

## ARTICLE

*Ab initio* Study on Ionization Energies of 3-Amino-1-propanol

Ke-dong Wang\*, Ying-bin Jia, Zhen-jiang Lai, Yu-fang Liu

College of Physics and Information Engineering, Henan Key Laboratory Photovoltaic Materials, Henan Normal University, Xinxiang 453007, China

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Fourteen conformers of 3-amino-1-propanol as the minima on the potential energy surface are examined at the MP2/6-311++G\*\* level. Their relative energies calculated at B3LYP, MP3 and MP4 levels of theory indicated that two most stable conformers display the intramolecular OH...N hydrogen bonds. The vertical ionization energies of these conformers calculated with *ab initio* electron propagator theory in the P3/aug-cc-pVTZ approximation are in agreement with experimental data from photoelectron spectroscopy. Natural bond orbital analyses were used to explain the differences of IEs of the highest occupied molecular orbital of conformers. Combined with statistical mechanics principles, conformational distributions at various temperatures are obtained and the temperature dependence of photoelectron spectra is interpreted.

**Key words:** *Ab initio*, 3-amino-1-propanol conformer, Vertical ionization energy, Hydrogen bond, Natural bond orbital

## I. INTRODUCTION

3-amino-1-propanol (3AP) is an important intermediate of medicine, which is used to synthesize cyclophosphamide tablets, prenylamine, and alcohol dl-pantotenilico. It is characterized by four independent torsional angles ( $\angle C-C-N-Lp$ ,  $\angle N-C-C-C$ ,  $\angle C-C-C-O$ , and  $\angle C-C-O-H$ ; Lp=lone pair). Rotating around each of the four internal axes (C-N, C-C, C-C and C-O) leads to three different rotamers, giving a total of  $3^4=81$  staggered conformations. Among these conformations, 41 correspond to non-equivalent energetical forms. On the other hand,  $-NH_2$  and  $-OH$  in this molecular could form intramolecular hydrogen bond (HB). These conformational and HB behaviors have brought many difficulties to the experimental and theoretical studies of the electronic structure of 3AP. The microwave [1], infrared [2, 3], Raman [3, 4] and electron diffraction [4, 5] experiments combined with *ab initio* calculations [2, 6–8] showed that the predominated conformation of the gas phase 3AP was characterized by an OH...N intramolecular HB. This intramolecular HB interactions affecting the electronic structures of 3AP were observed in the photoelectron spectra (PES) measured by Leavell *et al.* [9]. It was observed that ionization potential of the highest occupied molecular orbital (HOMO) which is the electron donor in HB of 3AP were temperature dependent, and decreased with increasing temperature.

The ionization potential of 3AP was markedly greater than the values for the analogs without HB. They qualitatively interpreted this difference via the stabilization energy of the lone pair involved in HB. There is no doubt that a more coherent account of the finding is required. Nevertheless, it is difficult to deduce the detailed structure information from the experiments, and the corresponding theoretical studies are necessary.

In this work, fourteen low-lying conformers of 3AP are studied. Their relative energy at different theoretical level are obtained, and their vertical ionization energies (IEs) of HOMO and the next highest occupied molecular orbital (NHOMO) are calculated. On the base of the calculated IEs and conformational distributions, the ionization bands moving with the temperature is interpreted.

## II. THEORETICAL METHODS

All the calculations were performed with Gaussian 03 programme [10]. 41 rotamers were used as the guess structures and fully optimized with the B3LYP/6-311G method, and then the obtained conformers were re-optimized at the MP2/6-311++G\*\* level and all without imaginary frequency. The relative energies of the fourteen low-lying conformers were calculated at the B3LYP and the extrapolated MP3 (including the third-order correlation corrections) [11] and MP4(SDTQ) [12] (including the fourth-order corrections and using the space of the single, double, triple and quadruple substitutions) method with aug-cc-pVTZ basis set [13]. MP2 optimized geometries were used for propagator calculations with aug-cc-pVTZ basis set. The P3 electron

\* Author to whom correspondence should be addressed. E-mail: wangkd@htu.cn, Tel.: +86-373-3326154

