PAPER

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Averaged electron collision cross sections for thermal mixtures of β-alanine conformers in the gas phase

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Abstract

A theoretical study of elastic electron scattering by gas-phase amino acid molecule β-alanine (NH_2–CH_2–CH_2–$COOH$) is presented. R-matrix calculations are performed for each of the ten lowest-lying, thermally-accessible conformers of β-alanine. Eigenphase sums, resonance features, differential and integral cross sections are computed for each conformer. The positions of the low-energy shape resonance associated with the unoccupied π^* orbital of the −COOH group are found to vary from 2.5 to 3.3 eV and the resonance widths from 0.2 to 0.5 eV depending on the conformation. The temperature-dependent population ratios are derived, based on temperature-corrected Gibbs free energies. Averaged cross sections for thermal mixtures of the 10 conformers are presented. A comparison with previous results for the α-alanine isomer is also presented.

Supplementary material for this article is available online

Keywords: R-matrix, conformers, resonances, differential cross sections, elastic cross sections

(Some figures may appear in colour only in the online journal)

1. Introduction

β-alanine (3-aminopropanoic acid, NH_2–CH_2–CH_2–$COOH$) is the simplest β-amino acid; it is an isomer of α-alanine in which the amino group is bonded at the β carbon with the respect of carboxylic group (–COOH). β-alanine is found in the interstellar medium and is most abundant amino acid in carbonaceus meteorites (IC chondrites) (Ehrenfreund *et al* 2001). Gas-phase reaction studies show that it can be produced preferentially compared to α-alanine (Blagojevic *et al* 2003). Biological interest in β-amino acids has increased in the recent years due to applications in many research areas of medicine and chemistry (Juaristi and Soloshonok 2005). β-alanine occurs naturally in human tissue and mammalian, such as brain and liver, and insect cuticles, as well as, in plants and fruits (Kasschau *et al* 1984). Despite β-amino acids not forming building blocks of proteins, β-alanine can be converted to α-alanine enzymatically (Hayashi *et al* 1961).

β-alanine exist in central nervous system (CNS) in low concentration and there are some suggestions that it could be designated as a neurohormone (Choquet and Korn 1988) and others as a neurotransmitter (Tiedje *et al* 2010).

In general, amino acids in solid phase or in aqueous environment are found in zwitterionic form (NH_3^+–R–COO^-); however, as isolated molecules in the gas phase they are generally detected in their neutral structure (NH_2–R–$COOH$). Amino acids are very flexible molecules: β-alanine has various singles chemical bonds which can freely rotate and can therefore generate numerous stable conformations, see figure 1. Intramolecular interactions, such as H bonds, are important for determining the relative stability of these conformers and the geometries. A detailed discussion of the low-lying conformers of β-alanine is given in the next section.

There appears to be no published theoretical or experimental data on cross sections for electron collisions by β-alanine molecules. Recently we performed an R-matrix
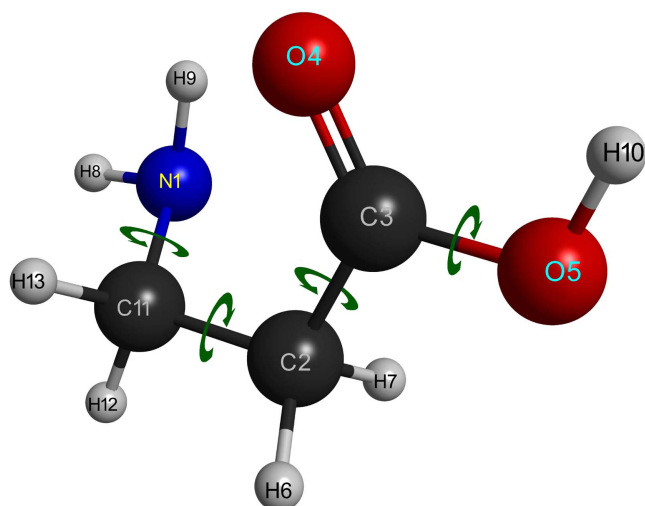
Figure 1. Structure of β-alanine. This amino acid is very flexible; the rotation of various bonds indicated generates many different conformers. (Figure generated with help of MacMolplt software Bode and Gordon 1998.)

study of low-energy electron scattering by α-alanine conformers in the gas phase (Fujimoto *et al* 2016). This study demonstrated that for comparison with gas-phase measurements the theoretical cross sections should be calculated as an average of cross sections of individual conformers weighted by its respective population ratio in the molecular beam at the temperature at which the experiment is performed. Amino acids, in general, are very flexible molecules and in the gas phase they are found in many neutral conformational forms. Our study on α-alanine showed that electron collision cross sections for specific conformation can be very different from those found for other conformers. This is particularly true if there are large differences in the permanent dipole moment between conformers.

A motivation for this study concerns DNA degradation by interaction with low-energy secondary electrons. Since the remarkable work of Boudaïffa *et al* (2000) who demonstrated plasmid DNA exposed to an electron beam with energy less than 20 eV could induce single and double strand brake on DNA molecules, interest in electron collisions with biological molecules has grown considerably. The mechanism of DNA damage is associated with electron attachment. Here the electron is captured, generally in an unoccupied orbital of some DNA building block, and forms a transient anion, called a resonance state. This temporary anion state can then decay into negative and neutral fragments. Knowledge about resonances associated with building blocks provides useful information for describing to fragmentation pathways.

In this work we present another study of low-energy electron collisions with molecules of biological interest, namely conformers of β-alanine. This molecule is thought to have many conformers in the gas phase; we focus on the 10 low-energy conformers which each should be present in significant quantity in the gas phase at a given temperature

due to their low energy relative to lowest conformer. For each of these conformers we calculate the individual cross sections. Temperature-dependent averaged cross sections are computed by weighting each conformer cross section by its populations at the given temperature. Resonance features are discussed for each conformers.

The organisation of article is as follows: section 2 presents a survey of what is know about the gas-phase conformers of β-alanine; section 3 gives an outline of the theory and details of the calculations. Section 4 presents and discusses our calculated data; this is followed by a summary of conclusions.

2. Conformers

As we are interested in studying the amino acid in the gas phase, we survey available theoretical and experimental studies about β-alanine conformers. The first structure calculation of β-alanine conformations that we are aware of was made by Ramek (1990), who performed calculations at the self-consistent field (SCF) level using a 4-31G split valence basis set and found 20 geometries which gave unique local minima in the potential energy surfaces. Ramek designated each unique structures as I, II, III etc following their relative energies (RE), where conformer I is the lowest-energy structure. This nomenclature has been generally adopted and is used by us here. Ramek's structural analysis indicated that intramolecular interactions, such as hydrogen-bonding, give stability to the conformers. Ramek *et al* (1992) made a comparative study using density maps of β-alanine and 3-aminopropanal to correlate spatial structures and bond lengths; they concluded that the CO group is important for the intramolecular interactions of β-alanine.

McGlone and Godfrey (1995), using a Stark-modulated free-expansion jet spectrometer, observed and assigned rotational spectra of β-alanine in the gas phase. With the help of SCF calculations and the experimental rotational constants they asserted that the only two conformers were observed. Heal *et al* (1996) investigated 20 conformers of β-alanine in neutral forms at the SCF level with a 6-31G** basis set and analysed the shape similarities between them using the shape group method.

