# A HAM/3 STUDY OF TOLUENE PES

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Abstract. Ionization potentials (or PES) of toluene were calculated by HAM/3 method. Systematic corrections of the calculated values were proposed bases upon HAM/3 results of benzene molecules. The corrected values agree very well with experimental ones obtained by photoelectron spectroscopy (PES).

HAM/3 (Hydrogenic Atoms in Molecules-version 3) (1-2) is a semi-empirical method that can calculate ionization potentials, excitation energies, electron affinities, and other molecular properties. There have been numerous works published (3-5) demonstrating usefulness of HAM/3 in interpretting photoelectron spectra (PES) of molecules. The objective of our work is to study PES of benzen substituents using HAM/3. In this short communication we show that a proper precaution is necessary to assign PES of toluene, a benzen substituent, based upon HAM/3 calculation.

Fig.1 shows energy levels (PES) of benzene and toluene. Experimental and theoretical PES of benzene are compared in the columns(A) and (B) in the figure. HAM/3 PES of benzene is in error in two respects; (1) The order of $3e_{2g}$ and $1a_{2u}$ are inverted in comparison to experiment, (2) The order of $3e_{1u}$ and $1b_{2u}$ is also wrong. HAM/3 PES of substituted benzenes, therefore, are expected to have similar sort of inversions of energy leves that are predominantly of the charactor of $3e_{2g}$, $1a_{2u}$, $3e_{1u}$ and $1b_{2u}$.

It is desirable to correct these energy levels before one compares HAM/3 PES with experimental one. A simple way of the correction may be to shift the energy levels that are dominated by the aforementioned energy levels. The amount of shift is such a way that the shifted level coincides with the corresponding experimental one. The $3e_{2g}$ and $3e_{1u}$ are shifted upwards, or shift by -0.79ev for the former and the latter by -0.48ev (see Fig.1, Column (B)).

On the other hand, the $1b_{2u}$ and $3a_{1g}$ are shifted downwards, or shift by +0.64ev and +0.79ev respectively.

A HAM/3 PES of toluene before the corrections are shown in the column (C) of Fig.2. The corrected PES is in the column (D). An experimental PES is in the column (E). If the column (D), the corrected HAM/3 PES, and the column (E), experiment, are compared close parallelism is noticable. Agreement between theory and experiment is excellent. It is now an easy matter to assign the observed PES.

Table 1 lists numerical values of the PES of toluene. The numbers with asterisk in the column, HAM/3, are corrected values, those in the parentheses are ones before correction. The ab initio PES with double zeta basis set in the literature (6) is also included in the table 1. The assignments based on $C_{2v}$ and "$D_{6h}$" are listed in the last two columns of the table. The HAM/3 PES reproduces experimental PES very well. Absolute average error of HAM/3 is 0.24ev. The corresponding value of ab initio DZ is 2.17ev, an order of magnitute is larger. The assignment of experimental PES based upon HAM/3 agrees fairly well with that of ab initio. The HAM/3 result of toluene demonstrates that the method is reliable if one takes proper precautions due to the inversions of orders of some benzene based orbitals.

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Table 1 PES of toluene calculated with HAM/3, (in eV).

| Expt[a]. | HAM/3[b] | DZ[a] | $C_{2v}$ | "$D_{6h}$". |
|---|---|---|---|---|
| 8.80 | 9.28 | 8.55 | $b_1$ | $e_{1g}(\pi)$ |
| 9.25 | 9.45 | 8.89 | $a_2$ | $e_{1g}(\pi)$ |
| 11.40 | 11.25*(12.04) | 12.72 | $a_1$ | $e_{2g}(\sigma)$ |
| 11.40 | 11.35*(12.14) | 12.81 | $b_2$ | $e_{2g}(\sigma)$ |
| 11.91 | 11.69 | 13.04 | $b_1$ | $a_{2u}(\pi)$ |
| 13.14 | 12.89*(13.37) | 14.40 | $a_1(b_2)$ | $e_{1u}(\sigma)$ |
| 13.14 | 12.99 | 15.09 | $b_2$ | $CH_3(\sigma)$ |
| 13.97 | 13.96 | 15.64 | $b_1$ | $CH_3(\pi)$ |
| 13.97 | 14.01*(14.49) | 15.76 | $b_2$ | $e_{1u}(\sigma)$ |
| 15.08 | 14.88*(14.24) | 16.90 | $b_2(a_1)$ | $b_{2u}(\sigma)$ |
| 15.42 | 15.25 | 17.02 | $a_1(b_2)$ | $b_{1u}(\sigma)$ |
| 16.45 | 16.71*(15.92) | 18.66 | $a_1$ | $a_{1g}(\sigma)$ |
| 18.42 | 17.89 | 21.48 | $a_1$ | $e_{1g}(\sigma)$ |
| 18.87 | 18.49 | 22.29 | $b_2$ | $e_{1g}(\sigma)$ |
| 21.40 | 20.99 | 25.34 | $a_1$ | $CH_3(\sigma)$ |
| 22.40 | 22.85 | 27.45 | $b_2$ | $e_{1u}(\sigma)$ |
| 23.70 | 23.53 | 28.43 | $a_1$ | $e_{1u}(\sigma)$ |
| | 26.71 | 31.40 | $a_1$ | $a_{1g}(\sigma)$ |
| AVE.ABSOL. ERROR | 0.24 | 2.17 | | |

