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Photophysical Properties of Photosensitizers and Quenchers

Addendum to http://murov.info/photophys.htm – Selected pages from the Thesis of Steven Murov. Some of the data has not been published elsewhere except in thesis form.

THE UNIVERSITY OF CHICAGO

THE PHOTOCHEMISTRY OF AROMATIC KETONES

A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF
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DEPARTMENT OF CHEMISTRY

BY
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I wish to express my deepest gratitude to Professors N. C. Yang and D. S. McClure for the patience, interest and insight with which they directed this research.

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TABLE 6

PHOSPHORESCENCE EMISSION DATA

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec)	Vib. Sp.(cm^{-1})	em. ø
1	1	benzophenone	EPA	4130	.0060	1630	.84
2	IM	benzophenone	MC	4166	.0050	1640	.60
3	IEIP	benzophenone	EIP	4137		1630	
4	IEIP	benzophenone	EIP			(slow sector speed)	
5	IA	benzophenone	AE	4125		1610	
6	ID_{10}	benzophenone-d_{10}	EPA	4123	.0058	1585	
7	$ID_{10}M$	benzophenone-d_{10}	MC	4162	.0053	1600	
8	2M	acetophenone	EPA	3860	.004, .03	1640	.74
9	2M	acetophenone	MC	3880	.0027	1695	.22
10	$2M_pD$	acetophenone	$_p$DMC	3885	.0027	1700	
11	2EIP	acetophenone	EIP	3868		1630	
12	2EIP	acetophenone	EIP			(slow sector speed)	
13	2EM	acetophenone	EM	3870		1640	
14	$2D_5$	acetophenone-d_5	EPA		.004, .03		.78
15	$2D_5$	acetophenone-d_5	EPA			(slow sector speed)	
16	$2D_5$	acetophenone-d_5	MC	3884	.0020	1730	
17	3	acetophenone-α-d_3	EPA	3865		1680	.70
18	4	4-methylacetophenone	EPA	3925	.084	1670	.61
19	4	4-methylacetophenone	EPA			(slow sector speed)	
20	4M	4-methylacetophenone	MC	3920	.027	1660	

TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp.(cm^{-1})	em.ø
21	5	3-methylacetophenone	EPA	3940	.074	Inac.	.64
22	5M	3-methylacetophenone	MC	3910	.023	Inac.	
23	5A	3-methylacetophenone	AE	3950		Inac.	
	6	2-methylacetophenone	EPA				<.02
24	7	3,4-dimethylacetophenone	EPA	3995	.167	dif.	.56
25	7	3,4-dimethylacetophenone	EPA			(slow sector speed)	
26	7M	3,4-dimethylacetophenone	MC	3960	.060	dif.	
27	8	3,5-dimethylacetophenone	EPA	4010	.11	dif.	.51
28	8M	3,5-dimethylacetophenone	MC	4003	.053	1630	
	9	2,4-dimethylacetophenone	EPA				<.02
	10	2,5-dimethylacetophenone	EPA				<.02
29	11	3,4,5-trimethylacetophenone	EPA	4060	.195	dif.	.46
30	11M	3,4,5-trimethylacetophenone	MC	4030	.139	dif.	
	12	2,4,5-trimethylacetophenone	EPA				<.02
31	13	2,4,6-trimethylacetophenone	EPA	39[illegible]0	.039	dif.	.34
32	13M	2,4,6-trimethylacetophenone	MC	3980	.024	dif.	
33	14	4-methoxyacetophenone	EPA	4000	.26	dif.	.68
34	14M	4-methoxyacetophenone	MC	3980	.35	dif.	

TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp.(cm^{-1})	em.ø
35	15	3-methoxyacetophenone	EPA	3950	.25	dif.	.35
36	15M	3-methoxyacetophenone	MC	3950	.25	f.s.	
37	16	4-trifluoromethylacetophenone	EPA	3970	.00074	Inac.	.29
38	16M	4-trifluoromethylacetophenone	MC	3985	.00070	1710	
39	17	3-trifluoromethylacetophenone	EPA	3900	.0012	Inac.	.32
40	17M	3-trifluoromethylacetophenone	MC	3936	.00098	1710	
41	18	3,4-methylenedioxyacetophenone	EPA	4340	.37	dif.	.30
42	18M	3,4-methylenedioxyacetophenone	MC	4224	.18	dif.	
43	19	2-acetylnaphthalene	EPA	4810	.95	f.s.	.050
44	19M	2-acetylnaphthalene	MC	4810	.82	f.s.	
45	$19D_3$	2-acetylnaphthalene-α-d_3	EPA	4810	1.71	f.s.	.078
46	$19D_7$	2-acetylnaphthalene-d_7	EPA	4795	1.58	f.s.	.079
47	22	o-benzylbenzophenone	EPA	4090	.0037	1625	.29
48	22M	o-benzylbenzophenone	MC	4135		1640	
	22HD	o-benzylbenzophenone-d	EPA		.0032		
49	23	2,4-dimethylbenzophenone	EPA	4110	.0032	1620	.54

TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp.(cm^{-1})	em.Ø
50	23M	2,4-dimethylbenzophenone	MC	4140	.0032	1650	
51	24	2,5-dimethylbenzophenone	EPA	4120	.0040	1640	.54
52	24M	2,5-dimethylbenzophenone	MC	4153	.0033	.650	
53	25	4-methylbenzophenone	EPA	4130	.0061	1630	
54	25M	4-methylbenzophenone	MC	4164	.0053	1650	
55	26	4,4'-dimethylbenzophenone	EPA	4120	.0064	1630	.86
56	26M	4,4'-dimethylbenzophenone	MC	4152	.0056	1670	
57	27	3,4-dimethylbenzophenone	EPA	4140	.0077	1630	
58	27M	3,4-dimethylbenzophenone	MC	4171	.0057	1640	
59	28	benzpinacolone	EPA	3990	.0071	1700	.63
60	28M	benzpinacolone	MC	4040	.0038	Inac.	
61	29	2-benzoylnaphthalene	EPA	4810	1.16	1560	.38
62	29M	2-benzoylnaphthalene	MC	4795	1.12	1590	
63	30	2-(O-toluoyl)naphthalene	EPA	4820	1.22	1610	.32
64	3M	2-(o-toluoyl)naphthalene	MC	4803	1.12	1590	

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TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp.(cm^{-1})	em.Ø
65	31	valerophenone	EPA	3835		1660	.77
66	31M	valerophenone	MC	3846		1680	
67	32	1-phenyl-5-methyl-5-hexene-1-one	EPA	3850		1640	.24
68	32M	1-phenyl-5-methyl-5-hexene-1-one	MC	3850		1640	
69	33	propiophenone	EPA	3830	.070,.021	1650	.70
70	33	propiophenone	EPA				
71	33	propiophenone	EPA			(slow sector speed)	
72	33M	propiophenone	MC	3836	.005,.11	1730	
73	33MS	propiophenone	MC			(slow sector speed)	
74	$33D_5M$	propiophenone-d_5	EPA	3819		1680	.76
75	$33D_5$	propiophenone-d_5	MC	3829		1720	
76	34	-phenylpropiophenone	EPA	3838		1710	.76
77	35	allylacetophenone	EPA	3840		1710	.067
78	35M	allylacetophenone	MC	3840		Inac.	
79	42	-phenylbutryophenone	EPA	3840		1650	.85
80	42M	-phenylbutryophenone	MC	3848		1690	
81	46	benzaldehyde	EPA	3995	.0023	1610	.56
82	46M	benzaldehyde	MC	3967	.0015	1680	
83	46EIP	benzaldehyde	EIP	4010			
84	47	4-methylbenzaldehyde	EPA	4013	.043	1610	
85	47M	4-methylbenzaldehyde	MC	3973	.019	1660	

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TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp.(cm^{-1})	em.Ø
86	48	4-methoxybenzaldehyde	EPA	4030	.15	dif.	
87	48M	4-methoxybenzaldehyde	MC	3980	.094	f.s.	
88	49	4-phenylacetophenone	EPA	4700	.25	dif.	
89	49M	4-phenylacetophenone	MC	4680		dif.	
90	50	1-indanone	EPA	3768	.0022,.23	1700	.56
91	50	1-indanone	EPA	(slow sector speed)		1650	
92	50	1-indanone-10^{-2}M	EPA				
93	50	1-indanone-10^{-3}M	EPA				
94	50	1-indanone-10^{-4}M	EPA				
95	50P	1-indanone	EPA+piperylene				
96	50	1-indanone	EPA	excitation		= 3400Å	
97	50	1-indanone	EPA	excitation		= 2500Å	
98	50	1-indanone	EPA	excitation spectrum			
99	50	1-indanone	EPA	excitation spectrum at slow sector speed			
100	50M	1-indanone	MC	3813	.0015,.16	1730	
101	50M	1-indanone	MC	(slow sector speed)			
102	50EIP	1-indanone	EIP	3770		1710	
103	50EM	1-indanone	EM	3780		1690	
104	$50D_2$	1-indanone-α-d_2	EPA	3769		1710	
105	$50D_4$	1-indanone-d_4	EPA	3765		1700	
106	$50D_6$	1-indanone-d_6	EPA	3771	.0028, .29	1700	.66
107	$50D_6M$	1-indanone-d_6	MC	(slow sector speed)			