Rosado *et al* (1997) measured vibrational spectra using Fourier transform infrared (FT-IR), Raman, matrix isolation infrared spectroscopy of β-alanine in zwitterionic and neutral forms. Some vibrational frequencies of β-alanine showed remarkable differences when measured in the crystalline state and in an argon matrix at low temperatures, in the latter they are found in neutral form. A photoionization mass spectroscopy study (Jochims *et al* 2004) of 5 amino acids including β-alanine reported fragmentation patterns, ion appearance energies and ionisation energies, but the composition of conformers in gas phase was not known.

Galano and Alvarez-Idaboy (2005) optimised 12 geometries of isolated β-alanine using second-order Møller–Plesset perturbation theory (MP2) at the MP2/6-311G(d, p)

and MP2/6-311++G(d, p) levels of calculation. High-level calculations with diffuse basis functions confirmed the importance of these kind of basis functions for describing intramolecular interactions and predicting correct RE, as well other molecular properties. Tian (2006) optimised geometries of 10 low-lying conformers of β-alanine using density functional theory (DFT) at the B3LYP/aug-cc-pVDZ level. Energetic calculations were performed, such as, stability order and ionisation potential (IP) and on some radical cations; the relevance of different types of hydrogen bond was considered to interpret the electronic molecular structure of the neutral conformers. This study simulated a theoretical photoelectron spectra (PES) and indicated the existence at least three gauche conformers (G1, G2 and G3) in the gas phase experiments. However, Tian and Yang (2007) reported theoretical photoionization dynamics where only two conformations, G1 and G2, were examined and they affirmed that thermostatic temperatures affect significantly molecular fragmentations induced by photoionization. Sanz *et al* (2006) observed and characterised the 4 lowest-energy conformers of β-alanine in a supersonic jet using a laser ablation molecular beam combined with Fourier transform microwave spectroscopy. They performed calculations on the 20 lowest-energy conformers using MP2 with a 6-311++G(d, p) basis set and determined spectroscopic parameters; by comparison with experimental results they assigned two further conformers beyond the two conformers identified previously by McGlone and Godfrey (1995). The conformers observed were I–V, following the nomenclature of Ramek (1990).

Dobrowolski *et al* (2008) measured FT-IR spectra of β-alanine in a low-temperature argon-matrix for the first time. To interpret these spectra they optimised the ten low-energy conformations at MP2/aug-cc-pVTZ and quadratic configuration interaction singles and doubles (QCISD)/aug-cc-pVDZ level of theory. To analyse conformer abundances they used total energies calculated at the QCISD level with an aug-cc-pVDZ basis with a correction to get relative Gibbs free energies at 298.15 K. The composition found was 40% in the lowest energy conformer I, 15% in IV, II, IX and around 5% in X, while the populations conformers VIII, VI, V, III, and VII each did not exceed 3.2%. Photoionization mass spectra and photoionization efficiency spectra were obtained using laser desorption and vacuum ultraviolet (VUV) synchrotron radiation by Zhang *et al* (2009a), who considered 3 neutral conformers of β-alanine to which they attributed pathways with conformation-specific dissociation channels to generate the fragment ions observed in the experiment.

Ribeiro da Silva *et al* (2010) reported an experimental and theoretical thermochemical study of α-alanine and β-alanine conformers where the Gibbs free energies of formation were calculated to estimate the population in the gas phase at 298.15 K. The composition for the β-alanine was 44.6% in the lowest-energy conformer I, 12.9% in II/VI and 9.9% in V, 6.9% in VI and 5.5% of conformer A and other minor contributions. According to their calculation the structures of conformers II and VI converge to the same minimum. Conformer A was not predicted to be one of the 20 low-energy structures listed by Ramek (1990). Dobrowolski

et al (2011) calculated the nuclear magnetic resonance parameters of 10 β-alanine conformers in gas phase using DFT at the B3LYP/aug-cc-pVTZ-su-1 level to correlate with chemical structure of the conformers and predict their population in the gas phase. The abundances estimated based on relative Gibbs free energy computed at the QCISD/aug-cc-pVDZ level were around 40% of β-alanine to the conformer I, 15% for IV, II, IX, 5% for X and not greater than 3.2% for each of VIII, VI, V, III.

Stepanian *et al* (2012) performed a complete *ab initio* potential energy surface scan at the MP2/aug-cc-pVDZ level and found 20 stable β-alanine conformers. However, based on criteria such as high stability due to RE and low barriers to interconversion, they proposed that only 5 stable structures of β-alanine should exist in low-temperature argon matrices. By analysis of experimental FT-IR spectra and with support from UV irradiation results, they affirmed that 4 conformers were definitely identified, namely conformers I, II, IV and V. Their predicted populations in argon matrix for the 5 conformers I, II, IV, V and VII, estimated based on the relative Gibbs free energies at 420 K and the conformational interconversion barriers, are 48.1%, 23.7%, 16.8%, 3.2% and 8.2%, respectively. These populations are in good agreement with the estimated experimental populations in argon matrices based on the intensities of spectral bands, except for conformer VII which was detected in trace amount. The Gibbs free energies were computed at the 'gold-standard' coupled-cluster singles and doubles plus perturbative triples with complete basis set [CCSD(T)/CBS] level for 11 lower-energies β-alanine conformers whose population was estimated.

Wong *et al* (2015) used a FT-IR matrix isolation spectroscopy technique to determine the composition and populations of β-alanine conformers in solid para-hydrogen and compared their results with their own measurements in argon matrix. They performed DFT calculations of the vibrational wavenumbers and intensities of eleven low-energy conformers at the B3LYP/aug-cc-pVTZ level to assign the spectra. Five conformers were identified in the parahydrogen matrix, namely I, II, III, IV and VII; conformer III was observed in a matrix environment for the first time. Only four conformers, I, II, IV and VII, were assigned in argon matrix, however conformer V was not observed in either the argon or the solid parahydrogen matrices in their measured spectra, in contrast to the previous results of Stepanian *et al* (2012). Wong *et al* (2015) also discuss the population of β-alanine in the gas phase based on the relative Gibbs free energies at 390 K.

In this work, we have studied the 10 lowest-energy conformers of β-alanine. The conformers are labelled as I–X, following the nomenclature of Ramek (1990). We used the geometries of β-alanine conformers optimised by Stepanian *et al* (2012) who carried out a complete potential energy surface search at the MP2/aug-cc-pVDZ level of theory. These geometric parameters are available in the supplementary material available online at stacks.iop.org/JPB/50/195201/mmedia as table SM1. To obtain the cross sections we have described the wave functions and other properties of conformers I–X at Hartree–Fock (HF) level using 6-311G* basis in the *R*-matrix calculations. Although Stepanian *et al*

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found 20 stable conformations in their potential energy surface scan, we consider only 10 conformers of β-alanine due to their lower RE. These conformers are the ones predicted to have a significant gas-phase population at the temperatures considered. While the results of the studies discussed above do not uniformly agree on the temperature-dependent population of different β-alanine conformers, there are some aspects of broad agreements. Below we consider the role conformers I–X and use populations proposed by Dobrowolski *et al* (2008), Ribeiro da Silva *et al* (2010), Wong *et al* (2015) and Stepanian *et al* (2012) to construct thermally-averaged results.

