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# Gamma-ray spectra of hexane (C<sub>6</sub>H<sub>14</sub>) in positron-electron annihilation process

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## HIGHLIGHTS

The role of the positrophilic electrons in annihilation process of hexane has been evidenced by excellent agreement with gas phase experiment. The study suggests that intermolecular interactions of liquid hexane may contribute to eliminate certain individuality of electrons in free molecules to averaged electron behaviours in liquid.

## ABSTRACT

Theoretical gamma-ray spectra of molecule hexane have been calculated and compared with the experimental results in both gas (Iwata(a) *et al.*, 1997) and liquid (Kerr *et al.*, 1965) phases. The present study reveals that in gas phase not all valence electrons of hexane contribute the same degree in the electron-positron annihilation of hexane. The electrons which dominate the positron-electron annihilation of molecules are called positrophilic electrons. The positrophilic electrons are predominately found to involve the electrons on the lowest occupied valence orbital (LOVO) of a free molecule in gas phase. When hexane is confined in liquid phase, however, the intermolecular interactions ultimately eliminate the free molecular orientation and selectivity for the positrophilic electrons in the gas phase. As a result, the gamma-ray spectra of hexane become an “averaged” contribution from all valence electrons, which is again in agreement with liquid phase measurement. The roles of valence electrons in annihilation process for gas and liquid phases of hexane have been recognized for the first time in the present study.

**Keywords:** Gamma-ray spectra of hexane; positron-electron annihilation; positrophilic electrons; lowest occupied valence orbital (LOVO).

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## 1. Introduction

Significant progress has been made to a more detailed understanding of the gamma-ray spectra of atoms and molecules (Kerr *et al.*, 1965, Chung and Hogg, 1967; Crawford, 1994; Danielson *et al.*, 2012; Dunlop and Gribakin, 2006; Ghosh, *et al.*, 1994; Green *et al.*, 2012; Gribakin, *et al.*, 2010; Iwata(a), *et al.*, 1997; Iwata(b), *et al.*, 1997; DeBlonde *et al.*, 1972; Tang, *et al.*, 1992; Wang, *et al.*, 2010; Wang(a), *et al.*, 2012; Wang(b), *et al.*, 2012), although more theoretical achievements have been obtained for atomic systems (e.g. Dunlop and Gribakin, 2006) than for molecules (e.g. Green, *et al.*, 2012; Wang, *et al.*, 2010; Wang(a), *et al.*, 2012). It is well known that the core electrons play a minor role in the electron-positron annihilation processes (Green, *et al.*, 2012; Wang, *et al.*, 2010; Wang(a), *et al.*, 2012; Gribakin, *et al.*, 2010; Iwata(b), *et al.*, 1997), due to significantly larger energies of core electrons in atoms and molecules. As a result, the valence electrons dominate the gamma-ray spectra, which is analogous to the electron scattering processes of molecules.

The interaction between a positron and the target is affected significantly by the total electrostatic potential (ESP) induced by all nuclei and electrons of the target. For an isolated atom, i.e., a one-centre system, the total ESP exhibits a spherical symmetry. As a result, the incoming positron will “feel” the same interaction at the same radius from the nuclei in space. For a multi-centre molecule, however, the total ESP usually does not exhibit a spherical symmetry except for highly symmetric cases such as methane (CH<sub>4</sub>) and fullerene (C<sub>60</sub>). The ESP of a multi-centre molecule exhibits polarity with the electrophilic and nucleophilic (or, positrophilic) sites which do not exist in atoms. It is known that not all valence electrons have the same contributions to the electronic processes of molecules (Green *et al.*, 2012; Wang, *et al.*, 2010; Wang(a), *et al.*, 2012; Gribakin, *et al.*, 2010; Iwata(a), *et al.*, 1997), such as

reactivity and ionization, depending on their orbital shape, symmetry and location. For example, in electron spectroscopy, electron transitions of a molecule can only happen for certain valence electrons (or orbitals), whereas other valence electron transitions of the same molecule can be forbidden.

When a positron is involved, however, the question becomes would each of the molecular electrons annihilate the positron equally, regardless of their orbital energy, shape, symmetry and location? If yes, why could the positron annihilate core electrons differently from the valence electrons with a low probability? If no, what are the electrons which are most likely to be annihilated with the positron, i.e., what are the positrophilic electrons and how to identify the positrophilic electrons? Previous studies (Green *et al.*, 2012; Wang, *et al.*, 2010; Wang(a), *et al.*, 2012; Wang(b), *et al.*, 2012) indicated that not all valence electrons make the same contributions to the positron-electron annihilation of atoms and small molecules in gas phase. A most recent study on methane (CH<sub>4</sub>) indicated (Ma and Wang, 2012) that the positrophilic electrons are not the electrons on the highest occupied molecular orbitals (HOMO) of methane, in agreement with an early study of Crawford (1994) that the annihilation happened underneath of the HOMOs of alkanes. In the present study, we provide more evidences on a larger alkane, i.e., n-hexane (C<sub>6</sub>H<sub>14</sub>), to understand positron-electron annihilation of gamma-ray spectra of a molecule.