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TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp. (cm^{-1})	em.Ø
108	$50D_6M$	1-indanone-d_6	MC	3813		1730	
109	51	1-tetralone	EPA	3931	.0076	1670	
110	51M	1-tetralone	MC	3956	.0031	1680	
111	52	naphthalene	EPA	4689	2.6[a]	f.s.	
112	52M	naphthalene	MC	4695		f.s.	
113	53	benzene	EPA	3390	7.0[a]	f.s.	
114	53M	benzene	MC	3390		f.s.	
115	54	toluene	EPA	3450	8.8[a]	f.s.	
116	55	durene	EPA	3570		f.s.	
117	56	anisole	EPA	3540	3.0[a]	dif.	
118	56M	anisole	MC	3540		dif.	
119	57	benzoic acid	EPA	3660	2.5[a]	f.s.	
120	58	4-methylbenzoic acid	EPA	3720		f.s.	
121	59	4-bromoacetophenone	EPA	4000	.0066	dif.	
122	59M	4-bromoacetophenone	MC	4020		dif.	
123	60	3-bromoacetophenone	EPA	3930	.0054	Inac.	
124	60D	3-bromoacetophenone	MC	3940		Inac.	
125	61	2-naphthaldehyde	EPA	4820	.37	f.s.	.035
126	61EIP	2-naphthaldehyde	EIP	4820	.25	f.s.	

TABLE 6--Continued

Spectra No.	Compound No.	Compound	Solvent	0-0 (Å)	τ (sec.)	Vib. Sp. (cm^{-1})	em.Ø
127	62	2-naphthaldehyde-d	EPA	4830	1.35	f.s.	.17
128	62EIP	2-naphthaldehyde-d	EIP	4828	.8	f.s.	
	63	1-acetylnaphthalene	EPA	5064	.13	f.s.	

d.f. diffuse structure
f.s. fine structure
Inac. inaccurate
EPA 5:5:2 ether:isopentane:ethanol
MC methylcyclohexane
EIP 1:1 ether:isopentane
EM 4:1 ethanol:methanol
AE 1:1 trifluoroacetic acid:ether
pDMC perdeuteromethylcyclohexane

[a]D. S. McClure, J. Chem. Phys., 17, 905 (1949).

There are other methods for locating the position of the ^3L_a states of compounds. The ^1L_a and ^3L_a states might be expected to have similar energy shifts upon substitution if we neglect the contribution from the charge transfer state. In other words, the changes induced by inductive and conjugative effects for the two states might be proportional. Once this proportionality factor has been obtained, the energy of the ^3L_a of a molecule may be predicted from a knowledge of the energy of its ^1L_a state. If such a proportionality exists, a plot of the $\Delta\nu$'s from benzene for the ^1L_a states of substituted benzenes versus the corresponding $\Delta\nu$'s for the ^3L_a states will yield a straight line with the proportionality constant as the slope of the line. We have made such a plot (see Figure 1). The 0-0 band of the ^3L_a state of benzene was taken as 29,500 cm^{-1} and the ^1L_a reference of benzene was taken from Petruska as 47,600 cm^{-1}.[73] Table 5 includes a compilation of the $\Delta\nu$'s of the two

[a]J. Petruska, J. Chem. Phys., 34, 1126 (1961).

[b]H. Sponer and Y. Kanda, ibid., 40, 778 (1964).

[c]D. Kearns, ibid., 36, 1608 (1962).

[d]D. S. McClure, ibid., 17, 905 (1949).

[e]D. F. Evans, J. Chem. Soc., 2753 (1959).

[f]R. A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, John Wiley and Sons, New York, 1951.

[g]D. W. Olds, J. Chem. Phys., 35, 2248 (1961).

[h]K. Takei and Y. Kanda, Spectro. Acta, 18, 1201 (1962).

