

Spin-Orbit Coupling in Aromatic Hydrocarbons: A Semiempirical Evaluation of the Radiative Lifetimes of Naphtalene and Anthracene

G. L. BENDAZZOLI

*Istituto di Chimica Fisica e Spettroscopia, Università di Bologna, Viale Risorgimento 4,
I-40136 Bologna, Italy*

G. ORLANDI

*Laboratorio CNR di Fotochimica e Radiazioni di Alta Energia, Via de' Castagnoli 1, I-40126
Bologna, Italy*

AND

P. PALMIERI

Istituto Chimico "G. Ciamician," Via Selmi 2, I-40126 Bologna, Italy

Abstracts

Singlet-triplet spin-orbit matrix elements, which govern the lowest ${}^3B_{1u} \leftarrow {}^1A_g$ transition in typical aromatic molecules like naphtalene and anthracene, are calculated with INDO molecular orbitals and the conventional spin-orbit one-electron hamiltonian. The correct order of magnitude of the triplet radiative lifetimes is obtained for the two molecules, when INDO MO coefficients are referred to a symmetrically orthogonalized basis. The possibility of using the semiempirical Hamiltonian is explored using *ab initio* wave-functions for a few test cases. Reasonably accurate doublet-doublet and singlet-triplet matrix elements have been computed.

On a calculé les éléments de la matrice spin-orbite singulet-triplet, qui déterminent la transition ${}^3B_{1u} \leftarrow {}^1A_g$ la plus basse dans des molécules aromatiques typiques comme le naphthalène et l'anthracène, à partir des orbitales moléculaires INDO et avec le Hamiltonien spin-orbite conventionnel à un électron. Un ordre de grandeur correct des durées de vie radiatives des triplets est obtenu pour les deux molécules, quand les coefficients INDO-MO sont attribués à une base symétriquement orthogonalisée. La possibilité d'utiliser un Hamiltonien semiempirique est examinée dans quelques cas de test à l'aide des fonctions d'onde *ab initio*. Des éléments de matrice doublet-doublet et singulet-triplet raisonnables sont obtenus.

Matrizelemente für die Spin-Bahn-Kopplung, die den tiefsten Singulett-Triplett-Übergang ${}^3B_{1u} \leftarrow {}^1A_g$ in typischen aromatischen Molekülen wie Nahptalin und Anthracen bestimmen, werden mit Molekülorbitalen von INDO-Typ und dem üblichen Einelektron-

operator für die Spin-Bahnkopplung berechnet. Die richtige Grössenordnung für die radiativen Lebensdauern der Triplette wird für beide Moleküle erhalten, wenn die INDO-mo-Koeffizienten auf einen symmetrisch orthogonalisierten Basissatz bezogen werden. Die Möglichkeit einen halbempirischen Hamiltonoperator zu verwenden wird mit Wellenfunktionen von "ab initio"-Typ für einige Testfälle untersucht. Ziemlich genaue Matrixelemente für Dublett-Dublett- und Singulett-Triplett-Übergänge sind erhalten worden.

1. Introduction

Among molecular properties governed by spin-orbit coupling, phosphorescence of organic and inorganic molecules has received large attention. Several attempts to evaluate theoretically the intensities of singlet-triplet transitions using semi-empirical [1] or *ab initio* [2] molecular wave-functions have been reported in the literature. In particular, phosphorescence lifetime in aromatic molecules has been discussed recently by Henry and Siebrand [3a] and Veeman and Van der Waals [3b]. In agreement with the experimental results [4] these authors were able to show that the most important spin-orbit interaction inducing the phosphorescence involves the high energy $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ states. Furthermore, they obtained the out-of-plane polarization and the correct order of magnitude for the lifetime of the process. However, their model is rather crude as the wave-functions for the electronic states are built using delocalized Hückel orbitals for the π electrons system and localized two-center carbon-carbon, carbon-hydrogen bonding and antibonding orbitals for the σ electrons.