The efforts to study annihilation of positron and electron in polyatomic molecules, such as normal hexane, began nearly half a century ago (Kerr *et al.*, 1965; Chuang *et al.*, 1967; DeBlonde *et al.*, 1972). In the well-known measurement of n-hexane (Kerr *et al.*, 1965), the momentum distributions in the two photon annihilating positron-electron process were studied by the same group (Chuang and Hogg) in 1967 who

developed a method based on analytic self-consistent field (SCF) wavefunctions of the carbon and hydrogen atoms of hexane. It was claimed that the positrons annihilate almost exclusively all the valence electrons in the C-H and C-C bonds of hexane (Chuang and Hogg, 1967). The concept of averaged contribution of all valence electrons to the positron-electron annihilation of hexane was quickly accepted, as the theoretical results of Chuang and Hogg (Chuang and Hogg, 1967) (in gas phase) agreed well with their experimental measurement of hexane of (Kerr *et al.*, 1965; DeBlonde *et al.*, 1972), but in liquid phase. Superposition of the multi-centred distribution of momenta averaged the valence electron contributions of the hexane molecules in liquid, hereby eliminating the individual valence electron information in a free molecule (in gas phase). As a result, the total theoretical momentum distribution agreed with the measurement in liquid. The study marked a significant achievement at that time due to limited resources for more detailed studies of larger molecules.

Nobody has reproduced the theoretical results of Chuang and Hogg for n-hexane (Chuang and Hogg, 1967) so far. Recently, Iwata(a) *et al.* 1997 measured the gamma-ray spectra of a series of alkanes including hexane in low-pressure gas phase using the state-of-the-art high resolution Angular Correlation of Annihilation Radiation (ACAR) technique. The gas phase measurement of hexane provides an excellent opportunity for a more detailed theoretical study of the low energy Doppler-shift of gamma-ray spectra of hexane, as the intermolecular interactions among hexane molecules in liquid can be neglected in gas phase. It is noted that in the gas phase measurement, the Doppler-shift of the hexane molecule is given by 2.25 keV (Iwata(a) *et al.* 1997), whereas by 2.93 keV in the earlier liquid hexane measurement (DeBlonde *et al.*, 1972). There is a significant difference of 0.68 keV in Doppler-shift of hexane

between the two measurements. The largest difference in Doppler-shift between the gas phase measurements of methane ( $\text{CH}_4$ ) and dodecane ( $\text{C}_{12}\text{H}_{26}$ ) is only 0.23 keV (Iwata(a) *et al.* 1997), which is nearly three times smaller than 0.68 eV. Such a significant discrepancy in Doppler-shift between two measurements cannot be simply explained as an instrumental/technical issue due to the advancement of the modern technology of Iwata(a) *et al.* , although the earlier measurement (Kerr *et al.*, 1965; DeBlonde *et al.*, 1972) was supported by their theoretical study (Chuang and Hogg, 1967). Such the large discrepancy in hexane measurements implies that a considerably large impact on the measurements attribute to the phase difference (i.e., gas phase and liquid phase). That is, different roles of the valence electrons played in the annihilation processes under gas and liquid conditions. The present study is to reveal the roles of electrons of n-hexane in the gamma-ray spectra in gas phase and liquid phase.

## 2. Theoretical treatment and results

The molecular electronic wave-functions of n-hexane are calculated using the Gaussian09 computational chemistry package (Frisch *et al.*, 2009). The model chemistry employed is the *ab initio* HF/TZVP model, i.e. the Hartree-Fock theory and the TZVP basis set (Schaefer *et al.*, 1994). The details of this HF/TZVP model can be referred to our previous studies (Green *et al.*, 2012; Wang *et al.*, 2010; Wang(b) *et al.*, 2012). The valence electron wave-functions of hexane produced using the HF/TZVP model are directly mapped into the momentum space (Ferrell, 1956). The spherically averaged gamma-ray spectra of the valence electrons are then calculated using the equations in Wang, *et al.*, 2010.

The structure of the normal hexane in three dimensional (3D) spaces is given in Fig.1 (a), together with the atom labelling and calculated atomic charges in brackets based on Mulliken population analysis (Frisch, *et al.*, 2009; Mulliken, 1955). Table 1 gives the calculated molecular geometric properties of n-hexane and compared with available literature values. As n-hexane has a  $C_{2h}$  point group symmetry so that only the unique geometric properties regarding the C-C and C-H bond lengths and bond angles are given in this table (other geometric parameters can be produced by point group symmetry). As shown in this table, the C-C and C-H bonds agree well with available results of Hunter and East (Hunter, *et al.*, 2002). Although small, the terminal C-C and C-H bonds, such as C(1)-C(6) and C(1)-H(9), are smaller than the centre bonds such as C(1)-C(4) and C(3)-H(17). The present study and Hunter and East (Hunter, *et al.*, 2002) also agree that the C(3)-H(17) bond is the longest C-H bond of n-hexane. The C-C bond angles of the n-hexane are in agreement with other literature results (Norman, *et al.*, 1961).

Fig.1 (b) reports the calculated total electron density of n-hexane mapped on the total molecular electrostatic potential (ESP) with the positive (blue) and negative (red) potentials represented by the color scheme. The interaction between a positron and a molecule or an atom can be represented by the total electrostatic potential (ESP) induced by all nuclei and electrons. The ESP is calculated ab initio in the present study. More details about ESP are given in an earlier study of Ma and Wang 2012. It is suggested by a recent study that the attractive potential and the chemical environment of a molecule play important roles in the annihilation process (Danielson, *et al.*, 2012). The calculated total ESP is the electrostatic Coulomb interactions of the hexane system with a positron, which can be employed as an

indicator of the positrophilic sites in the annihilation processes (which will be discussed later).

