

Computation of Electronic Absorption Spectra and Spectral Properties of Neutral 1-Methyl Chrysene and Its Positive Ion in H₃BO₃ Matrix by AM1 and PM3 Methods

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The theoretical electronic absorption spectrum of methyl chrysene, a polycyclic aromatic hydrocarbon in boric acid matrix, is calculated for the first time, using semi-empirical method. Earlier reported theoretical results of electronic spectrum were calculated in free state and the results compared with the spectrum of aromatic system in glassy or other matrices. The interaction between the trapped polycyclic aromatic hydrocarbons (neutral and ions) and its environment induces perturbations of the energy levels which results in large shifts of the electronic transitions as compared to isolated polycyclic aromatic hydrocarbon molecule. The spectroscopic and electronic parameters have been reported, using semi empirical methods, for the present probe in free, aqueous and H₃BO₃ matrix. The static polarizability values have also been calculated to check the Laser action of the 1-methyl chrysene and its cation.

Key Words: Computation, Absorption spectra, 1-Methyl chrysene, H₃BO₃.

INTRODUCTION

The potential importance of polycyclic aromatic hydrocarbons (PAHs) in astrophysics^{1,2} has motivated present study of ultraviolet and visible spectrum and spectroscopic properties of 1-methyl chrysene and its mono-positive ion. PAHs have been proposed as possible carriers of the visible, diffuse interstellar absorption bands (DIB)^{3,4} which extends from 4000 Å to near IR. These were discovered more than 85 years ago⁵ and their interstellar nature was recognized 12 years later⁶. There is no unique carrier for all DIBs and among other species, PAHs are believed to be the promising candidates. A large fraction of PAHs are expected to be ionized in the interstellar medium (ISM) and thus are expected to absorb lower energy photons (mainly in the visible and near-IR region of the spectrum) to a

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great extent than the neutral precursors⁷. Small PAHs absorb in visible range if they are in cationic form⁸, while in natural state they absorb in ultraviolet. To test this hypothesis, we have calculated quantum mechanically, the absorption peaks of 1-methyl chrysene in neutral and ionized states in boric acid glass. The present work is carried out, so as to identify whether any absorption bands of either 1-methyl chrysene or its mono-positive ion matches with any DIBs, in UV/Vis range. To our best of knowledge, this is the first time, semi empirical calculations are simulated in boric acid matrix.

COMPUTATION DETAILS

The molecule was placed in the xy-plane with two fold symmetry axis of the molecule along y-axis (Fig. 1). The molecular geometry of 1-methyl chrysene is first optimized at Molecular Mechanics (MM⁺) level. Semi-empirical method, Austin Model 1 (AM1) is then used for optimizing the full geometry of the system, using Polak-Ribiere (conjugate gradient) algorithm. The charge value 'Q' and the spin multiplicity 'S' is set accordingly for singlet and doublet state calculations. Unrestricted Hartree-Fock (UHF) is employed keeping RMS gradient of 0.01 Kcal/Å mol. The optimized geometry of 1-methyl chrysene in singlet state is shown in Fig. 1.

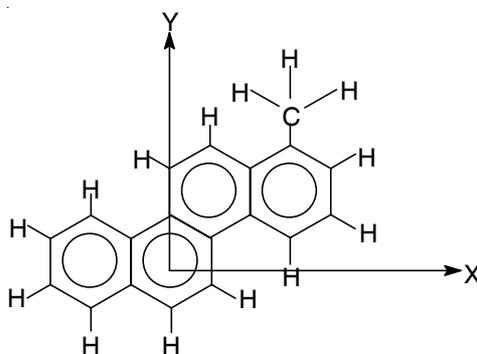


Fig. 1.

RESULTS AND DISCUSSION

We have computed the electronic spectrum and other spectroscopic properties, especially, the first ionization energy, which is found to be maximum, the wavelength (λ_{nm}) in aqueous media is minimum, attributed to be due to the strong electrostatic interactions with the molecule. Though, the spectra was computed by using Parametric method 3 (PM3), but has not been reported here because of almost the same absorption lines appeared as with AM1 method. The theoretical results are reported in Tables 1-4. The calculated electronic absorption spectra of 1-methyl chrysene (1

MeCH^o) is shown in Table-1. It can be seen from the result that the initial wavelengths of various transitions in all the states of the system found near visible/far IR region showing vibronic coupling, with more or less very weak oscillator strength. But at the transition number ten (t = 10) where the oscillator strength the least dipole moment value of the system in free state. The mean polarizability values are found to be practically same in all the three states, showing the shape of the molecule remain unchanged. Then 1-MCH^o can't have the lasing action *i.e.*, Laser property.