3. Calculations

3.1. The R-matrix method

Calculations of elastic collision cross sections for low-energy electrons with β-alanine molecules in the gas phase used the UKRMol implementation of the UK molecular *R*-matrix codes due to Carr *et al* (2012). This method is described in detail by Gillan *et al* (1995) and Tennyson (2010), here we only present an outline of the methodology of calculation.

In the *R*-matrix method the space is divided in two regions: the inner and outer region. The inner region is a sphere of radius a around the target molecule centre-of-mass, which is defined assuming that the whole electronic density of the molecular target is inside this sphere. Here a radius of $a = 10a_0$ was found to be sufficient. When the scattering electron is inside the sphere, the interactions with the N-electrons of the target are more important and we have to consider exchange, correlation and polarisation between them. The wave function of $(N + 1)$-electron system inside the sphere is given by

$$\Psi_k^{N+1}(x_1 \ldots x_{N+1}) = \mathcal{A} \sum_{ij} a_{ijk} \phi_i^N(x_1 \ldots x_N) u_{ij}(x_{N+1}) + \sum_i b_{ik} \chi_i^{N+1}(x_1 \ldots x_{N+1}), \quad (1)$$

where ϕ_i^N are the electronic wave functions of the target in the ith state and u_{ij} is a one-electron continuum wave function, which are expanded in partial waves up to some maximum value of ℓ, ℓ_{max}; $\mathcal{A}$ is an antisymmetrization operator which ensures that the $(N + 1)$-electrons are indistinguishable in the inner-region. The second summation in equation (1) contains L^2 configurations χ_i^{N+1} which involve placing the scattering electron in target orbitals; these configurations are used to include target polarisation effects. a_{ijk} and b_{ik} are coefficients determined variationally using a specially adapted code (Tennyson 1996).

To include polarisation effects we performed a systematic study including up to 30 virtual orbitals from the SCF calculation to generate two particle, one hole (2p, 1h) L^2 configurations, in singlet and triplet excited target states, in the second sum of equation (1). These calculations are generally called static-exchange-polarisation (SEP); this number

of virtual orbitals is also enough to converge simpler static-exchange (SE) calculations.

In the outer region it is not necessary take into consideration exchange and correlation effects, and a set of one-electron, coupled, second-order differential equations are solved to get the scattering observables as a function of electron collision energy.

As β-alanine conformers have permanent dipole moments, the long-range interaction is take into account using a Born closure procedure. In the *R*-matrix methodology the continuum orbitals are expanded up to partial waves of ℓ_{max}, here $\ell_{max} = 4$, and the higher partial waves are included in scattering *T*-matrices via analytic Born *T*-matrices, where the rotating dipole approximation is used to calculate rotational motion to avoid the divergence of nuclei fixed approximation (Padial *et al* 1981, Morrison 1988). Here final elastic cross sections are computed using the code POLYDCS (Sanna and Gianturco 1998) which sums rotational excitations cross sections ($J = 0 \rightarrow J' = 0, 1, 2, ...$) to convergence to allow computed cross sections be compared with measured cross sections which are generally rotationally-unresolved. Table SM2 in the supplementary material presents the rotational constants used in this work.

The systematic study to compute cross sections for each conformer broadly followed the strategy used in our previous studies (Fujimoto *et al* 2012, 2014). These studies provide more details of calculations such as, tests of *R*-matrix radius, number of virtual orbitals etc. We also previously performed *R*-matrix calculations on averaged cross sections of α-alanine conformers in gas phase (Fujimoto *et al* 2016) and demonstrated that the cross sections of the thermal mixture can be very different from the cross sections of the lowest-energy conformer. This is particularly true if the permanent dipole of some conformer is very different from that of the lowest-energy conformation and the relative population of this conformer is significant. Here we executed similar study for β-alanine, but some differences in methodology that we make clear below.

3.2. Populations of conformers

In this study we consider only the 10 lowest-energy conformers which are cited in works of Dobrowolski *et al* (2008), Ribeiro da Silva *et al* (2010), Stepanian *et al* (2012) and Wong *et al* (2015). Although some of these works consider more than 10 low-energy conformers, these higher-energies conformers are generally predicted to be less important. Therefore, we choose only the 10 lowest-energy conformers that are considered to have significant thermal population, for calculating the averaged cross sections.

Our description of the isolated targets used in the *R*-matrix calculations was performed at the SCF or HF level. It is well-known that small RE cannot be computed reliably enough at this level to estimate the Boltzmann populations (Császár 1996, Fujimoto *et al* 2016). Therefore, we choose to use calculated energetic data of the above authors for two reasons: (1) the RE are calculated using higher levels of

Table 1. Permanent dipole moments and various relative Boltzmann population ratio sets temperature-corrected for 10 β-alanine conformers at temperatures from 298.15 to 420 K.

Conformer	Dipole moment, D		Relative population ratio				
	our	MG	D-298 K	R-298 K	W-390 K	S1-420 K	S2-Ar
I	1.2601	1.2	0.410817	0.480389	0.225041	0.252527	0.481
II	2.6715	2.6	0.130378	0.091222	0.148407	0.153213	0.237
III	3.0168	3.0	0.022159	0.033387	0.027639	0.033709	
IV	1.5503	1.4	0.159649	0.073910	0.140827	0.106012	0.168
V	7.2728	6.8	0.022536	0.106261	0.052331	0.062471	0.320
VI	1.7809	1.1	0.024110	0.091222	0.085979	0.080796	
VII	2.7829	2.8	0.015811	0.040356	0.129176	0.077521	0.820
VIII	2.9740	3.1	0.032123	0.035469	0.033670	0.131596	
IX	1.8669	2.1	0.132598	0.023410	0.074838	0.060067	
X	1.9798	1.7	0.049819	0.024374	0.082092	0.042088	

Note. our—dipole moment calculated in HF/6-311G*. MG—dipole moment calculated in HF/6-31G** by McGlone and Godfrey (1995). D is the population based on Dobrowolski *et al* (2008). R is the population based on Ribeiro da Silva *et al* (2010). W is the population based on Wong *et al* (2015). S1 is the population based on Stepanian *et al* (2012). S2 is the population predicted by Stepanian *et al* (2012) in argon matrices.

correlation; (2) they present Gibbs free energies which are evaluated at temperatures near experimental conditions; these correct the relative total energies which are calculated at 0 K. This correction affects the stability order of the β-alanine conformers as shown by Stepanian *et al* (2012) in their figure 6(a), where significant differences in the relative stability of conformers when the temperature varies from 12 to 500 K can be seen. For example, conformer V is the second lowest-energy at 12 K and unlike most conformers, its Gibbs free energy increases with temperature and at 500 K it is the ninth lowest-energy conformer. This indicates that the relative populations show a strong dependence on temperature and that the relative stability order could be very different at different temperature. For example, conformer V has relative Gibbs free energy of 1.71 kJ mol^{-1} at 12 K and 4.88 kJ mol^{-1} at 420 K.