It is well known in organic chemistry that all the C-H bonds of hydrocarbons are polar bonds although normal alkanes such as n-hexane do not possess a permanent dipole moment. As shown in Fig.1(b), the negative potentials (red) concentrate on the carbon atoms, whereas the positive potentials (blue) concentrate on the hydrogen atoms, which is in agreement with the Mulliken population charges indicated in Fig.1 (a). As indicated by Tachikawa *et al* in their recent study (Tachikawa, *et al.*, 2011) the positron is attached to the electronic negatively charged nitrogen atom of the C-N bond of the CH<sub>3</sub>CN molecule rather than other atoms. In the case of hexane, the positron is likely to attach to the partially electronic negatively charged carbon atom of the C-H polar bond of n-hexane.

Fig1 (b) also indicated that the ESP distribution is not the same on all the carbon atoms nor on all the hydrogen atoms in the n-hexane, depending on the point group symmetry of hexane. For example, the negative potential (and charge, too) is more intensive at the terminal carbon atoms (i.e., C(1) and C(2)) and the C-C bond regions. As a result, these intensive negative potential regions are the more positron attractive regions. On the contrast, the partially positive potential regions such as vicinity of the hydrogen atoms are likely positron repulsive.

The probability of a positron to annihilate an electron from a molecular orbital *i* of the target molecule is estimated as (Crawford, 1994)

$$P_i = N \sum_j |C_{ij}|^2, \quad (1)$$



where  $C_{ij}$  are the coefficients of the atomic orbital (basis set)  $j$  to the molecular orbital  $i$  and  $N$  is the normalization factor (Crawford, 1994). The  $C_{ij}$  coefficients represent a particular molecular orbital  $i$  in the presentation of a set of given atomic orbitals (basis set),

$$\psi_i = \sum_j C_{ij} \phi_j \quad (2)$$

The  $C_{ij}$  coefficients are the solutions of the HF equation obtained using the self-consistent field. In quantum mechanics, Eq. (1) indicates that the probability of annihilation is target orbital dependent. As a result, the dominant orbitals are determined by the largest  $|C_{ij}|^2$  terms in Eq. (1) in the annihilation process in gas phase. However, the summation of all these  $|C_{ij}|^2$  terms for all (occupied) orbitals represents the probability of annihilation due to the intramolecular interactions in liquid phase. The electrons in such the dominant orbitals of the target molecule are positronphilic electrons (Ma and Wang, 2012).

The positrophilic electrons of n-hexane are the valence electrons which dominate the Doppler-shift of the gamma-ray spectra in gas phase. In our HF/TZVP calculations, the ground electronic state ( $X^1A_g$ ) of the normal hexane ( $C_6H_{14}$ ) with a  $C_{2h}$  point group symmetry has a closed shell configuration with 25 doubly occupied molecular orbitals which contains 19 valence orbitals. The calculated configuration ( $X^1A_g$ ) of hexane contains six inner valence orbitals

$$(4a_g)^2(4b_u)^2(5a_g)^2(5b_u)^2(6a_g)^2(6b_u)^2, \quad (3)$$

and thirteen outer valence orbitals

$$(1a_u)^2(1b_g)^2(7a_g)^2(7b_u)^2(2a_u)^2(8b_u)^2(8a_g)^2(2b_g)^2(9b_u)^2(3a_u)^2(9a_g)^2(3b_g)^2(10a_g)^2, \quad (4)$$

where orbitals  $4a_g$  and  $10a_g$  are the inner most valence orbital which is the lowest occupied valence orbital (LOVO) and the highest occupied molecular orbital (HOMO), respectively. Fig.2 gives the orbital distributions of the LOVO ( $4a_g$ ) and the HOMO ( $10a_g$ ). As seen in this figure, the HOMO contains a number of nodal planes whereas the  $4a_g$  orbital doesn't. As a result, the electrons in the HOMO possess higher (negative) energies than other valence electrons in the molecule.

With a sufficient energy, positron-electron annihilation spectrum of a molecule is largely determined by the wavefunction (orbital) of a valence electron in the molecule. A positron is accelerated in the vicinity of the target hexane by the molecule Coulomb attractive potential (red region in Fig.1 (b)) to annihilate a valence electron in the target. Valence electron distribution of the target hexane is determined by the wavefunctions (orbitals, such as those in Fig.2) which are dominated by the total ESP of hexane (balance of negative and positive components). As a result, the positron density closely relates to the negative potential of the target. Fig.3 shows positrophilic electrons  $6b_u$ ,  $6a_g$ , and  $4a_g$  of hexane, together with the superposition of the positrophilic electrons. It is noted that the positrophilic electrons of hexane all locate in the more concentrated inner valence space of n-hexane (Eq.(3)), in agreement with previous studies of alkanes that the electrons are annihilated underneath of the HOMO (Crawford, 1994).

Fig.4 compares the calculated gamma-ray spectra of n-hexane in the positron-electron annihilation process with available experimental measurements of n-hexane (Iwata(a), *et al.*, 1997; DeBlonde, *et al.*, 1972). Note that the “x” and circle (“o”) spectra are both from the same gas phase measurement of Iwata(a) *et al.* 1997. The “x” spectrum is the original data points from the measurement without manipulation,

whereas the “o”s are the two-Gaussian fit of the same measurement (Iwata(a), *et al.*, 1997). The red triangles (“ $\Delta$ ”) are the earlier measurement of Kerr, *et al.*, (1965) of liquid n-hexane, which has been transformed into gamma-ray spectra from the measured momentum distributions (Iwata(a), *et al.*, 1997) based on equations in Wang, *et al.*, 2010. The black solid spectrum is the calculated Doppler-shift in gas phase from the dominant positrophilic electrons of n-hexane, and the red dash spectrum represents the calculated Doppler-shift in liquid phase from all the valence electrons of n-hexane. The present results from positronphilic electrons in gas phase show an excellent agreement with the measurement ( $\times$ ) of Iwata(a), *et al.*, 1997. On the other hand, our calculations from all valance electrons of hexane result in good agreement with the measurement in liquid phase ( $\Delta$ ) of Kerr *et al.*, 1965, DeBlonde, *et al.*, 1972. It is noted that in the same gas phase experiment of hexane (Iwata(a), *et al.*, 1997), the Doppler-shift obtained from the actual experiment ( $\times$ ) is 2.45 keV whereas the two-Gaussian fit of the same measurement is given by 2.25 keV. That is, an experimental fitting/data handling related discrepancy in the gamma-ray measurement can be as large as  $\pm 0.20$  keV (or  $\pm 8.2\%$ ).