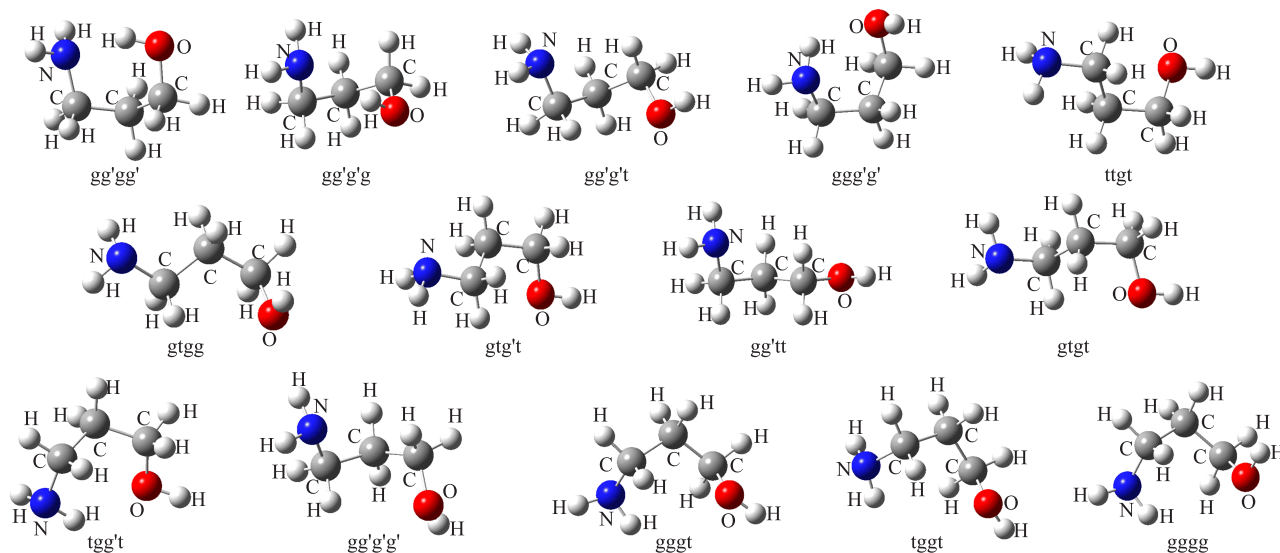


FIG. 1 Fourteen low-lying conformers of 3-amino-1-propanol.

propagator approximation [14] with the quality basis sets have been shown to give excellent agreement with experimental PES for nucleic acid bases [15, 16] and some organic molecules [17, 18]. Average errors of 0.1–0.2 eV are typical for this kind of calculation. All virtual and occupied valence molecular orbitals (MO) were retained in the propagator calculations.

For every vertical IE calculated with electron propagator theory, there corresponds a MO such that

$$\begin{aligned} \phi^{\text{MO}}(x_i) = N^{-1/2} \int \Psi^{(N-1)}(x_1, x_2, \dots, x_{i-1}, x_{i+1}, \\ \dots, x_N) \Psi^{(N)}(x_1, x_2, \dots, x_N) dx_1 dx_2 \dots \\ dx_{i-1} dx_{i+1} \dots dx_N \end{aligned} \quad (1)$$

where  $N$  is the number of electrons in the neutral molecule and  $x_i$  is the space-spin coordinate of electron  $i$ .  $\Psi^{(N)}$  and  $\Psi^{(N-1)}$  are the total electronic wave functions for the molecule ground (initial) state and the final ion state. The MO can further be simplified to be proportional to canonical Hartree-Fock (HF) orbital in P3 approximation. Pole strength is equal to the integral over all space of the absolute value squared of the Dyson orbital, representing the perturbation to the results of Koopmans' theorem. The approximations are validated only when the pole strengths lie between 0.85 and unity.

The natural bond orbital (NBO) [19] analysis transfers the delocalized MOs into the localized ones that are closely tied to chemical bond concepts. The interaction between filled (*e.g.*, the lone-pair) and anti-bonding orbitals represents the deviation of the molecule from the Lewis structure and can be used as a measure of the delocalization due to the intramolecular HBs studied in this work. The energy lowering due to the delocalization caused by the intramolecular HB interactions

can be treated by the second-order perturbation energy  $E(2)$  in the NBO theory,

$$E(2) = -\frac{n_\sigma F_{ij}^2}{\Delta\varepsilon} \quad (2)$$

where  $n_\sigma$  is the population of the lone-pair ( $n$ ) orbital,  $F_{ij}$  is the Fock matrix (or Kohn-Sham matrix in DFT) element between the NBOs  $i(n)$  and  $j(\sigma^*)$ , and  $\Delta\varepsilon$  is the energy level differences between these two orbitals. This method has been successfully used to analyze both inter- and intramolecular interactions [20, 21].