Moreover, the accurate evaluation of spin-orbit matrix elements with the conventional effective spin-orbit Hamiltonian

$$H_{SL} = \sum_{\text{all nuclei}} \sum_N \xi^N L^N(i) \cdot S(i) \quad (1)$$

has been recently discussed by Moore and McWeeny [5]. These authors suggested using symmetrically orthogonal orbitals to evaluate matrix elements over the Hamiltonian (1) in molecular computations.

For these reasons we felt it would be interesting to reinvestigate this problem using scf-mo wave-functions expanded over a Löwdin orthogonal basis. According to Ref. [5], matrix elements of spin-orbit operator are expressed

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$$\langle \psi_a | H_{SL} | \psi_b \rangle = \sum_{\text{all nuclei}} \sum_N \xi^N (D_S^{ba})_{ij} \langle \phi_j | L_\lambda^N | \phi_i \rangle \quad (2)$$

where ξ^N is the spin-orbit coupling constant for the free atom N , ϕ_i and ϕ_j are Löwdin orbitals associated to nucleus N , $(D_S^{ba})_{ij}$ is an element of the transition spin-density matrix connecting states ψ_a and ψ_b , and L_λ^N the appropriate component of the angular momentum operator about nucleus N . This approach is believed to have the following advantages:

- (i) All valence electrons of the molecule are explicitly included from the outset and treated on the same footing.
- (ii) All energy gaps are obtained directly without requiring the use of questionable empirical parameters.
- (iii) The theoretical implications connected to the use of eq. (1) are taken into account.

The accuracy of diagonal and off-diagonal matrix elements as given by eq. (2) has been preliminarily tested in Section 2 against experimental values of spin-orbit coupling constants for simple linear molecules in Π states and against full *ab initio* computations for SO_2 based on the exact spin-orbit Hamiltonian [2]

$$H_{SL} = \frac{g\beta^2}{4\pi\epsilon_0 c^2} \left\{ \sum_{n,v} Z_n L^n(i) \cdot S(i)/r_{ni}^3 - \sum_{i,j} (2L^i(j) + L^j(i)) \cdot S(i)/r_{ij}^3 \right\} \quad (3)$$

where g is the free electron g factor, β is the Bohr magneton, $L^i(j)$ is the orbital angular momentum of particle j about the i th particle and $S(i)$ the spin operator, and ϵ_0 is the permittivity of free space. Index n in eq. (3) refers to nuclei and i, j to electrons.

For some radical ions it has been found that the accuracy of these matrix elements can be considerably improved by an adequate choice of the atomic constants ξ^N . On the other hand, results on the neutral SO_2 molecule, indicate that the free atom ξ constants are probably adequate to derive singlet-triplet spin-orbit matrix elements in aromatic molecules. Thus the overall intensity of the ${}^3B_{1u} \leftarrow {}^1A_g$ transitions in naphthalene and anthracene have been computed using the carbon free atom spin-orbit coupling constant ($\xi^C = 28 \text{ cm}^{-1}$). The evaluation of the matrix elements over the operator of eq. (1) requires the choice of a computational scheme. For very large molecular systems the adoption of a semiempirical procedure is almost unavoidable. Therefore we used the INDO procedure to obtain the molecular wave-functions.

2. The Atomic Spin-Orbit Coupling Constants ξ^N

As examples of diagonal spin-orbit matrix elements computed from eqs. (1) and (2), we report in Table I the spin-orbit coupling constants for the series of radicals CS_2^+ , COS^+ , CO_2^+ in ${}^2\Pi$ ground states. For the latter two radicals, an excited state of ${}^2\Pi$ symmetry was also considered. In all cases, *ab initio* SCF wave-functions derived from a basis of double-zeta quality [6, 7] were used. In column (a) of Table I are reported the values of spin-orbit coupling constants computed by using standard values of ξ^N [8]. For CO_2^+ , the computed value is in better agreement with the experiment if compared to previous computations where all [2] or part [9] of the spin other-orbit terms were explicitly included. Since for the symmetric radicals CO_2^+ , CS_2^+ in the ${}^2\Pi_g$ states the computed coupling constants must coincide with the atomic constant for oxygen and sulphur

respectively, the discrepancies with respect to experimental values can be interpreted in terms of modifications of the formal charge and of electronic configurations of these atoms due to molecule formation. In Table II are reported atomic spin-orbit coupling constants for S and O for different ionization degrees of the two atoms in the electronic configurations s^2p^n and sp^{n+1} , derived from the fine structure of the spectroscopic terms [10, 11]. Using a simple interpolation procedure and the results of a Mulliken population analysis of the molecular wave-functions, values of ξ^N better suited for the computations of spin-orbit matrix elements in these molecules were derived. A considerable improvement is then obtained for all computed molecular coupling constants (Table I, column (b)).