### 3. Discussion

The significant discrepancy in Doppler-shift between two measurements of n-hexane in gas phase and liquid phase indicates that the impact of the phase (i.e., gas phase and liquid phase) is considerably large in the measurements, apart from instrumental and technical issues. The most significant difference between the gas phase and the liquid phase of the same substance is the intermolecular forces. In gas phase (vacuum), a molecule is almost free from intermolecular interactions. A positron most likely annihilates the positrophilic electrons of the free target molecule

determined by the ESP of the molecular target, as the target moves free in the three dimensional space allowing the selectivity of such annihilation.

Unlike atoms, most molecules are non-spherical without shell structures. Valence electrons of a molecule distribute into valence molecular orbitals which locate in various regions of the molecule depending on the orbital energies. As a result, the positrophilic electrons are in the orbitals which take similar shape to the molecular ESP, so that the incoming positron is likely to target the region with the largest electron density in a molecule in the annihilating process. The probability,  $P_i$ , of a particular electron(s) annihilated by a positron which is determined by Eq. (1) is individual valence orbital dependent. As a result, a simple superposition (sum) contribution of all individual valence electrons to the total momentum distributions (gamma-ray spectra) leads to the detail loss of the individual electrons in a target (Wang(a), *et al.*, 2012). This superposition underestimates the positrophilic electrons or over estimates the electrons with only minor roles in the annihilation as previously seen in small molecules (Wang(b), *et al.*, 2012). For example, under plane wave approximation, the calculated Doppler-shift ( $\Delta\epsilon$ ) of the positrophilic electrons of  $O_2$  ( $2\sigma_g$ ) is 2.87 keV ( $\Delta\epsilon_{exp}$  is 2.73 keV), whereas such superposition of all valence electrons ( $\Delta\epsilon$ ) of  $O_2$  is 4.00 keV and all electrons (core + valence) ( $\Delta\epsilon$ ) is 4.22 keV under the same model (Wang(b), *et al.*, 2012).

In liquid phase, however, the hexane molecules aggregate together by intermolecular forces. The hexane molecules cannot move freely in the liquid phase, rather, the molecules are confined in the vicinity of ether other in liquid phase. The neutralization of the positrophilic and electrophilic areas of the target in liquid

eliminates the selectivity of the positrophilic valence electrons, so that all valence electrons of the target need to be included in the spectra.

#### **4. Conclusions**

In summary, the present study calculates gamma-ray spectra of hexane in gas phase and liquid phase, respectively, using the positrophilic electron model and all-valence electron model. The results are in excellent agreement with earlier measurements of the same molecule in gas phase as well as in liquid phase. Such the excellent agreement with measurements confirms that the gamma-ray spectra of hexane are indeed dominated by the positrophilic electrons in gas phase. The present study further indicates that positrophilic electrons of a target molecule are determined by the electrostatic potential (ESP) of the target molecule and the positron. In particular, the positrophilic electrons are dominated by the electrons on the lowest occupied valence orbital (LOVO) of the target hexane. While in gas phase the positrophilic electrons dominate contributions to the gamma-ray spectra, the intermolecular interactions in hexane liquid phase eliminate the selectivity of the electrons so that all valence electrons in liquid contribute to the annihilation process. To our knowledge, it is the first time that the present study accurately calculates the Doppler-shift of gamma-ray spectra of hexane in gas and liquid conditions using *ab initio* quantum mechanical methods, supported by experimental measurements.

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## Figure captions

Figure 1: (a) Bird-view of the structure and atomic labeling scheme of n-hexane ( $C_6H_{14}$ ). Mulliken population charges are also given on each atoms. Note that due to the  $C_{2h}$  point group symmetry, the atomic labels are based on the unique atoms. (b) The total electrostatic potential (ESP) of hexane is mapped on the optimised ball-stick structure of n-hexane. The colour bar represents the values of the ESP (red: negative and blue: positive).

Figure 2: The orbital distributions of the inner most orbital  $4a_g$  and the HOMO,  $10a_g$ .

Figure 3: (a) The contour color-filled map of the positrophilic orbitals of  $4a_g$ ,  $6a_g$ ,  $6b_u$  and  $6b_u+6a_g+4a_g$ . (b) 3D-surface of negative potential (orange) with the electron density of the positrophilic electrons " $6b_u+6a_g+4a_g$ " (cyan).

Figure 4: Gamma-ray spectra of n-hexane molecule in positron-electron annihilation process compared with two experimental measurements. The numbers in brackets are the Full Widths at Half Maximum (FWHM, i.e. the Doppler shift) in keV.