Our previous work (Fujimoto *et al* 2016) used the RE of conformers of α-alanine to estimate its temperature-dependent composition in the gas phase with the RE kept constant with temperature at their 0 K values. Comparison of the averaged cross sections which accounted for theoretical populations showed good agreement with measured populations. However, in this work we use the temperature-corrected relative Gibbs free energies calculated by Dobrowolski *et al* (2008) and Ribeiro da Silva *et al* (2010) at 298.15 K, by Wong *et al* (2015) at 390 K and by Stepanian *et al* (2012) from 298.15 to 500 K to estimated the relative population. Stepanian *et al* (2012) calculated the relative Gibbs free energies in the range 12–500 K. Table 1 presents relative populations for the 10 lowest-energy conformers. Our populations differ slightly from those given in the original papers in the cases where the original work considered more than ten conformers. β-alanine starts to sublime near 360 K and decompose above 400 K, depending on the condition which the experiment is conducted. Thus, we have calculated averaged cross sections for populations between 298 and 500 K because we expect that the measurement of cross sections would be performed at this range of temperature.

Table 1 also presents our computed dipole moment for each conformer. We note that while each conformer possess a permanent dipole, that of conformer V is significantly bigger than for the other conformers. Table 1 compares our calculated dipole moments at the HF/6-311G* level with results of McGlone and Godfrey (1995) obtained at the HF/6-31G** level. Good agreement is found; the small discrepancies can mainly be attributed to our use of geometries optimised by Stepanian *et al* (2012) in at the MP2/aug-cc-pVDZ level of theory.

3.3. Averaged cross sections

We have calculated cross sections for each of conformers with R-matrix method. The averaged integral (ICSs) or differential cross sections (DCSs) for 10 lowest-energy conformers weighted by population ratio is given by

$$(\text{CS})^{\text{avg}}(T) = \sum_i c_i(T)(\text{CS})_i, \qquad (2)$$

where the $c_i(T)$ are the temperature-dependent population ratios and $(\text{CS})_i$ is the SEP DCS or ICS of ith conformer.

4. Results and discussion

Here we show our results for elastic electron β-alanine collisions in the gas phase at energies from 1 to 10 eV and calculated at the SEP level including 30 virtual orbitals. The results comprise eigenphase sum, resonance positions, ICSs and DCSs individual conformers as well as the averaged ICS and DCS weighted by population ratios.

4.1. Eigenphase sums and resonance features

Figure 2 exhibits eigenphase sums for the 10 lowest energy conformers I–X of β-alanine. The behaviour of the eigenphase sums allows us to detect the existence of resonance features. The automated detection and fitting procedure
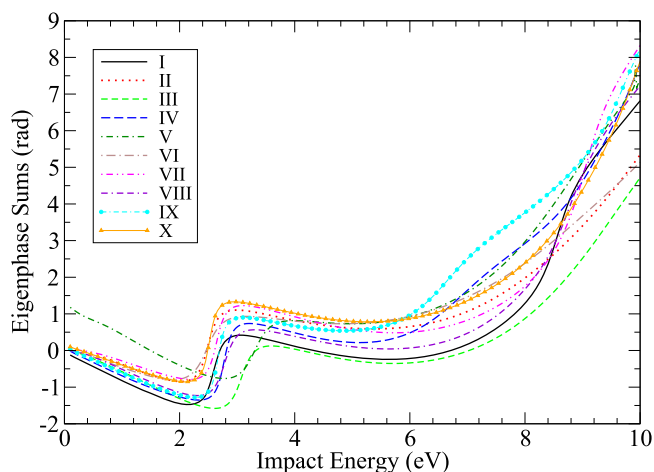
Figure 2. Eigenphase sums for 10 conformers of β-alanine computed at the SEP level.

implemented by Tennyson and Noble (1984), which fits resonance positions and widths to a Breit–Wigner form, was used; the results are presented in table 2. We emphasise that the treatment of polarisation effects is the same for each conformer; 30 virtual orbitals were used in each case and the resonance position and width for can be considered relatively well converged. The resonance position and width of each conformer depend on the stabilisation of the temporary anion, which depends on the level of structure calculation and, in particular, the number of virtual orbitals employed rather than any variation in temperature.

Our calculations make no allowance for the rotational temperature. Tests on previous calculations for the cross sections for water (Faure *et al* 2004) showed that, within the adiabatic nuclei approximation we use here, these cross sections showed negligible variation with temperatures up to 1000 K (Tennyson 2014, unpublished).

The eigenphase sums for all conformations show basically two structures which correspond to the resonances: low-energy near 2.8 eV and higher-energy around 9 eV. Table 2 shows the position of the lower-energy resonance varies from 2.6 to 3.5 eV, depending of the conformer. These lower-energy resonance structures are present in all amino acids and do not show a large energy spread because, as discussed previously (Aflatooni *et al* 2001, Ptasińska *et al* 2005), they are shape resonances associated with the carboxyl group where the electron is temporarily captured by the lowest unoccupied π^* orbital. The difference of about 0.9 eV in the resonance position may be attributed to the stabilisation of –COOH group depending of the conformer as the intramolecular interactions, such as H bonding, is distinct for each of conformer. These resonances are relatively long-lived for shape resonances as can be seen by the sharp resonance whose widths vary from 0.2 to 0.5 eV. The formation mechanism for the higher-energy resonance is not well-established: it has been suggested for glycine that it could be related to core-excited resonance (Tashiro 2008) or a shape resonance associated with the σ^* unoccupied orbital of OH group (Scheer *et al* 2007) of amino acids. These resonances

are broader: the positions of higher energy resonance ranges from 8.0 to 9.8 eV and the widths from 1.8 to 3.6 eV; they are not found for all conformers.

4.2. Differential cross sections

Figure 3 shows the DCS for each of 10 conformers of β-alanine, computed at the SEP level including Born correction, for impact energies of 1, 3, 5 and 10 eV. Table SM3 of supplementary material gives the DCS for each conformers for the energy range from 1 to 10 eV in steps of 1 eV. All the DCS exhibit similar behaviour and are of similar magnitude except for conformer V which has a much larger cross section. The main reason for this is that the conformer V has a very large permanent electric dipole which enhances the long-range interactions and results in a larger cross section. Conformers which have larger dipole moments, in order of decreasing dipole they are V, VIII, III, II and VII, have enhanced cross sections particularly at lower impact energies as seen at 1 and 3 eV of figure 3. Basically the size of the dipole moment determine the approximate magnitude of the DCS. At 1 eV conformer V, which has a dipole moment of 7.3 D and shows the largest DCS, the conformers III and VIII are the second larger DCS with dipole near 3 D, followed by conformer II and VII which have dipole near 2.7 D. We note that issues with measurements at forward scattering angles means that measurements do not always fully reflect the importance of dipolar effects in elastic cross sections (Zhang *et al* 2009b).

We compute averaged DCS whereby the individual DCS of each of 10 conformers were weighted by their population ratio and summed. The population ratios were taken from the literature for temperatures of 298.15 K (Dobrowolski *et al* 2011, Ribeiro da Silva *et al* 2010), 390 K (Wong *et al* 2015) and 420 K (Stepanian *et al* 2012). All these authors have estimated the population ratio using the Gibbs free energy temperature-corrected. Figure 4 plots the averaged DCS for the sets of Dobrowolski *et al* (2011) (D), Ribeiro da Silva *et al* (2010) (R) at 298.15 K, Wong *et al* (2015) (W) at 390 K and also two sets from Stepanian *et al* (2012), one is theoretical (S1) and the other deduced to be found in argon matrix (S2). The S2 set contains only the 5 conformers that were used by Stepanian *et al* (2012) to assign their argon matrix FT-IR spectra, namely conformers I, II, V, IV and VII. Despite the differences in the population, we find that the averaged DCSs are rather similar and are all larger than the DCS of the lowest-energy conformer I; this contrast is increased at lower collision energies. At higher energies near 10 eV all the averaged sets become very close and difference to the DCS of conformer I is also reduced. Comparisons with the figure 3 it can be concluded that even though the DCS of conformer V is much bigger than other conformers, the population this conformer is small at the temperatures considered and consequently this conformer does not contribute significantly to the average.