In evaluating phosphorescence or intersystem crossing decay rates, one needs matrix elements connecting states of different multiplicity. In this case the choice of the ξ constants are more difficult as charge and electronic configuration may differ in the two states. In principle, one may expect that an *ad hoc* choice of the atomic parameter has to be made. To investigate this point we considered the SO_2 molecule for which $T_1 \leftarrow S_0$ transition moments have been evaluated both with the effective Hamiltonian of eq. (1) using the standard [8] values of ξ , and with

TABLE I. Spin-orbit coupling constants (cm^{-1}) for CO_2^+ , CS_2^+ , and COS^+ radicals. In column (a) standard values [8] are assumed for the atomic constants in the spin-orbit Hamiltonian given in eq. (1). In column (b) the atomic constants are obtained by interpolating values in Table II, using the results of a population analysis. *Ab initio* molecular wave-functions derived from double-zeta quality bases are used for all molecules.

Molecule	Electronic state	(a)	(b)	Experimental [17]
CO_2^+	$\tilde{X}^2\Pi_u$	- 103	- 106	- 95.5
	$\tilde{A}^2\Pi_g$	- 151	- 165	- 159.5
COS^+	$\tilde{X}^2\Pi_i$	- 114	- 120	- 121
	$\tilde{A}^2\Pi$	- 305	- 363	- 372
CS_2^+	$\tilde{X}^2\Pi_g$	- 382	- 408	- 440.39

TABLE II. Experimental atomic coupling constants (cm^{-1}) for oxygen and sulphur in the s^2p^n and sp^{n+1} configurations.

Atomic charge	Valence configuration	Spectroscopic term	Coupling constants	
			Oxygen	Sulphur
0	s^2p^4	3P	155	390
	sp^5	3P	-	361
1	sp^4	$^2P, ^4P$	188	439
2	s^2p^2	3P	199	545
3	s^2p	2P	257	633
	sp^2	$^2P, ^4P$	234	641
4	sp	3P	301	760
5	p	2P	358	842

the exact spin-orbit Hamiltonian. The square of the transition moment together with relevant spin-orbit matrix elements are reported in Table III. The overall transition moments and the significant matrix elements computed with the two procedures are in satisfactory agreement.

Therefore we conclude that the Hamiltonian (1) with standard free atom constants can be used to discuss the phosphorescence of aromatic molecules like naphthalene and anthracene, since the electronic charge is evenly distributed among the atoms both in the ground and excited states.

TABLE III. *Ab initio* (a) and semiempirical (b) selected spin-orbit matrix elements (cm^{-1}) $|\langle \psi_i | H_{SO} | \phi_j \rangle|$ for SO_2 . The same limited CI wave-functions [14] over a basis of STO-4.31G orbitals [18] were used in both computations. The component of the multiplet is specified by the spin quantum number given in parenthesis. The square of the transition moment μ (a.u.) of the ${}^3B_1 \leftarrow {}^1A_1$ transition is also reported.