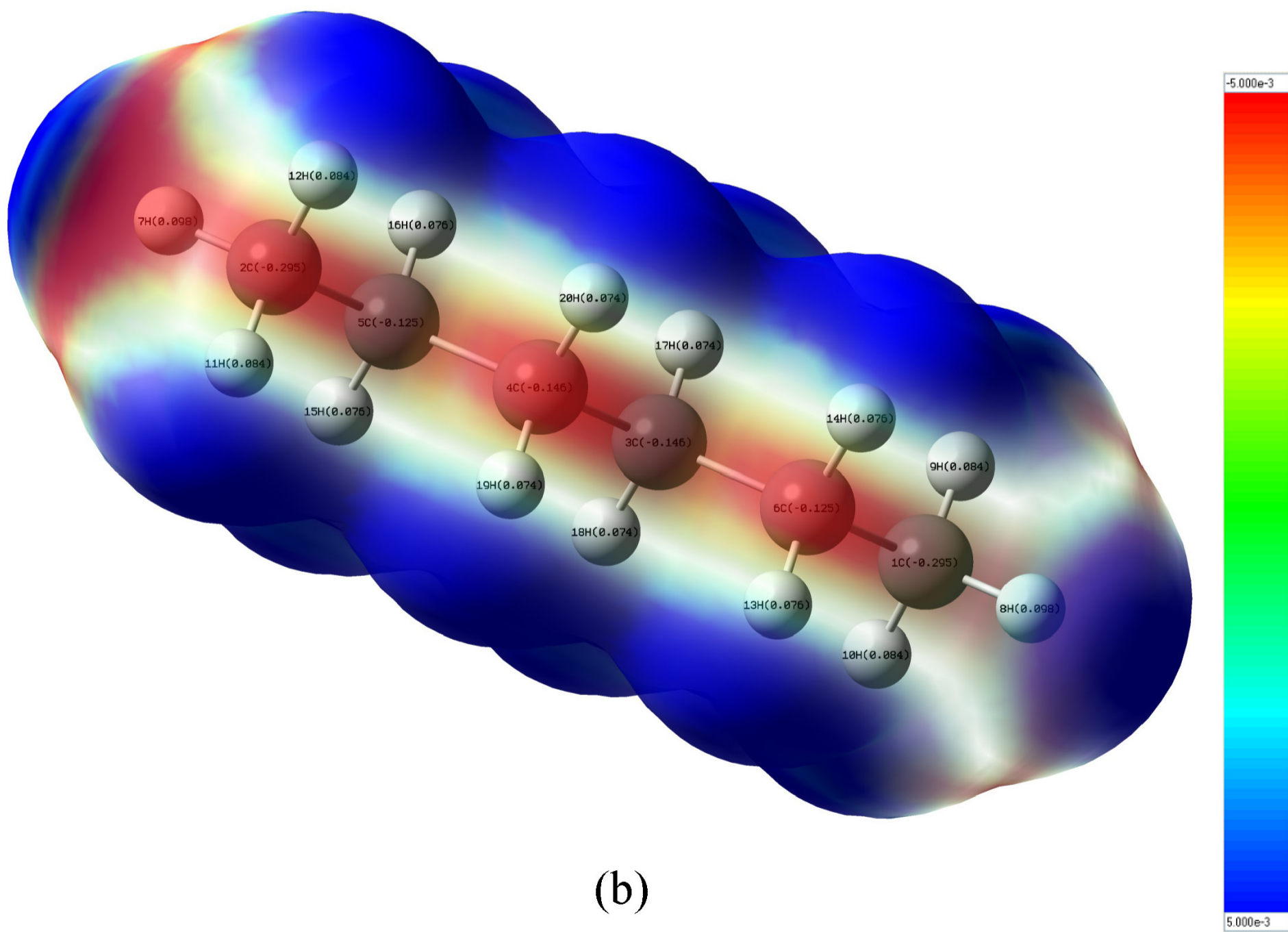
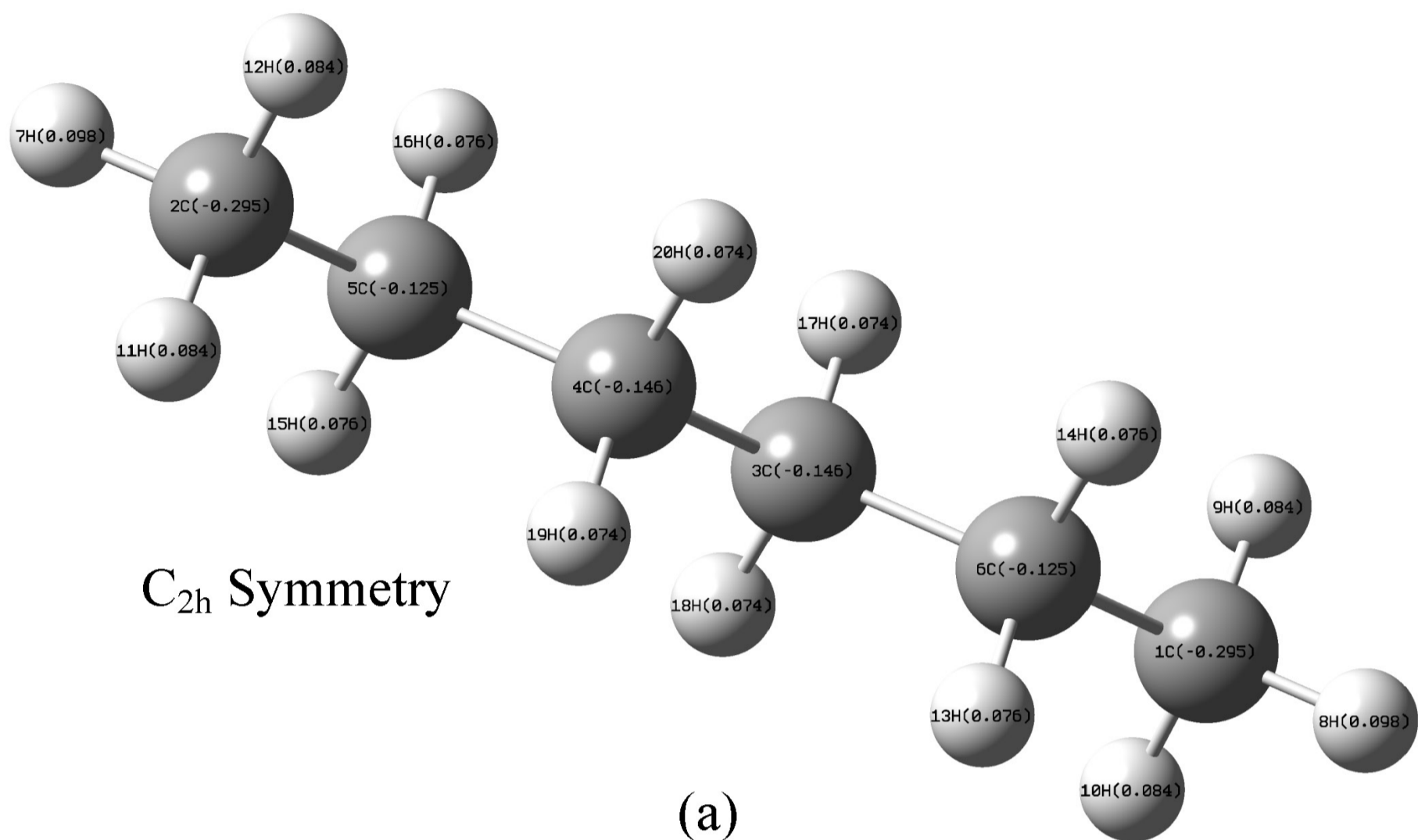
× is the measurement for the low-pressure gas phase provided by Iwata(a), et al. 1997.