To evaluate the effects of temperature on the averaged cross sections we used the relative Gibbs free energies due to Stepanian *et al* (2012), who calculated them at temperatures

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Table 2. Resonance parameters for 10 β-alanine conformers: positions (widths) in eV.

	Resonance parameters		
Conformer	Position (width)	Position (width)	Position (width)
I	2.5955(0.2999)	8.5697(0.5213)	
II	2.4921(0.3045)		
III	3.0757(0.3854)	10.2592(0.0119)	
IV	2.7713(0.2423)	7.1150(1.8876)	
V	3.3102(0.5092)	8.9776(2.3050)	9.9219(0.0029)
VI	2.4781(0.4839)		
VII	2.6414(0.2708)	9.0447(0.5911)	
VIII	2.7833(0.3617)	8.7817(0.7672)	
IX	2.6675(0.2070)	6.7416(1.3853)	9.7470(0.9397)
X	2.5178(0.2123)	9.8645(0.8257)	
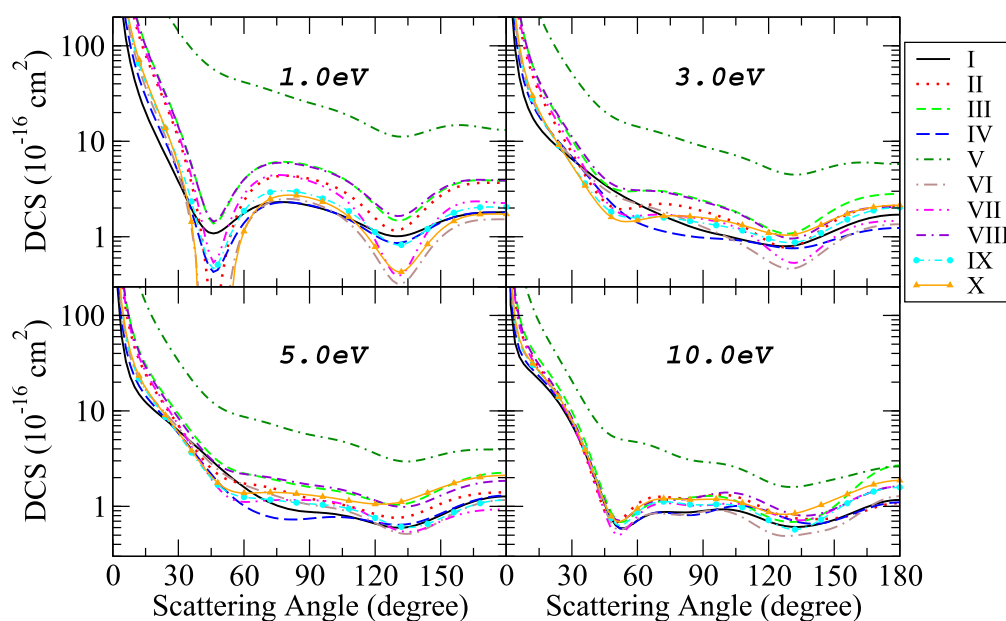
Figure 3. Elastic DCSs for electron collision with β-alanine conformers for impact energies at 1, 3, 5 and 10 eV. Results are for SEP calculations including Born correction.

ranging from 12 to 500 K, to estimate the temperature dependence of population ratio. As their electronic structure calculations for the conformers were all performed the same high level of theory (CCSD(T)/CBS), the comparison should be even handed. We used population ratios at temperatures of 298.15, 390, 420 and 500 K to computed conformer-averaged cross sections; these are near the conditions where the measurements could be carried out considering the sublimation temperature of β-alanine. The results are presented and compared in figure 5. Table 3 shows the population ratios for temperatures of 298.15, 390, 420 and 500 K based on relative Gibbs free energies as calculated by Stepanian *et al* (2012) but considering only 10 conformers of β-alanine. The relative population of conformer I decrease from 38.2% up to 20.5% as the temperature increase. The proportion of conformer II also reduces from 17, 0% to 13.9%. Conformer V, which has a very large dipole, decrease its relative population from 9% to 5% when the temperature increases from 298.15 to 500 K. In general, the population ratio of all other conformers,

increases with temperature. Figure 5 shows that as the temperature increases the averaged DCS decreases for all impact energies. This is mainly due to the decreasing relative population of conformer V. For a 1 eV impact energy the averaged DCS decreases by around 20% as the temperature varies from 298.15 to 500 K. For impact energies near 10 eV the difference is around 10% or less. The averaged cross sections is higher than that for conformer I at all impact energies, because the relative population of conformer I reduces as the temperature increases and the contributions of conformers II, III, VII and VIII, which have larger dipole moments than conformer I, become relatively more important. From these results we can conclude that even though conformer I, the lowest-energy structure, gives the largest contribution to the composition in the gas phase, it is expected that the averaged cross sections will be larger than the conformer I cross section at all temperatures were electron collisions are likely to be important.
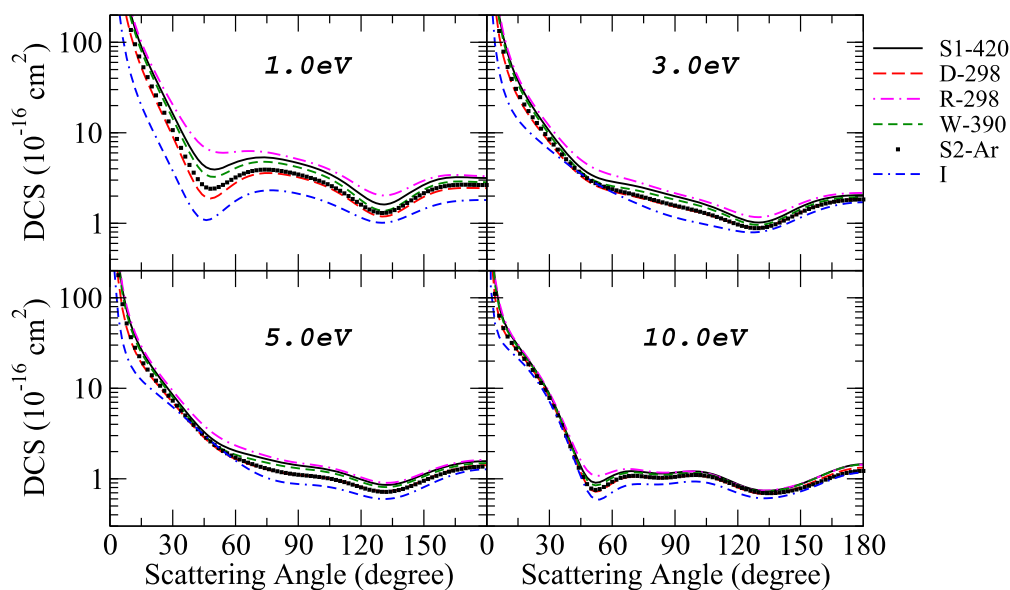
Figure 4. Comparison between averaged Born-corrected DCS using different sets of population ratio at different temperatures of 298.15, 390 and 420 K. The population sets are from Dobrowolski *et al* (2011) (D), Ribeiro da Silva *et al* (2010) (R) at 298.15 K, Wong *et al* (2015) (W) at 390 K and also two sets from Stepanian *et al* (2012) one is theoretical (S1) and another found in argon matrix (S2). The results are presented for impact energies of 1, 3, 5 and 10 eV; for comparison the DCS for conformer I is also given.