### III. RESULTS AND DISCUSSION

Figure 1 depicts the structures of the fourteen low-lying conformers. The obtained conformations are labeled by rotation around the central two C–C bonds using the letter g ( $\angle\text{N–C–C–C}=60^\circ$  or  $\angle\text{C–C–C–O}=60^\circ$ ), g' ( $\angle\text{N–C–C–C}=-60^\circ$  or  $\angle\text{C–C–C–O}=-60^\circ$ ) or t ( $\angle\text{N–C–C–C}=180^\circ$  or  $\angle\text{C–C–C–O}=180^\circ$ ), preceded and followed by the letters which indicate the geometry adopted by the  $\angle\text{C–C–N–Lp}$  (Lp=lone pair) and  $\angle\text{C–C–O–H}$  axes, respectively; the letters g, g' and t, refer to values of the appropriate dihedral angles are close to  $60^\circ$ ,  $-60^\circ$ , and  $180^\circ$ , respectively. In gg'gg' and gg'g'g conformers, the length of OH...N is 1.99 and 2.32 Å respectively. And in ggg'g', NH...O is 2.31 Å. All of them are smaller than the sum of the van der Waals radii (N+H=2.7 Å and O+H=2.60 Å) [22] indicating OH...N or NH...O intramolecular HBs formed in these three conformers. This result is in agreement with the HF and MP2 calculations from Cacela *et al.* [3]. The strength of these HBs will be discussed in the following text.

TABLE I Calculated relative energies (in kJ/mol) of 3AP.

	MP2 <sup>a</sup>	B3LYP <sup>b</sup>	MP3 <sup>c</sup>	MP4 <sup>d</sup>	$A_{296}^e/\%$	$A_{473}^e/\%$
gg'gg'	0	0	0	0	93.08	69.41
gg'g'g	8.10	10.57	8.01	8.15	3.3880	8.724
gg'g't	10.41	12.20	12.15	13.04	0.4644	2.515
ggg'g'	11.43	11.33	11.01	11.83	0.7586	3.419
ttgt	13.67	12.88	14.33	15.75	0.1543	1.262
gtgg	13.95	12.76	13.74	15.37	0.1802	1.390
gtg't	13.31	13.10	13.95	15.57	0.1656	1.319
gg'tt	13.53	13.66	14.25	15.87	0.1472	1.225
gtgt	13.56	13.21	14.19	15.70	0.1577	1.279
tgg't	13.61	13.74	14.13	14.92	0.2161	1.558
gg'g'g'	13.35	13.74	14.02	14.81	0.2258	1.601
gggt	11.73	14.39	12.73	13.15	0.4446	2.447
tggt	13.57	14.74	14.33	14.96	0.2125	1.542
gggg	12.52	14.19	12.79	13.36	0.4067	2.314

<sup>a</sup> Including the ZPVE, scaled by 0.94.

<sup>b</sup> B3LYP/aug-cc-pVTZ.

<sup>c</sup> MP3/aug-cc-pVT.

<sup>d</sup> MP4(SDTQ)/aug-cc-pVTZ.

<sup>e</sup> Abundance percentages obtained using the MP4 results.

Table I lists the relative energies computed with B3LYP, MP2, MP3, and MP4(SDTQ) methods. Although the different calculations predict the different stability orders, all the theoretical calculations predict the gg'gg' conformer is the most stable one and gg'g'g conformer the next stable. Theoretical studies carried out at the HF/4-31G [6–8] and B3LYP [2, 3] levels have established the importance of the intramolecular OH...N interaction increasing the stability in this type of compounds. It is noted that the ggg'g' conformer having NH...O HB is predicted to be the third stable one at B3LYP, MP3, and MP4 level in the present calculations. This is also in agreement with the theoretical results [2, 3, 6–8] that NH...O HB was present in four of the minima in the potential energy surface of 3AP.

The exponential function abundance is proportional to  $\exp(-\Delta E/RT)$ , *i.e.*  $A \propto -\Delta E/RT$  where  $\Delta E$  is the relative energy,  $R$  is the gas constant, and  $T$  is temperature. The conformational distributions obtained at the MP4/aug-cc-pVTZ level at the various temperatures are also shown in Table I. The abundance  $A$  of the most stable gg'gg' conformer is 93.08% at 296 K and decreases to 69.41% when the temperature rises to 473 K.

The first two vertical ionization energies of fourteen low-lying conformers of 3AP calculated at P3/aug-cc-pVTZ level of theory are compiled in Table II and compared with experimental results from Ref.[9]. In addition to the P3 results which include electron correlation and orbital relaxation effects, the values based on the Koopmans' theorem (HF/aug-cc-pVTZ) are also given.

TABLE II Vertical IE (in eV) of 3AP based on MP2/6-311++G\*\* optimized geometries.

