	82	7
$36^{1}_{1}\,37^{0}_{4}$	94	0.02	*92*	*5*
$36^{1}_{0}\,37^{0}_{1}\,48^{0}_{2}$	117	0.01		
$36^{1}_{2}\,37^{0}_{1}$	117	0.01	115	11
$36^{1}_{1}\,37^{0}_{6}$	124	0.01	--	--
$36^{1}_{2}\,37^{0}_{3}$	141	0.01	140	15
$36^{1}_{2}\,37^{0}_{5}$	170	0.03	168	12

a) from Table S4 of this work; b) from Fig. 16 of J. A. Syage, P. M. Felker and A. H. Zewail, J. Chem. Phys. 81, 4685 (1984); b) relative intensities.

Table S7. Fluorescence spectrum from the $S_1(36^0\ 37^1)$ vibronic level.

Computed spectrum[a]			Observed spectrum			
Vibronic levels	E(cm^{-1})	FC·100	SFZ[b]		SMI[c]	
			E(cm^{-1})	Int[d]	E(cm^{-1})	Int[d]
$36^0_0\ 37^1_1$	0	32	0	100	0	100
$36^0_0\ 37^1_3$	22	23	23	78	22	81
$36^0_1\ 37^1_0$	49	17				
$36^0_0\ 37^1_5$	51	11	49	82	49	65
$36^0_1\ 37^1_2$	67	7	67	11	66	17
$36^0_0\ 37^1_7$	82	4	82	7	81	12
$36^0_1\ 37^1_4$	94	2	*92*	*5*	92	7
$36^0_0\ 37^1_9$	117	1	115	11	115	9
$36^0_2\ 37^1_1$		0				
$48^0_2\ 37^1_1$		2				
$36^0_1\ 37^1_6$	124	1	--	--	--	--
$36^0_2\ 37^1_3$	141	1	140	15	138	15
$48^0_2\ 37^1_3$	140	2				
$36^0_2\ 37^1_5$	170	1	168	1 2	165	8
$48^0_2\ 37^1_5$		1				

a) This work, Table S4; b) from Fig. 16 of J.A. Syage, P. M. Felker and A. H. Zewail, J. Chem. Phys. 81, 4685 (1984); c) from Fig. 8 of T. Suzuki, N. Mikami and M. Ito, J. Phys. Chem. 90, 6431 (1986); d) relative intensities.

S6. *References*

[46] F. Duschinsky, Acta Physicochim. USSR 7, 551 (1937).