[i]Y. Kanda, R. Shimada, and Y. Kakenoshita, ibid., 19, 1249 (1963).

[j]V. L. Ermolaev, Uspekhi Fiz. Nauk, 80, 333 (1963).

[k]API Research Project 44, Ultraviolet Spectral Data.

states. The values for the ^1L_a states used are those from Petruska.[73] He took the wavelength at which $\epsilon = 3160$ on the low energy side of the band as the position of the band. For the triplet states one can usually observe the 0-0 band and this was taken as the triplet state energy. A reasonably straight line was obtained (see Figure 1) with a slope of 0.5. Thus the ^3L_a state of a phenyl carbonyl compound should be shifted from the ^3L_a state of benzene one-half as much as its ^1L_a state is shifted from the ^1L_a state of benzene.

The predicted and experimental values for the ^3L_a states for several acetophenones, benzaldehydes, and 1-indanone are included in Table 5. There is an average difference of 440 cm^{-1}

between the two sets of data and an average difference of 375 cm^{-1} if the two trifluoromethyl acetophenones are not included on the basis that they both have low-lying n,π^* triplets. The data indicate that the crossover from a n,π^* to a ^3L_a low-lying triplet state must lie very near to acetophenone. In other words, acetophenone may have a low-lying n,π^* triplet but will have a ^3L_a state only slightly above it and the substitution of a methyl may reverse the two states.

In summary, the two methods used predict that substitution of an electron donating group in acetophenone may be sufficient to make the lowest triplet state π,π^* in character. For electron withdrawing groups, the predictions show that the ^3L_a state is above the n,π^* triplet state.

The text to the left, Table 5 and the graph that follow describe an attempt to predict the triplet energy level (^3L_a) from an estimate of the energy level of the ^1L_a determined from absorption spectroscopy. Included are the triplet energy levels of many benzene derivatives. The graph that results indicates a fair correlation between the energies of the two states.