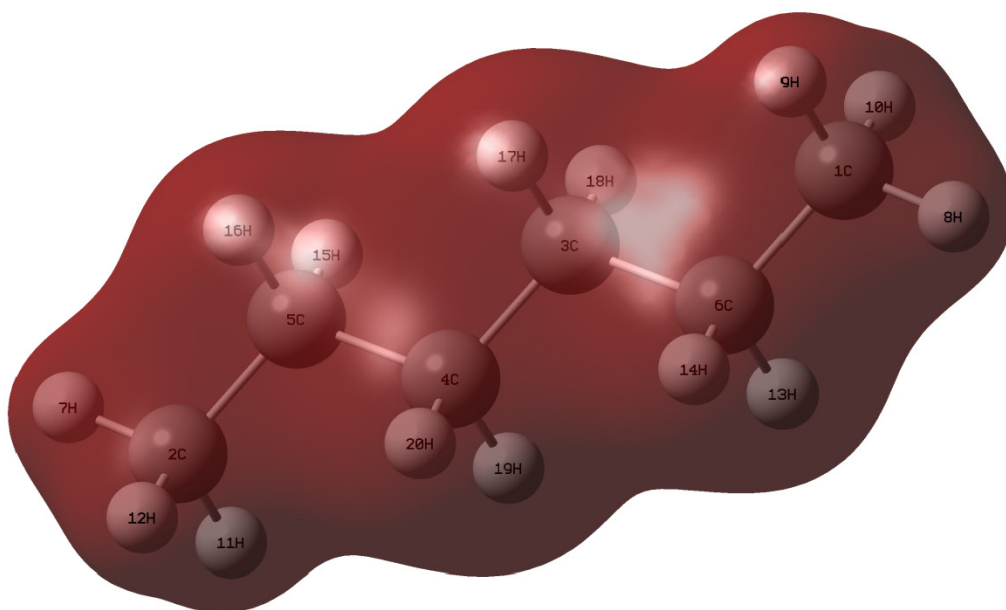
Δ is the measurement of organic liquid hexane of DeBlonde, et al, 1972.

o is the two-Gaussian fitted experimental spectra from the same experiment of Iwata(a), et al. 1997.

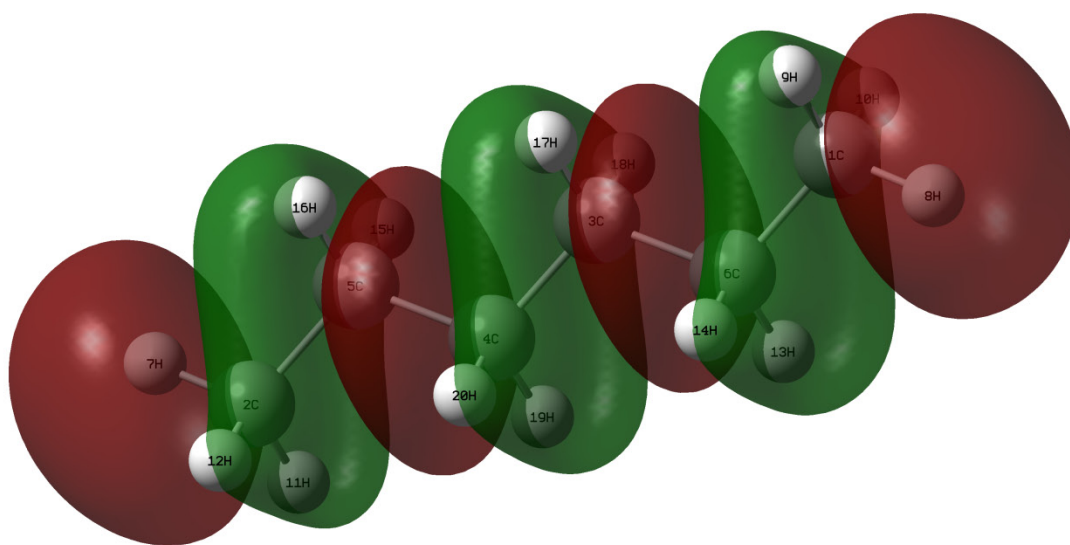
— is the calculated gamma-ray spectra of n-hexane in gas phase obtained from dominant positrophilic electrons of hexane and

- - - is calculated gamma-ray spectra of n-hexane in liquid phase obtained from superposition of all valence electrons of hexane. All spectra are normalized to unity at zero.