ψ_i	ψ_j	(a)	(b)
$1\ {}^1A_1$	$1\ {}^3B_1(\mp 1)$	113	97
$1\ {}^1A_1$	$1\ {}^3A_2(\mp 1)$	56	44
$1\ {}^1A_1$	$2\ {}^3A_2(\mp 1)$	42	40
$1\ {}^1A_1$	$2\ {}^3B_1(\mp 1)$	30	26
$1\ {}^1A_1$	$1\ {}^3B_2(0)$	1	2
$1\ {}^1A_1$	$2\ {}^3B_2(0)$	32	30
$1\ {}^1A_1$	$3\ {}^3B_2(0)$	56	68
$1\ {}^3B_1(\mp 1)$	$2\ {}^1A_1$	47	56
$1\ {}^3B_1(\mp 1)$	$3\ {}^1A_1$	3	4
$1\ {}^3B_1(\mp 1)$	$1\ {}^1B_2$	8	16
$1\ {}^3B_1(\mp 1)$	$2\ {}^1B_2$	31	37
$1\ {}^3B_1(\mp 1)$	$3\ {}^1B_2$	28	40
$1\ {}^3B_1(0)$	$1\ {}^1A_2$	62	51
$1\ {}^3B_1(0)$	$2\ {}^1A_2$	1	0
$ \mu ^2$		5.2×10^{-6}	3.5×10^{-6}

3. The ${}^3B_{1u} \leftarrow {}^1A_g$ Transitions in Naphthalene and Anthracene

The INDO MO were obtained by adopting the reference system reported in Figure 1. The highest occupied and lowest virtual MO's are $1a_u$ and $2b_{1g}$ for naphthalene and $2b_{3g}$ and $3b_{2u}$ for anthracene. In the single-configuration approximation, the lowest triplet state is therefore correctly predicted to be of B_{1u} symmetry in both molecules and to arise from the $1a_u \rightarrow 2b_{1g}$ and the $2b_{3g} \rightarrow 3b_{2u}$ excitations, respectively. Although the computed transition energies (0.2198 a.u. for naphthalene and 0.1503 a.u. for anthracene) to the B_{1u} states are larger than the experimental values [12], the trend of transition energies in the two molecules is correctly predicted.

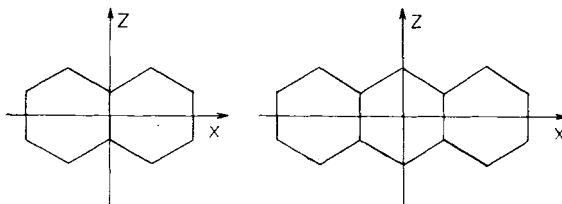


Figure 1. Reference system for naphthalene and anthracene.

Using the perturbation expansion of the moment of the ${}^3B_{1u} \leftarrow {}^1A_g$ transition, one obtains

$$\begin{aligned} \langle {}^1A_g | r | {}^3B_{1u} \rangle = & \sum_{\lambda} \sum_n \langle {}^1A_g | H_{SL} | n^3\lambda \rangle \langle n^3\lambda | r | {}^3B_{1u} \rangle / [E({}^1A_g) - E(n^3\lambda)] \\ & + \sum_{\lambda'} \sum_{n'} \langle n'^1\lambda' | H_{SL} | {}^3B_{1u} \rangle \langle {}^1A_g | r | n'^1\lambda' \rangle / [E({}^3B_{1u}) - E(n'^1\lambda')] \quad (4) \end{aligned}$$

where λ, λ' specify the symmetry of the excited states and indexes n, n' identify different states within the same symmetry.

Matrix elements in eq. (4) have been computed using the INDO wave-functions and energies. In such a case, the main source of error depends upon the description of the ground and excited ${}^3B_{1u}$ states and in the energy differences in the denominator of eq. (4). The wave-functions of the perturbing excited states do not necessarily need to be accurate, if the perturbation expansion is sufficiently complete. For this reason we have avoided the use of empirical data in the evaluation of the singlet-triplet transition moments. We will be principally concerned with the out-of-plane polarized component, which is known by its symmetry and through experiments [13] to be responsible for the intensity of the transition. Selection rules for matrix elements in eq. (4) have been discussed in detail in Ref. [3a]. A summary of the relevant information is also presented in Table IV of this paper to clarify the content of the following numerical tables. In the choice of the perturbing singlet and triplet states, we have also exploited the one electron nature of the semiempirical spin-orbit Hamiltonian (1) and considered in the summation (4) matrix elements between states differing by one orbital. In all our previous computations, spin-orbit matrix elements having only spin-orbit contributions have been found negligible [14]. In naphthalene, this reduces the number of the perturbing states to those associated with the $1a_u \rightarrow b_{2g}^*$, $b_{3u} \rightarrow 2b_{1g}^*$ singlet and with the $1a_u \rightarrow b_{3u}^*$, $b_{2g} \rightarrow 2b_{1g}^*$ triplet excitations. Similarly for anthracene, the $2b_{3g} \rightarrow b_{1u}^*$, $a_g \rightarrow 3b_{2u}^*$ singlet and the $2b_{3g} \rightarrow a_g^*$, $b_{1u} \rightarrow 3b_{2u}^*$ triplet excitations have been considered.