Conformer	HOMO		NHOMO	
	HF <sup>a</sup>	P3 <sup>b</sup>	HF <sup>a</sup>	P3 <sup>b</sup>
gg'gg'	10.91	9.84	11.50	10.18
gg'g'g	10.97	9.91	11.74	10.40
gg'g't	10.56	9.50	11.82	10.60
ggg'g'	10.53	9.46	11.78	10.60
ttgt	10.39	9.34	12.23	10.93
gtgg	10.67	9.61	11.97	10.71
gtg't	10.49	9.43	12.10	10.90
gg'tt	10.68	9.62	11.90	10.66
gtgt	10.51	9.45	12.02	10.82
tgg't	10.18	9.10	12.33	11.07
gg'g'g'	10.61	9.56	11.91	10.59
gggt	10.48	9.42	12.04	10.83
tggt	10.36	9.31	12.23	10.96
gggg	10.59	9.53	11.93	10.73
Exp. with $T=296$ K [9]	9.77	9.77	10.48	10.48
Exp. with $T=473$ K [9]	9.55	9.55	10.61	10.61

<sup>a</sup> HF/aug-cc-pVTZ method based on Koopmans' theorem.

<sup>b</sup> P3/aug-cc-pVTZ.

Discrepancies between the Koopmans and P3 results indicate that relaxation and correlation corrections vary from 1.0 eV to 1.3 eV.

It is seen from Table II that the different conformers have different IEs. The gg'gg' and gg'g'g conformers have greater IE of HOMO ( $IE_{\text{HOMO}}$ ) than the other conformers of 3AP without OH...N HB. In order to interpret the  $IE_{\text{HOMO}}$  differences between these two conformers (gg'gg' and gg'g'g) and the other ones, the NBO analyses [19] for all possible intramolecular HBs for all conformers of 3AP are summarized in Table III. It is shown that the intramolecular OH...N HB in gg'gg' conformers is the strongest and the same type HB in gg'g'g is the next strongest, and NH...O HB in ggg'g' is the most weak. If there is no OH...N HB in 3AP, the  $IE_{\text{SHOMO}}$  for all conformers will have similar IEs. In the NBO theory, the  $n_{\text{N}} \rightarrow \sigma_{\text{OH}}^*$  interaction leads to the lowered energy levels of the occupied orbital. The energy  $E(2)$  lowered by this delocalization interaction for gg'gg' conformer is 0.38 eV and for gg'g'g is 0.08 eV. Thus the energy level of HOMO (mainly with  $n_{\text{N}}$  character) for gg'gg' and gg'g'g conformers are lower than those without the OH...N HB. Thereby, the corresponding  $IE_{\text{SHOMO}}$  of these two conformers are higher than the others. This approach is successfully used to interpret the PES of proline [15] in which a remarkably strong OH...N HB is observed. In the same way, the  $IE_{\text{NHOMO}}$  of ggg'g' conformer should be higher than the others. But the fact is not so. Similar result of N-methylglycine [23] can be found, which is worthy of

TABLE III Intramolecular HB lengths  $d$  and NBO analyses of the HBs of the conformers.

Conformer	$d/\text{\AA}$	NBO analyses		
		$\Delta\varepsilon/\text{a.u.}$	$F_{ij}/\text{a.u.}$	$E(2)/(\text{kJ/mol})$
gg'gg' $n_N \rightarrow \sigma_{\text{OH}}^*$	1.99	0.81	0.076	36.83
gg'g'g $n_N \rightarrow \sigma_{\text{OH}}^*$	2.32	0.79	0.033	7.19
ggg'g' $n_O \rightarrow \sigma_{\text{NH}}^*$	2.31	0.76	0.023	3.59

further investigations.

Leavell and his co-workers measured PES of 3AP more than twenty years ago [9]. They observed that  $\text{IE}_{\text{HOMO}}$  was temperature dependent. When the temperature increased from 296 K to 473 K, the position of the first ionization peak which was assigned to the ionization from  $n_N$  changed from 9.77 eV to 9.55 eV. According to the present calculations, 3AP coexists in 81 conformers. All these conformers may contribute to the PES by the weights of the equilibrium abundances. Considering that the higher total energy of conformer the less abundances, the fourteen low-lying conformers are taken into account in interpreting the PES. The two most stable gg'gg' and gg'g'g conformers having  $\text{OH} \cdots \text{N}$  HBs bears most of the abundance: 96.47% at 296 K and 78.13% at 473 K, and contributes to the ionization peaks to a large extension. At the same time, both of them have larger  $\text{IE}_{\text{SHOMO}}$  of  $n_N$  than the other conformers. As the temperature increases to 473 K, the contributions from these two conformers decrease and other conformers with less stability become more important, which make the ionization peaks move: the  $n_N$  peak to lower IE. This method has been successful in interpreting the PES of 2-aminoethanol [24].

#### IV. CONCLUSION

By *ab initio* calculations, fourteen low-lying conformers of 3AP were discussed. The two most stable gg'gg' and gg'g'g conformers have the intramolecular  $\text{OH} \cdots \text{N}$  HBs. These HBs effect on the molecular electronic structures is discussed on the basis of calculated IEs and NBO analyses. When taking into account the abundances of the different conformers, the PES peaks moving with the temperature is explained.

#### V. ACKNOWLEDGMENTS

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