Continuation Table 1.

a. Ref. 6

b. Numbers with asterisks are corrected values and those in parentheses are before correction.

c. Assignments in parentheses are those of ref. 6.

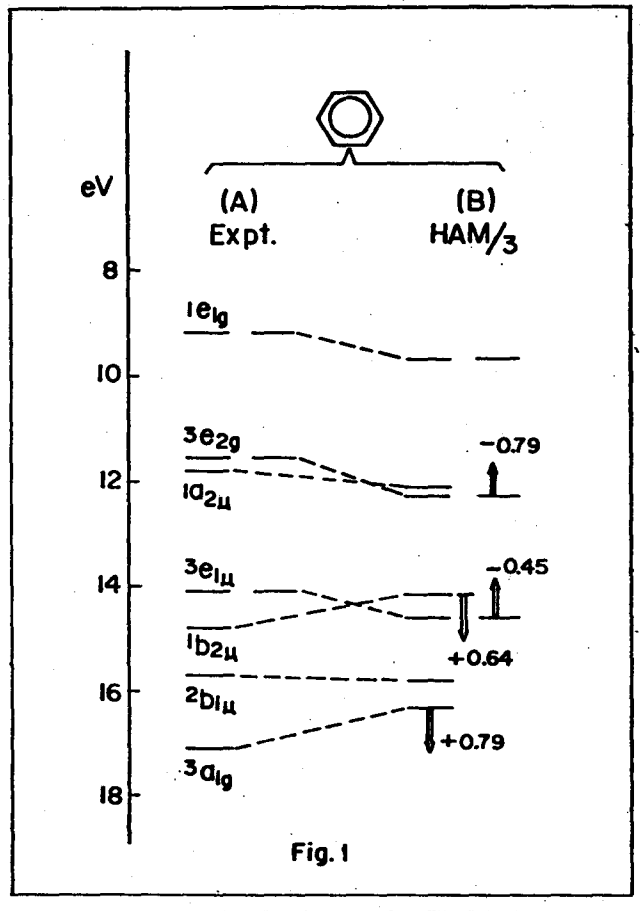

Fig. 1

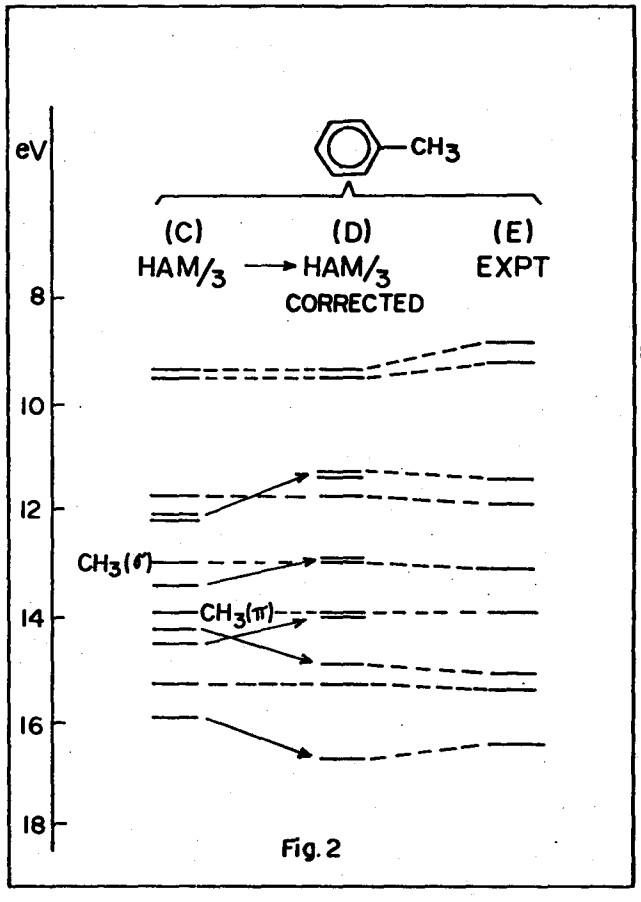

Fig. 2

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