In the evaluation of matrix elements a definite choice has to be made for the INDO atomic orbitals. Given the nature of the integral approximations in this method, it seems natural to consider its atomic basis as orthogonal [15]. For this reason, at variance with the conventional choice, we identify such basis with a

TABLE IV. Symmetry properties in the D_{2h} point group of the operators and molecular wavefunctions in expansion (3).

Transition dipole component	y	B_{2u}
Angular momentum components	L_x	B_{3g}
	L_y	B_{2g}
	L_z	B_{1g}
Spin factors	$\alpha\beta$ - $\beta\alpha$	A_g
	$\alpha\alpha$	$B_{2g} + B_{3g}$
	$\alpha\beta + \beta\alpha$	B_{1g}
	$\beta\beta$	$B_{2g} - B_{3g}$
Orbital factors	λ	B_{3g}
	λ'	B_{2u}

symmetrically orthogonal one. The matrix elements over Löwdin orbitals have been expanded as a combination of many-center integrals over Slater orbitals. Numerical values for matrix elements and energies of the perturbing states are listed in Tables V and VI for naphthalene and anthracene, respectively. The importance of the choice of the atomic basis is shown in Table V, where matrix elements are reported for the Löwdin orthogonalized and for the Slater-type basis. We see that the individual matrix elements are significantly different in the two cases and, as a result, the phosphorescence lifetime changes by more than one order of magnitude. Since the Löwdin basis involves a consistent consideration of the overlap effects, the implication is that these terms are very important in the evaluation of the phosphorescence lifetime. One can also notice that going from the non-orthogonal to the orthogonal basis, matrix elements involving $\sigma \rightarrow \pi^*$ states increase considerably, while the opposite effect is observed for $\pi \rightarrow \sigma^*$ states.

The two resulting lifetimes for naphthalene and anthracene are of the correct order of magnitude and appear in the same order as the experimental ones. Furthermore, if we empirically take into account the neglect of correlation in the evaluation of transition moments [16], the agreement with the experiments becomes very good. This would suggest that to correctly estimate spin-orbit effects on singlet-triplet electronic transitions one should rely more on the completeness of the perturbative expansion (4) [5], rather than on the accuracy of the description of highly excited electronic states.

A qualitative picture of the "mechanism" which allows the ${}^3B_{1u} \leftarrow {}^1A_g$ transition can be derived from the analysis of matrix elements in Tables V and VI. In agreement with Ref. [3], we found that all types of excitations ($\sigma \rightarrow \pi^*$ singlet and triplet, and $\pi \rightarrow \sigma^*$ singlet and triplet) give non-negligible contributions to the transition moment and that large contributions come from $\pi \rightarrow \sigma^*$ singlet and triplet states having antibonding character with respect to C-C bonds of the aromatic rings. However, it seems likely that this type of analysis is sensitive to the choice of the orbitals and to the nature of the molecular wave-function.

TABLE V. Spin-orbit (cm^{-1}) and dipole (a.u.) matrix elements for naphthalene. MO coefficients are referred to (a) symmetrically orthogonal orbitals and (b) Slater orbitals. τ^a is the radiative lifetime of the $^3B_{1u}$ state in seconds. The energies E (a.u.) are referred to the ground state of the molecule.