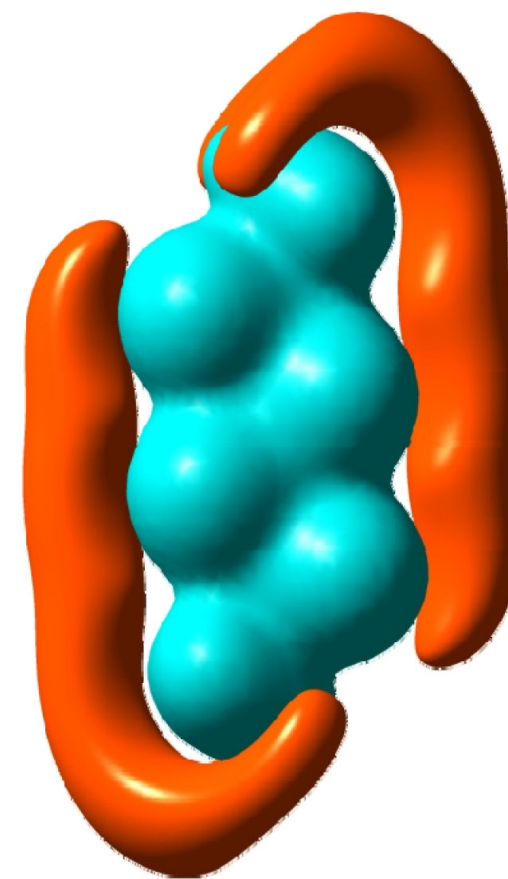
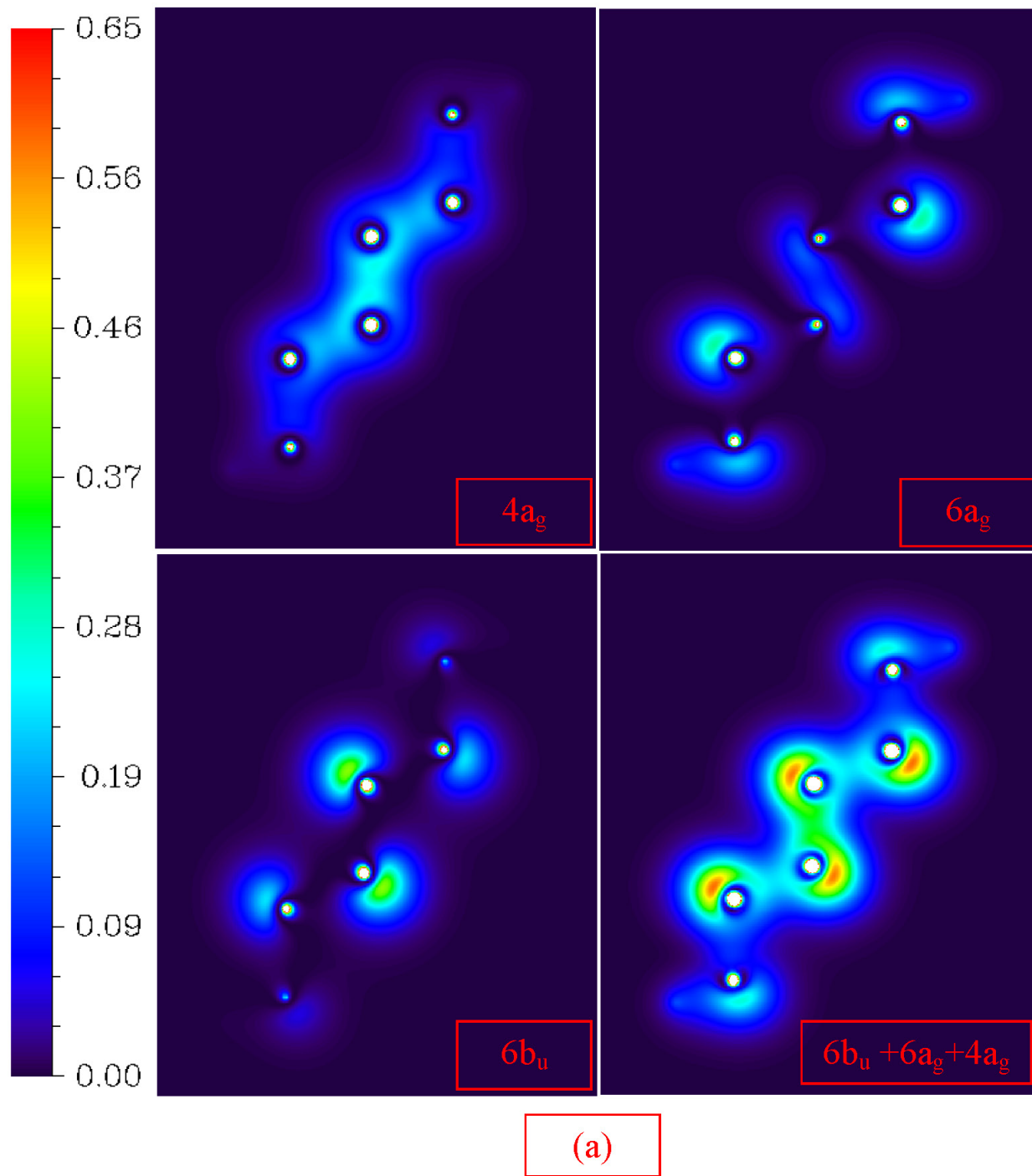




