Calculations of gamma-ray spectral profiles of linear alkanes in the positron annihilation process

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ABSTRACT

The positron–electron annihilation gamma-ray spectra of linear alkanes C_nH_{2n+2} ($n = 1$–12) have been studied systematically. A profile quality (PQ) parameter, χ, is introduced to assess the agreement between the obtained theoretical profiles and the experimental measurements in the entire region of energy shift of the spectra. Together with the Doppler shift ($\Delta\varepsilon$) of the gamma-ray spectra, the two parameters, χ and $\Delta\varepsilon$, are able to provide a more comprehensive assessment of the calculated gamma-ray spectra with respect to available experiment. Applying the recently developed docking model, the present study determines the positrophilic electrons for individual alkanes from which the gamma-ray spectral profiles are calculated. The results achieve an excellent agreement with experiment, not only with respect to the Doppler shift, but also with respect to the gamma-ray profiles in the photon energy region up to 5 keV. The study further calculates the gamma-ray spectra of other linear alkanes in the series without available experimental measurements, such as heptane (C_7H_{16}), octane (C_8H_{18}), decane ($C_{10}H_{22}$) and undecane ($C_{11}H_{24}$). The results obtained show a dominance of the positrophilic electrons in the lowest occupied valence orbital (LOVO) in the positron–electron annihilation process, in agreement with previous studies.

1. Introduction

Recently, it was theoretically revealed that specific valence electrons, i.e., the positrophilic electrons in methane and hexane, dominate their annihilation spectra in gas phase. [1,2] Under the low-energy positron plane wave positron (LEPWP) approximation, [7] the $2a_1$ electrons of methane [1] are identified as the positrophilic electrons which dominantly locate in the lowest occupied valence orbital (LOVO). [2] A further study of polar molecules, such as fluorinated methanes, [3] showed that the LOVO electrons again dominate the contribution of the positrophilic electrons in the molecules, in agreement with the results obtained for non-polar molecules. As a result, the docking model which determines the positrophilic electrons from valence electrons of a molecule was introduced. [3] The calculated gamma-ray spectra of the molecules, polar and non-polar, using the docking model agreed well with the experiments. [3] It was further indicated that these positrophilic electrons which are dominated by the LOVO

electrons of a molecule play an important role in positron–electron annihilation process.

In recent studies, [1–3] it is demonstrated that under the LEPWP approximation, [7] the positrophilic electrons are determined by docking the electron density distributions into the local molecular attraction potential (LMAP) of the molecule, both of the electron densities and LMAP are calculated quantum mechanically.[3] In this docking model, the influence of positron wave function is very small and therefore, can be neglected and the LMAP becomes the dominant term to reflect the molecular force field effect on the positron wavefunction. [3] The electrons docking into the positron attractive potential possess the dominant probabilities to annihilate a positron.

The present study applies the docking model under the LEPWP approximation to determine positrophilic electrons, in order to calculate the γ-ray positron–electron annihilation spectra of a completed series of linear alkane molecules in gas phase, i.e., C_nH_{2n+2} ($n = 1$–12), for which accurate measurements are available for many of the molecules. [4] Theoretical expressions of the gamma-ray spectra in the positron–electron annihilation process are given in the Section 2. The calculated results of the linear alkanes are compared with available measurements to validate the theoretical

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model. The model has been applied to study alkanes in the series which do not have experimental measurement available in Section 3, and finally, the conclusions are drawn in Section 4.

2. Theoretical treatment

The local molecular attraction potential (LMAP) which is presented to accommodate the docking in the positron–electron annihilation process, is given by [3]

$$U(r) = -\rho_p(r) \times V_{mol}(r). \tag{1}$$

where $\rho_p(r)$ is the positron density and $V_{mol}(r)$ is the total electrostatic potential, which are calculated quantum mechanically. The local molecular attraction potential (LMAP) is used to describe the physical interaction between a positron and a molecule.

The total electrostatic potential of a molecule represents electrostatic Coulomb interactions with a positive unit charge in a molecule, which includes nuclear $V_{nuc}(r)$ and electronic $V_{ele}(r)$ interactions in a molecule,

$$V_{mol}(r) = V_{nuc}(r) + V_{ele}(r) = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{\rho_e(r')}{|r - r'|} dr'. \tag{2}$$

Substitution of $V_{mol}(r)$ into Eq. (1), the LMAP $U(r)$ becomes

$$U(r) = -\rho_p(r) \times V_{nuc}(r) - \rho_p(r) \times V_{ele}(r)$$
$$= -\sum_A \frac{\rho_p(r) \times Z_A}{|r - R_A|} + \int \frac{\rho_p(r) \times \rho_e(r')}{|r - r'|} dr', \tag{3}$$

where the $\rho_e(r')$ is the electron density. Under the LEPWP approximation, [7] the positron density $\rho_p(r) \approx 1$. As a result, the LMAP only depends on $V_{mol}(r)$ for the positrophilic and electrophilic sites on the molecule in the annihilation processes [3]

$$U(r) = -\sum_A \frac{Z_A}{|r - R_A|} + \int \frac{\rho_e(r')}{|r - r'|} dr'. \tag{4}$$

Under the Born–Oppenheimer approximation, the wave function of the positrophilic electrons in the ith orbital can be expanded by Gaussian type functions (GTFs)

$$\psi_i(r) = \sum_{klmn} C_{klmn} x^k y^l z^m \exp(-a_n r^2). \tag{5}$$

where the expansion coefficient C_{klmn} represents the ith molecular orbital obtained by self-consistent methods and $x^k y^l z^m \exp(-a_n r^2)$ are basis functions.