			$ \langle ^1A_g H_{SL} n^3\lambda \rangle $		$\langle n^3\lambda y ^3B_{1u} \rangle$		$E(n^3\lambda)$
n	λ		(a)	(b)	(a)	(b)	
1	$^3B_{3g}$	$(1a_u \rightarrow 6b_{3u})$	1.994	1.488	0.137	0.076	0.428
2	$^3B_{3g}$	$(1a_u \rightarrow 7b_{3u})$	2.007	1.414	-.111	-.061	0.481
3	$^3B_{3g}$	$(1a_u \rightarrow 8b_{3u})$	5.179	2.977	0.265	0.136	0.595
4	$^3B_{3g}$	$(1a_u \rightarrow 9b_{3u})$	4.417	2.364	-.173	-.082	0.622
5	$^3B_{3g}$	$(1b_{2g} \rightarrow 2b_{1g})$	2.721	3.682	-.666	-.1057	1.170
6	$^3B_{3g}$	$(2b_{2g} \rightarrow 2b_{1g})$	1.094	1.576	-.046	-.072	0.668
7	$^3B_{3g}$	$(3b_{2g} \rightarrow 2b_{1g})$	6.541	7.126	0.122	0.172	0.528
8	$^3B_{3g}$	$(4b_{2g} \rightarrow 2b_{1g})$	0.191	0.110	0.015	0.011	0.309
			$ \langle n'^1\lambda' H_{SL} ^3B_{1u} \rangle $		$\langle ^1A_g y n'^1\lambda' \rangle$		$E(n'^1\lambda')$
n'	λ'		(a)	(b)	(a)	(b)	
1	$^1B_{2u}$	$(1a_u \rightarrow 5b_{2g})$	0.470	0.378	-.071	-.050	0.446
2	$^1B_{2u}$	$(1a_u \rightarrow 6b_{2g})$	2.462	1.482	0.203	0.167	0.493
3	$^1B_{2u}$	$(1a_u \rightarrow 7b_{2g})$	2.906	1.433	0.682	0.426	0.620
4	$^1B_{2u}$	$(1a_u \rightarrow 8b_{2g})$	2.257	0.920	-.419	-.245	0.670
5	$^1B_{2u}$	$(1a_u \rightarrow 9b_{2g})$	4.161	1.782	-.110	-.052	0.709
6	$^1B_{2u}$	$(1b_{3u} \rightarrow 2b_{1g})$	2.804	4.901	0.092	0.137	1.652
7	$^1B_{2u}$	$(2b_{3u} \rightarrow 2b_{1g})$	0.021	0.121	0.474	0.634	1.044
8	$^1B_{2u}$	$(3b_{3u} \rightarrow 2b_{1g})$	5.240	7.535	0.211	0.268	0.842
9	$^1B_{2u}$	$(4b_{3u} \rightarrow 2b_{1g})$	0.138	0.094	-.063	-.067	0.488
10	$^1B_{2u}$	$(5b_{3u} \rightarrow 2b_{1g})$	0.535	0.463	0.052	-.064	0.435

^a τ : (a) unscaled = 11, scaled = 33 [16]; (b) unscaled = 169; experimental = 23 [19a], 75 [19b].

4. Conclusions

We have presented theoretical computations of singlet-triplet transition intensities for two typical aromatic molecules, i.e. naphthalene and anthracene. The computations are based on INDO wave-functions and on a semiempirical spin-orbit Hamiltonian. The feasibility of using such a Hamiltonian was independently tested using *ab initio* molecular wave-functions. Reasonably accurate results were obtained, both for doublet-doublet and singlet-triplet matrix elements. Although the results obtained for radiative lifetimes are essentially similar to those obtained by a simpler treatment, the present approach relies on a very small number of empirical parameters. Apart from the use of semiempirical wave-functions, only

TABLE VI. Spin-orbit (cm^{-1}) and dipole (a.u.) matrix elements for anthracene in the Löwdin basis. The energies E of the states are given in a.u. using the ground-state energy as reference. τ^a is the radiative lifetime of the ${}^3B_{1u}$ state in seconds.