In our previous work on electron collisions with α-alanine (Fujimoto *et al* 2016) we used relative (0 K) energies from electronic structure calculations instead of the temperature-corrected relative Gibbs free energy to calculate the Boltzmann population ratio. For α-alanine our predicted averaged cross sections used theoretical populations based on the CCSD(T) electronic structure calculations which are in reasonable agreement with populations deduced from experiment (Farrokhpour *et al* 2012). Figure 6 presents a comparison between our averaged DCS, SEP including Born correction for β-alanine, weighted with population ratios estimated from RE and obtained using Gibbs free energy for temperatures of 298.15 and 420 K. The three population sets are based on the calculations of Stepanian *et al* (2012): S1 is based on Gibbs free energies; RE is based on zero-point vibration energy (ZPVE) corrected RE and S2-Ar are population ratios predicted to exist in argon-matrix. To calculate the relative population in the RE set we used the ZPVE corrected RE of Stepanian *et al* (2012) calculated at the B3LYP/aug-cc-pVTZ level and presented in the table 2 of their paper. When using RE, the order of stability is preserved for all temperatures, although the relative composition, i.e. Boltzmann population ratio, is temperature dependent. These population ratios are valid for molecules whose RE do not vary significantly with temperature.

The use of RE in RE set, equivalent to the 0 K energies with no temperature-dependent entropy contribution, gives larger cross sections mainly because of increase in the population of conformer V, which varies from 24% to 22% as the temperature increases from 298.15 to 420 K. When the relative Gibbs free energy is considered the population of conformer V in S1 set varies from 9% to 5% for the same temperature range. As conformer V has the largest cross section, its population strongly influences the averaged cross

sections. Comparison of the averaged DCS computed using the S2-Ar set shows that the use of Gibbs free energy to estimate the population in S1 set gives closer agreement than use of RE in RE set. We note that the averaged DCS estimated using population sets within the same approach, for example using relative Gibbs free energies (S1 set) or ZPVE RE (RE set), show smooth variation when the temperature varies from 298.15 to 420 K. Therefore, the approach used to estimate relative population is more significant than temperature variation. The population ratio based on ZPVE RE for temperatures from 298 to 500 K are presented in table SM4 of supplementary material.

4.3. Integral cross sections

In this section we present results for ICS computed at the SEP level without and with Born correction for each of 10 low-energy conformers of β-alanine, as well as the population-averaged ICS, for impact energies ranging from 1 to 10 eV. All results include 30 virtual orbitals in our calculation at SEP level.

The ICS computed without Born correction are shown in the figure 7 for each of 10 conformers. As the long-range interaction due to the dipole moment is mainly treated in the outer region, due to the centrifugal barrier term, for partial waves up to $\ell = 4$, the resonance features is much more prominent in these results. The positions and widths of lower-energy resonance for 10 conformers can be seen in the figure 7. The position of the resonance peaks vary from near 2.4 eV for conformer II up to near of 3.4 eV for conformer V although for the majority of the resonances peak round 2.6 eV. These low-energy resonance peaks are related to the structures observed and discussed in eigenphase sums plots in figure 2.
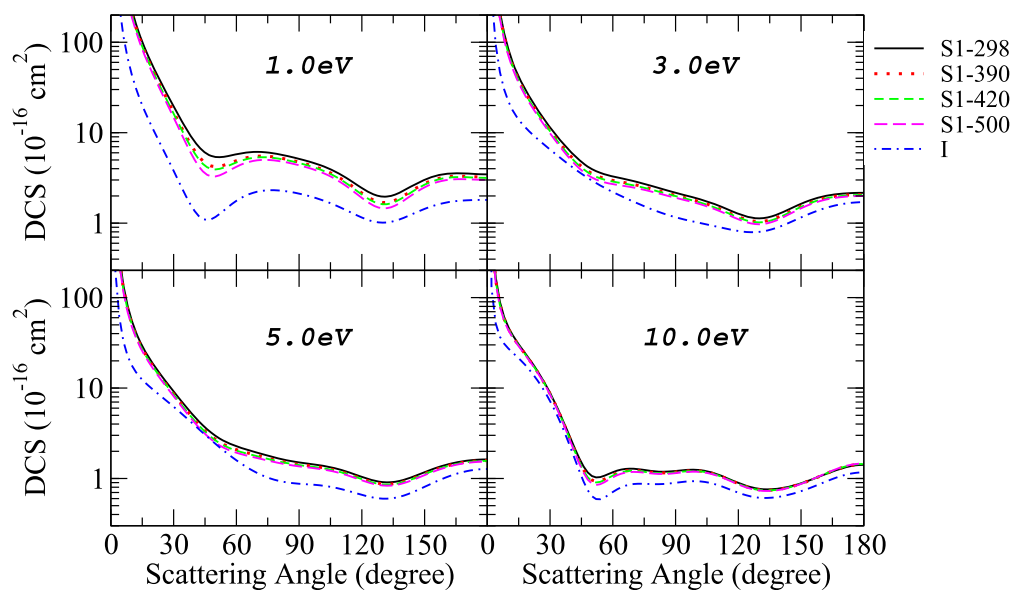
Figure 5. Temperature-dependence in averaged Born-corrected DCS using population ratio at temperatures of 298.15, 390, 420 and 500 K. The population set is S1 from Stepanian *et al* (2012). The results are presented for impact energies of 1, 3, 5 and 10 eV; results for pure conformer I are also given.

Table 3. Temperature-dependence of relative population ratio based on Stepanian *et al* (2012) results for 10 β-alanine conformers.

	Boltzmann population ratio			
Conformer	298.15 K	390 K	420 K	500 K
I	0.3823	0.2767	0.2525	0.2046
II	0.1707	0.1589	0.1532	0.1393
III	0.0202	0.0310	0.0337	0.0396
IV	0.0730	0.1000	0.1060	0.1165
V	0.0901	0.0678	0.0625	0.0504
VI	0.0488	0.0743	0.0808	0.0931
VII	0.0421	0.0699	0.0775	0.0936
VIII	0.1292	0.1330	0.1316	0.1265
IX	0.0259	0.0521	0.0601	0.0798
X	0.0178	0.0362	0.0421	0.0566

Note. Population ratio was calculated by relative Gibbs free energies from Stepanian *et al* (2012).

Figure 8 shows our ICS results including Born correction for 10 β-alanine conformers. Here the full long-range dipole effects are included in the calculations leading increased ICS and a smoothing out of the resonance structures. For pure dipole scattering the ICS depends on the square of the dipole moment and it can be seen that Born-corrected cross sections increase in line with the square of the calculated dipole moments presented in table 1. As the dipoles increase the relative height of resonance peaks are diminished so much that for conformer V is no longer possible to observe the resonance features in the ICS near 3.4 eV.