$4a_g$



$10a_g$



(b)

(a)

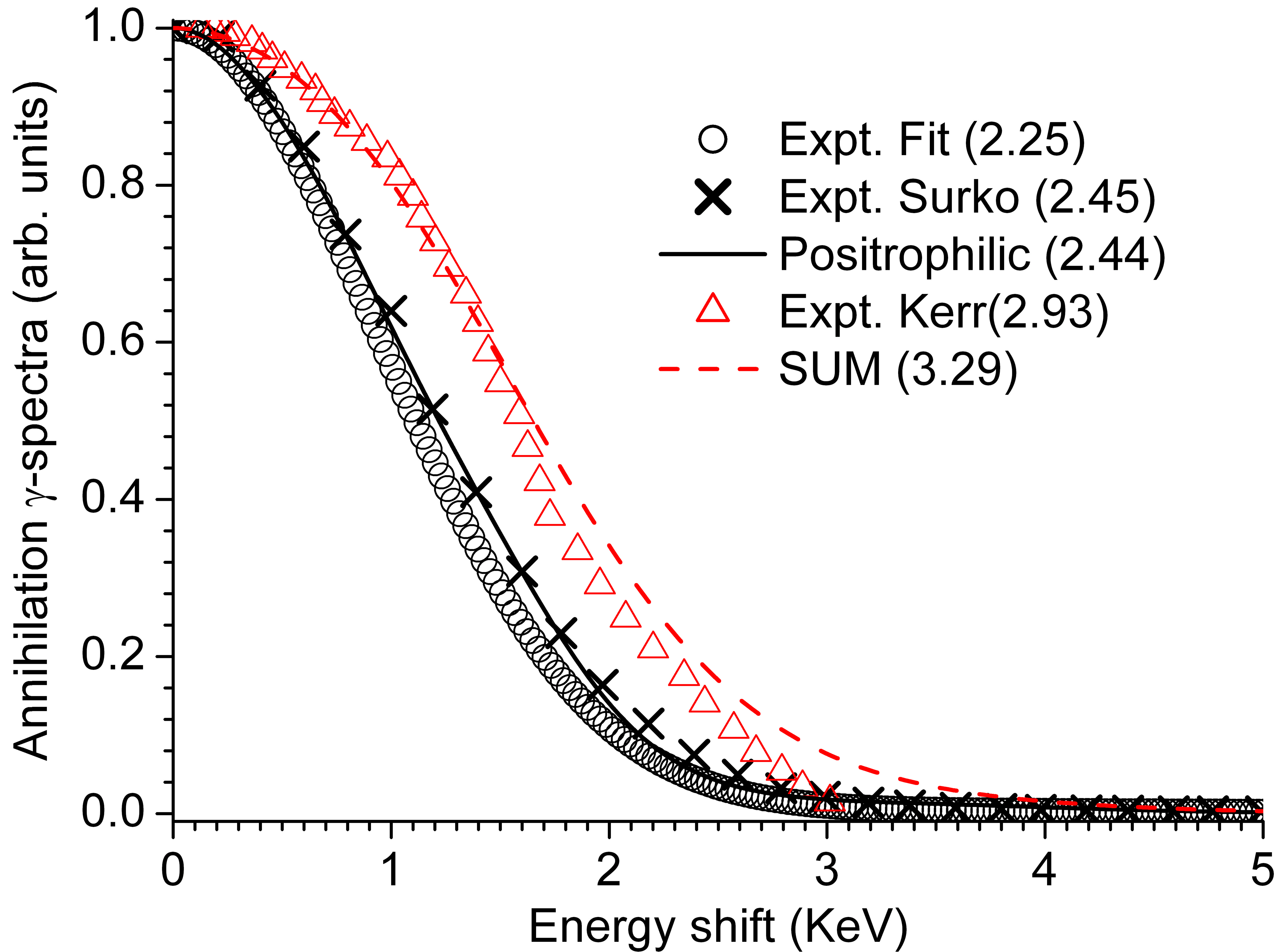


Table 1 Geometric parameters of n-hexane (gas phase) obtained using the HF/TZVP model\*.

Hexane(C <sub>2h</sub> )	This work	Literature values	
C(1)-C(6)	1.5337	1.5246 <sup>a</sup>	
C(3)-C(6)	1.5358	1.5256 <sup>a</sup>	
C(3)-C(4)	1.5355	1.5254 <sup>a</sup>	
Bond lengths (Å)	C(1)-H(8)	-	
	C(1)-H(9)	1.1048	1.090 <sup>a</sup>
	C(6)-H(13)	1.1075	1.090 <sup>a</sup>
	C(3)-H(17)	1.1087	1.094 <sup>a</sup>
Bond angles (°)	C(2)-C(5)-C(4)	113.163	113.6 <sup>b</sup>
	C(5)-C(4)-C(3)	113.607	114.1 <sup>b</sup>

\*The atomic labeling scheme of n-hexane refers to Figure 1(a). (a) from Hunter and East, 2002; (b) from Norman and Mathisen, 1961.