n	λ	$ \langle {}^1A_g H_{SL} n^3\lambda \rangle $	$\langle n^3\lambda y {}^3B_{1u} \rangle$	$E(n^3\lambda)$
1	${}^3B_{3g}$: $(2b_{3g} \rightarrow 9a_g)$	1.947	0.154	0.397
2	${}^3B_{3g}$: $(2b_{3g} \rightarrow 10a_g)$	0.705	0.100	0.432
3	${}^3B_{3g}$: $(2b_{3g} \rightarrow 11a_g)$	0.039	0.035	0.423
4	${}^3B_{3g}$: $(2b_{3g} \rightarrow 12a_g)$	1.613	0.040	0.506
5	${}^3B_{3g}$: $(2b_{3g} \rightarrow 13a_g)$	5.068	0.259	0.596
6	${}^3B_{3g}$: $(2b_{3g} \rightarrow 14a_g)$	4.837	0.192	0.604
7	${}^3B_{3g}$: $(1b_{1u} \rightarrow 3b_{2u})$	0.282	-.041	1.395
8	${}^3B_{3g}$: $(2b_{1u} \rightarrow 3b_{2u})$	2.582	0.546	1.119
9	${}^3B_{3g}$: $(3b_{1u} \rightarrow 3b_{2u})$	0.734	0.003	0.705
10	${}^3B_{3g}$: $(4b_{1u} \rightarrow 3b_{2u})$	0.145	0.007	0.559
11	${}^3B_{3g}$: $(5b_{1u} \rightarrow 3b_{2u})$	6.624	-.093	0.503
12	${}^3B_{3g}$: $(6b_{1u} \rightarrow 3b_{2u})$	0.074	-.007	0.404
n'	λ'	$ \langle n'^1\lambda' H_{SL} {}^3B_{1u} \rangle $	$\langle {}^1A_g y n'^1\lambda' \rangle$	$E(n'^1\lambda')$
1	${}^1B_{2u}$: $(2b_{3g} \rightarrow 7b_{1u})$	0.031	-.009	0.390
2	${}^1B_{2u}$: $(2b_{3g} \rightarrow 8b_{1u})$	0.642	-.065	0.415
3	${}^1B_{2u}$: $(2b_{3g} \rightarrow 9b_{1u})$	2.103	0.169	0.462
4	${}^1B_{2u}$: $(2b_{3g} \rightarrow 10b_{1u})$	1.927	-.311	0.479
5	${}^1B_{2u}$: $(2b_{3g} \rightarrow 11b_{1u})$	1.141	0.304	0.578
6	${}^1B_{2u}$: $(2b_{3g} \rightarrow 12b_{1u})$	1.548	0.387	0.625
7	${}^1B_{2u}$: $(2b_{3g} \rightarrow 13b_{1u})$	2.843	0.421	0.654
8	${}^1B_{2u}$: $(2b_{3g} \rightarrow 14b_{1u})$	3.952	-.142	0.702
9	${}^1B_{2u}$: $(1a_g \rightarrow 3b_{2u})$	0.001	0.035	1.870
10	${}^1B_{2u}$: $(2a_g \rightarrow 3b_{2u})$	2.690	0.190	1.576
11	${}^1B_{2u}$: $(3a_g \rightarrow 3b_{2u})$	0.487	-.317	1.091
12	${}^1B_{2u}$: $(4a_g \rightarrow 3b_{2u})$	0.190	0.351	1.056
13	${}^1B_{2u}$: $(5a_g \rightarrow 3b_{2u})$	5.064	-.186	0.779
14	${}^1B_{2u}$: $(6a_g \rightarrow 3b_{2u})$	0.518	-.041	0.615
15	${}^1B_{2u}$: $(7a_g \rightarrow 3b_{2u})$	0.200	-.049	0.460
16	${}^1B_{2u}$: $(8a_g \rightarrow 3b_{2u})$	0.102	0.004	0.292

^a τ : unscaled = 66; scaled = 198 [16]; experimental = 60 [19c], 180 [19b].

the spin-orbit coupling constant for the carbon atom was taken from experiment (28 cm^{-1}). Therefore, the procedure is, in principle, of general applicability. We hope that this method will prove useful in discussing problems met in the photochemistry of large organic molecules.

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