Averaged ICS (SEP with Born correction) are presented in figure 9 where various sets of Boltzmann population ratio are used. All population sets are based on relative Gibbs free energies but use different temperatures and levels of structure calculations available in the literature. The population sets are

from Dobrowolski *et al* (2008) (D) performed at QCISD/aug-cc-pVDZ level, Ribeiro da Silva *et al* (2010) (R) at G3 level, Wong *et al* (2015) (W) in B3LYP/aug-cc-pVTZ and Stepanian *et al* (2012) (S1-theoretical and S2-argon matrix) at CCSD(T)/CBS level of theory. Figure 9 shows that results computed using the R set are around 60% larger those from D set at the same temperature of 298.15 K. The key difference between the sets is the relative contribution of conformer V, which has the largest cross sections of all conformers. According to the Stepanian *et al* calculations, the contribution of conformer V should become less important as the temperature increase, so the magnitude of ICS would be expected to decrease with temperature. However, the averaged ICS using W set is higher than the results from D set, the contribution of the conformer V is near 5% for W set at 390 K and around 2% for D set at 298.15 K according to table 2. The D and W population sets were obtained using two different methodologies which both should include a high level of correlation in their quantum mechanical calculations; however their small differences in relative population lead to significant differences in predicted thermally-averaged cross sections. The results from S1 set at 420 K are closer to those using the R set at 298.15 K while S2 at 420 K are near to the D set at 298.15 K. These results suggest that level of structure calculation has a more significant influence on the value of the relative Gibbs free energy and consequently the predicted composition than the temperature variation in the range considered.

The dependence on the temperature of the averaged Born-corrected SEP ICS is plotted in figure 10. The population ratios are based on Stepanian *et al*'s relative Gibbs free energy for conformer I–X and when the range of temperature vary from 298.15 to 500 K the ICS decrease near 20%. The explanation can be found in table 3, where the population ratio for conformer V decrease from 9% to 5% when the
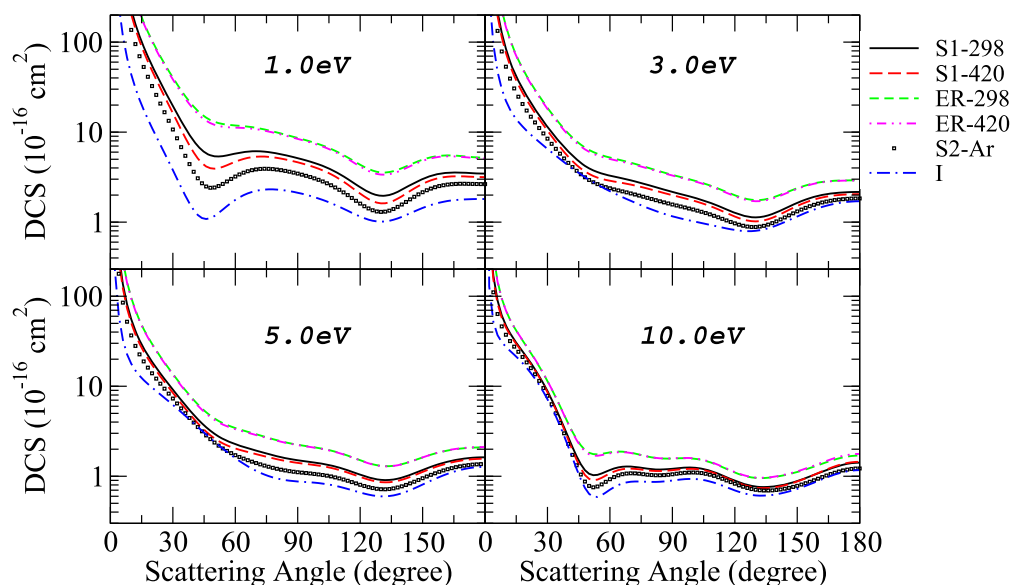
Figure 6. Temperature-dependence and approach-dependence in averaged Born-corrected DCS using population ratio at temperatures of 298.15 and 420 K. S1 is the population set obtained via relative Gibbs free energies; ER is the set based on ZPVE relative energies, both from Stepanian *et al* (2012). Results are presented for impact energies of 1, 3, 5 and 10 eV; a comparison with pure conformer I is also given.
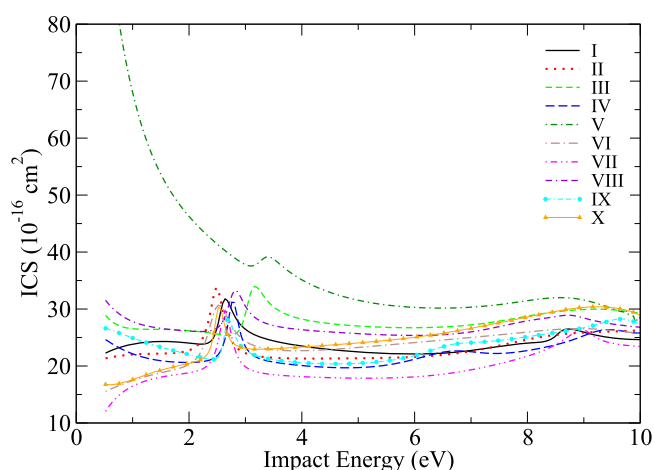

Figure 7. Integral cross section for elastic electron scattering by 10 β-alanine conformers in SEP model with no Born correction. The low-energy resonance features are apparent.
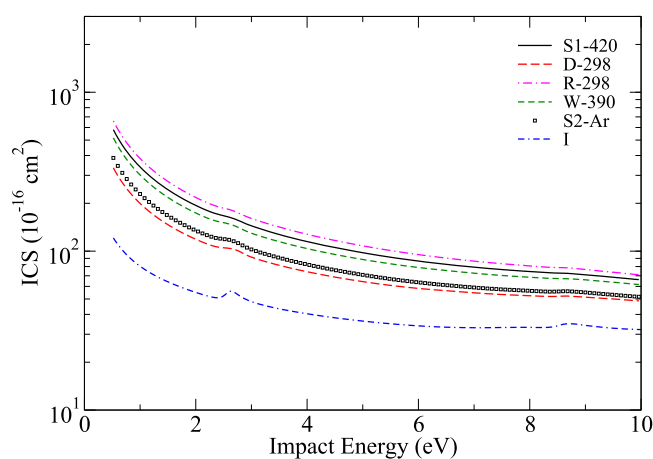

Figure 9. Comparison of ICSs, computed with SEP plus Born correction, for different population sets elastic electron scattering by β-alanine conformers.
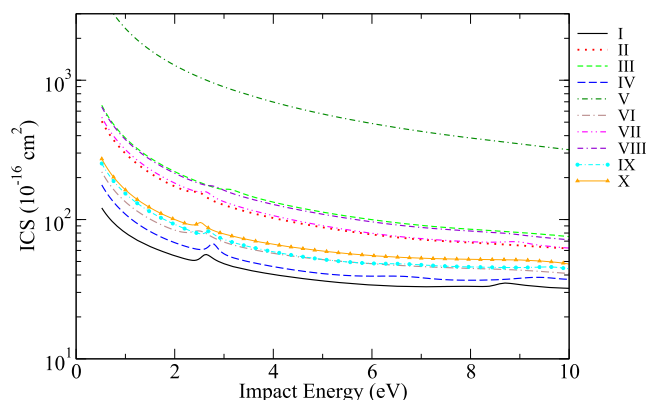
temperature increase and, in general, the conformers which have higher cross sections have lower relative population so the average is going down. The comparison of ICS with conformer I shows that the average ICS can be four (lower energy) or two (higher energy) times bigger depending on the impact energy. The resonance features are smoothed in the averaged ICS compared with conformer I, although the resonance peak positions are close together.