TABLE-1
SINGLET STATE ELECTRONIC ABSORPTION OF 1-METHYL
CHRYSENE (1-MeCH^o), USING AM1 METHOD

t	Molecular point group: C ₁			Calculated values								
	λ_{ba} (nm)	λ_{aq} (nm)	λ_{fs} (nm)	d			s			f		
				ba	aq	fs	ba	aq	fs	ba	aq	fs
1	509.00	507.43	494.44	1	1	1	t	t	s	0.00	0.00	0.00
2	386.88	390.70	372.20	1	1	1	t	t	t	0.00	0.00	0.00
3	359.56	363.93	353.68	1	1	2	s	s	t	0.44	0.47	0.00
4	347.72	355.33	353.15	1	1	2	t	t	t	0.00	0.00	0.34
5	333.22	332.35	329.09	1	1	1	t	t	s	0.00	0.00	0.01
6	325.93	327.73	322.35	1	1	1	s	s	s	0.00	0.03	0.00
7	292.21	285.85	303.01	1	1	1	t	t	t	0.00	0.05	0.00
8	269.47	267.20	262.53	1	1	1	s	s	t	0.07	1.94	0.00
9	257.22	257.66	257.50	1	1	1	t	t	t	0.00	0.00	0.05
10	250.68	248.50	249.83	1	1	1	s	s	s	1.93	1.94	2.21
11	240.99	241.13	238.95	1	1	1	t	t	s	0.00	0.00	0.00
12	240.67	237.32	238.35	1	1	1	s	s	s	0.12	0.34	0.00
13	231.70	235.27	230.24	2	1	1	t	s	s	0.00	0.10	0.82
14	231.61	234.43	229.09	2	1	2	s	t	t	0.36	0.00	0.00
15	226.92	228.71	228.85	1	1	2	t	s	s	0.44	0.52	0.26
16	215.87	213.92	213.80	1	1	1	t	s	t	0.00	0.01	0.00
17	210.54	213.11	211.48	1	1	1	s	t	s	0.01	0.00	0.00
18	197.16	197.18	195.17	1	1	1	s	s	s	0.44	0.28	0.37

t = transition no.; λ_{ba} = wavelength in boric acid matrix, λ_{aq} = wavelength in aqueous medium; λ_{fs} = wavelength in free state; d = degeneracy; s = spin multiplicity; f = oscillator strength.

In H₃BO₃ matrix, it is practically the van der-Waal interactions. For the cationic species (1-MeCh⁺), the oscillator strength is very weak and most of the allowed transitions are in the UV range, showing the tight binding of the cationic species with the surrounding environment (Table-2). Computed electronic and energetic parameters of neutral 1-MeCh^o in all states are shown in Table-3. It can be seen from the results that the molecule, in all, is found to be endothermic in nature. The ΔE values (LUMO-HOMO).

TABLE-2
 DOUBLET STATE ELECTRONIC ABSORPTION SPECTRA OF
 1-METHYL CHRYSENE (1-MeCH⁺), USING AM1 METHOD

t	Molecular point group: C ₁			Calculated values								
	λ_{ba} (nm)	λ_{aq} (nm)	λ_{fs} (nm)	d			s			f		
				ba	aq	fs	ba	aq	fs	ba	aq	fs
1	1281.75	1057.52	1159.56	1	1	1	d	d	d	0.00	0.07	0.00
2	1010.33	831.80	955.22	1	1	1	d	d	d	0.17	0.11	0.18
3	409.32	421.30	415.57	1	1	1	d	d	d	0.36	0.32	0.35
4	351.06	362.33	344.18	1	1	1	d	d	t	0.01	0.04	0.00
5	337.96	342.46	340.40	1	1	1	t	t	t	0.02	0.07	0.01
6	322.30	305.64	317.94	1	1	1	t	t	t	0.07	0.14	0.14
7	288.55	299.29	287.97	1	1	1	t	t	t	0.04	0.02	0.06
8	279.24	278.37	281.93	1	1	1	t	d	t	0.03	0.10	0.00
9	272.13	272.58	269.93	1	1	1	d	d	d	0.00	0.18	0.00
10	256.70	259.15	254.77	1	1	1	d	t	d	0.01	0.41	1.07
11	243.75	250.59	244.97	1	1	1	d	t	d	0.53	0.05	0.08
12	241.41	242.49	242.18	1	1	1	d	t	d	0.04	0.21	0.46
13	239.29	240.26	239.49	1	1	1	t	d	d	0.11	0.82	0.00
14	234.25	230.76	233.83	1	1	1	t	d	t	0.06	0.22	0.03
15	225.14	220.50	227.10	1	1	1	t	t	t	0.77	0.39	0.91
16	208.64	207.28	207.59	1	1	1	d	t	d	0.00	0.05	0.00
17	201.82	199.73	202.93	1	1	1	d	d	d	0.40	0.37	0.39

t = transition no.; λ_{ba} = wavelength in boric acid matrix, λ_{aq} = wavelength in aqueous medium; λ_{fs} = wavelength in free state; d = degeneracy; s = spin multiplicity; f = oscillator strength, ba = boric acid; aq = aqueous; fs = free state.