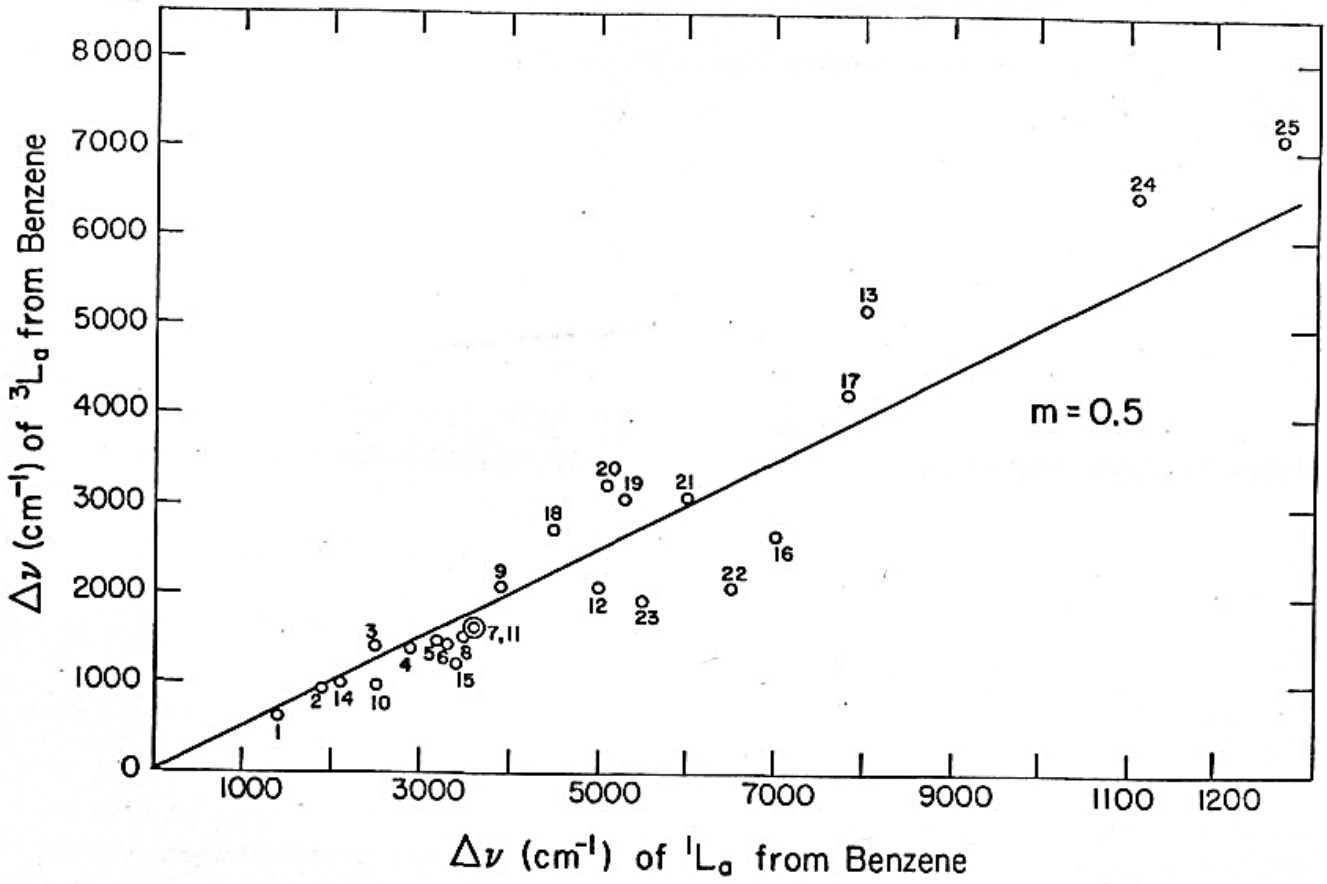
TABLE 5

ENERGY SHIFTS FROM BENZENE OF THE ^1L_a AND ^3L_a TRANSITIONS FOR BENZENE DERIVATIVE

No.	R_1	R_2	R_3	R_4	R_5	R_6	$\Delta\nu^1L_a$ (cm^{-1})	Ref.	$\Delta\nu^3L_a$ (cm^{-1}) (Exp)	$\Delta\nu^3L_a$ (cm^{-1}) (Pred)	Ref.
1	CH_3						1400	a	610		b
2	CH_3	CH_3					1900	a	930		b
3	CH_3		CH_3				2500	a	1380		b
4	CH_3			CH_3			22900	a	1355		b
5	CH_3	CH_3		CH_3			3200	a	1450		c
6	CH_3		CH_3		CH_3		3300	a	1425		b
7	CH_3	CH_3	CH_3		CH_3		3600	a	1600		c
8	CH_3	CH_3		CH_3	CH_3		3500	a	1505		b
9	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	3900	a	2080		b
10	Cl						2500	a	940		e
11	Cl		Cl				3600	a	1600		c
12	Cl			Cl			5000	a	2080		c
13	Cl	Cl	Cl	Cl	Cl	Cl	8000	a	5180		g
14	OH						2100	a	970		e
15	OCH_3						3400	a	1200		d
16	NH_2						7000	a	2670		e
17	-C≡CH						7800	a	4750		e
18	-CN						4500	a	2720		h
19	CH_3	CN					5300	a	3050		h

TABLE 5--Continued

No.	R_1	R_2	R_3	R_4	R_5	R_6	$\Delta\nu^1L_a$ (cm^{-1})	Ref.	$\Delta\nu^3L_a$ (cm^{-1}) (Exp)	$\Delta\nu^3L_a$ (cm^{-1}) (Pred)	Ref.
20	CH_3		CN	ø			5100	a	3230		h
21	CH_3			CN			6000	a	3090		h
22	COOH						6500	a	2070		i
23	$COOCH_3$						5500	k	1935		i
24	ø						11100	f	6500		j
25	ø			OH			12800	f	7150		j
26	$COCH_3$						7800		3700	3900	
27	$COCH_3$		CH_3				8200		4000	4100	
28	$COCH_3$			CH_3			9400		4000	4700	
29	$COCH_3$		CH_3	CH_3			9700		4200	4800	
30	$COCH_3$		CH_3		CH_3		9000		4500	4500	
31	$COCH_3$		CH_3	CH_3	CH_3		10300		4700	5100	
32	$COCH_3$						8700		4200	4300	
33	$COCH_3$		CF_3				6900		4100	3400	
34	$COCH_3$			CF_3			6900		4400	3400	
35	$COCH_3$						11600		5800	5800	
36	$COCH_2CH_3$						7600		3300	3800	
37	CHO						8200		4300	4100	
38	CHO			CH_3			11000		4300	5500	
39							7400		4200	3700	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4000
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2000
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3000
5000
7000
9000
1100
1200
Δν (cm⁻¹) of ³La from Benzene
Δν (cm⁻¹) of ¹La from Benzene
m = 0.5
1
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