Finally, to illustrate the isomer effect we compare our cross sections for β-alanine with our previous results for α-alanine (Fujimoto *et al* 2016). In the figure 11 we compare the averaged-ICS-SEP with Born correction, two data sets for β-alanine, weighted by S1 at 403 K and S2-Ar sets, and two for α-alanine, weighted by theoretical population based on RE calculated in CCSD(T) level at 403 K and another experimental population deduced by Farrokhpour *et al* (2012)
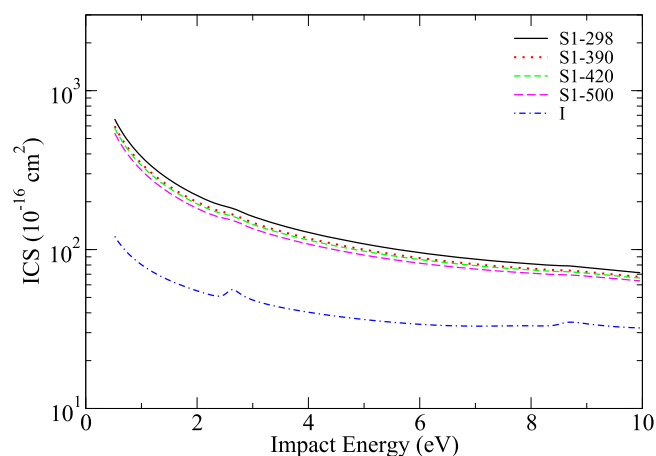

Figure 8. Integral cross section for elastic electron scattering by 10 β-alanine conformers in SEP model with Born correction.

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Figure 10. Temperature-dependence in averaged Born-corrected ICS-SEP using population ratio at temperatures of 298.15, 390, 420 and 500 K. The population set is S1 based on Stepanian *et al* (2012) calculations. A comparison with conformer I is also presented.
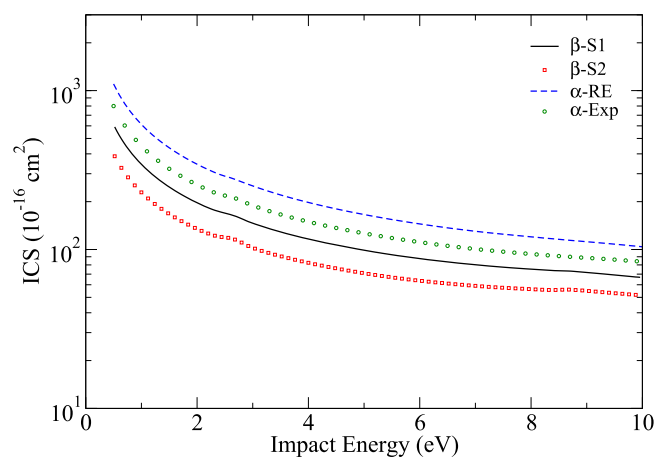

Figure 11. Comparison between averaged-ICS-SEP results for β-alanine and α-alanine isomers. The population sets are: S1-403 K and S2-Ar for β-alanine and RE and experimental at 403 K for α-alanine conformers.

at 403 K. Both α-alanine cross section are bigger than those for β-alanine, basically because the thermal composition of α-alanine contains two conformers, IIA and IIB, which have relative population near 16% each and dipoles of 6.10 and 6.15 D, respectively. While the conformer V of β-alanine has dipole of 7.3 D and a population near 6%. The figure SM1 in the supplementary material gives a comparison between the DCSs α- and β-alanine with the population sets of figure 11.

To emphasise resonance feature, figure SM2 of the supplementary material plots the averaged-ICS-SEP without Born correction for α- and β-alanine with the population sets of figure 11. The lower-resonance associated with the unoccupied π^* orbital of –COOH has roughly the same resonance position and width in both isomers. This indicates that the temporary anion is stabilised by a similar amount, independent of the detailed environment given by the intramolecular interactions, in α and β isomers. This can also be seen by comparing resonance features presented in table 2 above for β-alanine with table 2 from Fujimoto *et al* (2016) for α-alanine.

5. Conclusions

We present a theoretical study of elastic electron scattering by 10 gas-phase conformers of β-alanine. The cross sections calculations are performed with the UKRMol codes at the static exchange plus polarisation (SEP) level with 30 virtual orbitals, in the range from 1 to 10 eV impact energies. The cross sections for individual conformers are calculated and the average are take into account weighted by population ratio at a given temperature. Population ratios are obtained from relative Gibbs free energy temperature-corrected to the values near the usual experimental conditions. β-alanine is solid and must be heated to be sublimed, so we considered temperatures from 298.15 K up to 500 K and used calculated relative Gibbs free energies from the literature. The eigenphase sums for individual conformers all show a low-energy shape resonance associate with occupation of the π^* unoccupied orbital of carboxylic group by the scattering electron. The resonance energy varies from about 2.5 to 3.3 eV, depending on the geometry of conformer; intramolecular interactions are responsible in difference in the temporary anion stabilities. Figure 4 compares averaged DCS and shows that cross sections estimated at 298.15 K could give averaged DCS lower than that one at 420 K depending on the population ratio set employed. However, when we compare averaged DCS calculated at different temperatures but using population ratio estimated from the same level of calculation data, the averaged cross sections reduce with an increase in temperature. The reduction is around 20% as the temperature increases from 298.15 to 500 K.

Our previous study (Fujimoto *et al* 2016) on α-alanine used RE, calculated at 0 K, to estimate conformer populations near 400 K where electron-collision experiments have been conducted. In this work for β-alanine, we use the relative temperature-corrected Gibbs free energy available in the literature to estimate the population. We show that including the effect of entropy in the model leads to population ratios which are very different at 400 K compared to 12 K, with some conformers swapping positions in the order of abundances. These significant composition changes are reflected in changes in the temperature-dependent conformer-averaged cross sections. Although our conclusion about the dependence of the averaged cross sections on temperature is similar to that of our previous work, if we had use the same method to estimate the population (relative 0 K energies), the effects varying the temperature from 298.15 to 420 K would have been significantly less. The dipole moments of β-alanine conformers vary from 1.2 D to near 7.3 D. Treating these correctly requires the Born correction to our cross sections to allow for the long-range electron-dipole interactions. Our averaged cross sections are strongly influenced by the proportion of the highly polar conformer V in the given population ratio. This is the effect which makes the averaged β-alanine cross sections more sensitive to the methodology used than those for α-alanine.

The averaged cross sections of α-alanine are bigger than β-alanine, due to the high contribution of conformers, which have large cross sections because of large dipole moments, to

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the average. And also to the substantial relative population of conformers at a given temperature.

Finally, we find that the averaged cross sections are all higher than the cross sections of the lowest-energy conformer I. This means that for large and flexible molecules, such as amino acids and many other biomolecules, the electron impact cross sections for molecules in gas phase should consider the thermal mixture when comparisons are made with experimental measurements rather simply than lowest-energy conformer. The low-energy barriers related to the rotations of functional groups means that it is not possible to observe each conformer separately in the electron scattering cross sections measurement.

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