through AM1 and PM3 methods, in aqueous media is least and maximum in free state. This further confirms the strong electrostatic and van der Waal interactions of the system in water and boric acid matrix, respectively. This observation is similar to the earlier computed values of spectral lines discussed here, which can be further substantiated by the most relevant molecular parameter (chemical descriptor) needed to model the photophysics of inter-stellar PAHs⁹, by using AM1 and PM3 methods. All calculations have been carried out by using Hyper Chem. 7.51 software package¹⁰. The spectrum is calculated in boric acid for the first time, so that the measured spectrum of system can be directly compared with the observed values in the boric acid environment. In matrix, the spectrum is calculated by doping the 1-methyl chrysene and its cation in 216 solvent molecules (H₃BO₃/H₂O) which have been optimized at Mm⁺ level, prior to doping. The spectral properties are computed in boric acid, aqueous and free state to observe the magnitude of perturbation in different phases. In addition, the polarizability values are also carried out by keeping a field of 0.005 a.u.

TABLE-3
COMPUTED ELECTRONIC AND ENERGETIC PARAMETERS OF
1-MeCH^o IN BORIC ACID MATRIX (ba), AQUEOUS MEDIUM (aq)
AND FREE STATE (fs)
SINGLET STATE (1-meCH^o)

Parameters	ba		aq		fs	
	AM1	PM3	AM1	PM3	AM1	PM3
ΔE	7.90	8.60	7.70	8.15	8.44	8.30
IP	7.42	8.76	7.80	7.93	8.69	8.74
μ	3.20	4.90	3.25	1.24	0.28	0.26
X [^]	181.56	173.82	181.12	172.70	180.86	172.07
H _f	1364.65	1409.30	1485.13	1236.85	63.68	58.56
B.E.	-2611.69	-2567.03	-2491.20	-2776.69	-39.12.65	-3917.76

$\Delta E(\text{ev}) = \text{LUMO-HOMO}$; IP(eV) = Ionization potential; μ (Debye) = Dipole moment; X = Polarizability; H_f (Kcal/mol) = Heat of formation; B.E. (Kcal/mol) = Binding energy; [^]with a field of 0.005 a.u.

The computed parameters of 1 MeCh⁺ are given in Table-4. The BE and dipole moment values in all the three states are less and more than that of neutral system, respectively. It is evident also from the fact that the ionized species show strong electrostatic interactions. The size of the molecular species is contracted in comparison to the neutral species (higher values of polarizabilities of cationic species).

TABLE-4
COMPUTED ELECTRONIC AND ENERGETIC PARAMETERS OF
1-MeCh⁺ IN BORIC ACID MATRIX (ba), AQUEOUS MEDIUM (aq)
AND FREE STATE (fs)
SINGLET STATE (1-meCh⁺)

Parameters	ba		aq		fs	
	AM1	PM3	AM1	PM3	AM1	PM3
ΔE	5.85	5.38	5.61	4.81	7.01	6.96
IP	10.63	10.67	10.18	11.18	12.39	12.52
μ	15.33	15.99	14.80	8.56	0.22	0.12
X [^]	239.53	224.76	249.54	240.91	247.70	238.04
H _f	1503.86	1573.07	1391.41	1410.49	243.62	241.32
B.E.	-2472.46	-2403.25	-2066.47	-2565.00	-3732.71	-3735.01

$\Delta E(\text{ev}) = \text{LUMO-HOMO}$; IP(eV) = Ionization potential; μ (Debye) = Dipole moment; X = Polarizability; H_f (Kcal/mol) = Heat of formation; B.E. (Kcal/mol) = Binding energy; [^]with a field of 0.005 a.u.

Conclusion

Semi-empirical methods like AM1 and PM3 can be quite successful in predicting the electronic absorption spectrum of poly aromatic hydrocarbons which exist in interstellar system. Moreover, various kinds of interactions can also be simulated through quantum chemical calculations.

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