Therefore, the electron density can be calculated as,

$$\rho_e(r) = \sum_i \eta_i |\psi_i(r)|^2, \tag{6}$$

where $\psi_i(r)$ is the wave function of the electron in the ith orbital of the target in the ground electronic state, and the positron density is given by,

$$\rho_p(r) = \sum_k \eta_k |\varphi_k(r)|^2. \tag{7}$$

here $\varphi_k(r)$ is the wave function of the incident positron with momentum k and η is the occupation number.

The real space wave functions are then directly mapped into the momentum space [6]

$$A_{ik}(\mathbf{P}) = \int \psi_i(\mathbf{r})\varphi_k(\mathbf{r})e^{-i\mathbf{P}\cdot\mathbf{r}}d\mathbf{r}. \tag{8}$$

where $\mathbf{P}$ is the total momentum of the annihilation photons. The probability distribution function at the photon momentum $\mathbf{P}$ in two-photon annihilation is then given by

$$W_i(\mathbf{P}) = \pi r_0^2 c |A_{ik}(\mathbf{P})|^2, \tag{9}$$

where r_0 is the classical electron radius, c is the speed of light. The spherically averaged gamma-ray spectra for each type of electrons are then calculated by using general equations, [6,7]

$$w_i(\varepsilon) = \frac{1}{c} \int \int_{2|\varepsilon|/c}^{\infty} W_i(\mathbf{P}) \frac{P dP d\Omega_P}{(2\pi)^3}. \tag{10}$$

The Doppler shift is therefore, calculated using Eq. (10).

Gamma-ray spectrum of a molecule is a profile over a photon energy range of up to $\Delta\varepsilon$ (5 keV) shift from the central 511 keV position ($P = 0$) when $P \neq 0$. Certainly, the Doppler shift ($\Delta\varepsilon$, i.e, the full width at half maximum (FWHM)) has been recognised as the most important parameter to quantify the spectra of molecules [1–7] and is closely correlated to electron momentum distribution of the molecule.[7] However, the full width at half maximum (FWHM, $\Delta\varepsilon$) parameter can be a necessary but not a sufficient condition to ensure the goodness of the calculated momentum profiles. For a satisfied agreement between theory and measurement, in this study, we introduced the second parameter, i.e., profile quality (χ) which is given by the root-mean square deviation (RMSD) between the theoretical and the experimental results of the gamma-ray spectrum of a molecule,

$$\chi = \sqrt{\frac{\sum_{i-1}^{N} (\sigma_{T,i} - \sigma_{E,i})^2}{N}} \times 100\%. \tag{11}$$

Where $\sigma_{E,i}$ is the points in the two-Gaussian (2G) fitted experimental gamma-ray spectrum, while $\sigma_{T,i}$ is the corresponding theoretically calculated profile. Here N is the total number of the data points, which is given by $N = 3001$ in the present study for up to 5 keV. This number of points is a sufficiently large number to represent the agreement of the gamma-ray spectral profile. All spectra are normalized to one in arbitrary unit at 511 keV and therefore, all energy shifts are relative to the position at 511 keV.

Theoretical calculations for the electronic structures of alkanes are *ab initio* Hartree–Fock (HF) calculations, which are combined with the TZVP basis set. [8] In this basis set atomic carbon orbitals are constructed by the 5s9p6d scheme of Gaussian type functions (GTFs), while atomic hydrogen orbitals are constructed by the 3s3p scheme of GTFs. The molecular wave functions are then obtained quantum mechanically using the HF/TZVP model and based on the optimised structural parameters. [9,10,13] All electronic structural calculations are implemented using the Gaussian 09 computational chemistry package. [11]

3. Results and discussions

In the series of linear alkanes, C_nH_{2i+2} ($n = 1$–12), accurate gamma-ray experimental measurements [4] are available for methane to hexane ($n = 1$–6), nonane ($n = 9$) and dodecane ($n = 12$), whereas the alkanes with $n = 7$, 8, 10 and 11, that is, heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}) and undecane ($C_{11}H_{24}$) do not have such the measurements. As a result, the theoretical model will be validated using the available experimental results before being applied to study the alkanes without measurements.

Our previous studies [1–3,7,10] have clearly indicated that the contributions to the Doppler shift of gamma-ray in a molecule is orbital dependent. For example, the γ-ray spectra of the smallest alkane molecule, CH_4, [1] reveal that the positrophilic electrons are dominated by the $2a_1$ electrons in the LOVO of this molecule.