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

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Abstract

A theoretical study of elastic electron collisions with 9 conformers of the gas-phase amino acid α-alanine ($CH_3CH(NH_2)COOH$) is performed. The eigenphase sums, resonance features, differential and integral cross sections are computed for each individual conformer. Resonance positions for the low-energy π^* shape resonance are found to vary from 2.6 to 3.1 eV and the resonance widths from 0.3 to 0.5 eV. Averaged cross sections for thermal mixtures of the 9 conformers are presented. Both theoretical and experimental population ratios are considered. Thermally averaged cross sections obtained using the best theoretical estimates give reasonable agreement with the observed thermal cross sections. Excited conformers IIA and IIB make a large contribution to this average due to their large permanent dipole moments.

S Online supplementary data available from stacks.iop.org/jpb/49/215201/mmedia

Keywords: electron collisions, *R*-matrix, conformers

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

1. Introduction

α-Alanine, ($CH_3CH(NH_2)COOH$), is the second simplest α-amino acid found in the nature, and it is a building block of proteins (Császár and Perczel 1999). α-Alanine is a solid at room temperature and its crystal has a zwitterion form (Dunitz and Ryan 1966, Simpson and Marsh 1966). However, α-alanine vaporizes at temperatures near 120° C and it is well-known that in the gas phase it exists as a mixture of charge-neutral conformers (Godfrey *et al* 1993, Blanco *et al* 2004). As is often observed for amino acids (Iijima *et al* 1991), α-alanine is a very flexible molecule and it exists as a great variety of conformers; figure 1 illustrates possible rotations of α-alanine. In the gas phase, intramolecular interactions are important for stabilizing different spatial arrangements of atoms.

There is a lot of work on the alanine conformers in gas phase. Initially, Iijima and Beagley (1991) used electron diffraction to study a gas phase sample. They assumed that the vapour of α-alanine was basically composed of a single conformer which had a high rotational barrier around the C2–C3 bonds (following the carbon numbers in the figure 1), which therefore hindered conversion to other conformers. In contrast, subsequently, many experimental and theoretical studies showed that in the gas phase, several neutral conformers of α-alanine can coexist at temperatures for which the experiments studies are performed, because their total energies only differ by around 0.1 eV. Godfrey *et al* (1993) analysed the observed rotational spectra of alanine in the gas phase aided by theoretical calculations performed at the self-consistent field restricted Hartree–Fock (RHF) level of theory using a 6-31G* Gaussian type orbital (GTO) basis set. They concluded that they observed two conformers, which were identified as I and III. The relative concentration observed in their Stark-modulated free-expansion jet at 255 °C was estimated to be 8:1 (I:III). Cao *et al* (1995) optimized energies and geometries for 13 conformations at various levels of theory, RHF/6-31G** up to second-order Møller–Plesset perturbation theory (Møller and Plesset 1934): MP2/6-311G*, and partially confirmed the previous results of

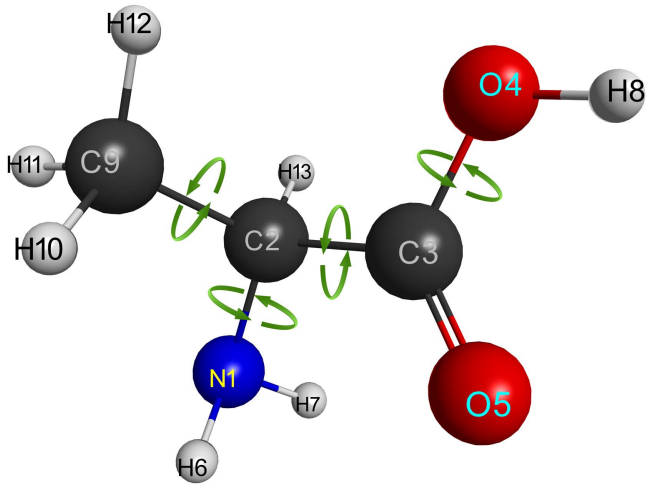

Figure 1. Structure of *L*-α-alanine. This amino acid is very flexible molecule, the rotation of various bonds generates many different conformers of α-alanine amino acid. (figure generated with help of MacMolplt software) (Bode and Gordon 1998).

Godfrey *et al*. However, Cao *et al* found that at the MP2 level conformer V was predicted to have the same set of experimental rotational constants and dipole moment of conformer I; they therefore concluded that was not possible to unambiguously assign which conformer were being detected by microwave spectroscopy. Gronert and O'Hair (1995) also searched for stable structure of conformers of alanine as well as serine and cysteine. They started the study at the semi-empirical Austin Model 1 (AM1) (Dewar *et al* 1985) level and then refined the geometries using RHF/6-31G* up to MP2/6-31+G* level of theory. For alanine, Gronert and O'Hair found 10 conformers; they reported rotational constants and dipole moments for all of them. Finally, Császár (1996) performed *ab initio* calculations at different levels of theory including high level of correlation such as the so-called 'gold standard' coupled clusters single double (perturbative triples), CCSD(T). As α-alanine is a very flexible molecule, intramolecular interactions, due to hydrogen bonding and steric effects, are important so the choice of appropriate diffuse and polarized basis functions are important for predictions of the correct geometries and relative energies. By analysis of minima on the potential energy surface for neutral α-alanine, Császár found 13 conformers and reported accurate geometries, various properties and spectroscopic constants of simulation of rotational and vibrational spectra. Császár's theoretical relative energy predictions include zero-point vibrational energy corrections, differ significantly from the experimental limits given by Godfrey *et al* (1993) in their combined rotational study and structural study. This indicated the need for an improved description of the gas-phase electron diffraction of α-alanine. Császár's structural results support the molecular constants measured for two low relative energy conformers. A more recent, *ab initio*, focal point analysis by Jaeger *et al* (2010) essentially confirmed Császár's results.

Based on Császár relative energies and considering a temperature of 500 K, one can expect the presence of several conformers in appreciable relative concentration in the gas phase. Kaschner and Hohl (1998) used density functional theory (DFT) to compute relative energies and geometries of some amino acids and small oligopeptides. These authors reported results for 6 alanine conformers and observed that the LDA (local-density approximation) approach overestimates the strength of hydrogen bonds and cannot reproduce the correct ordering compared with *ab initio* calculations. Kaschner and Hohl's calculations confirmed that, in the gas phase, glycine and alanine prefer the neutral rather than the zwitterionic form. Lesarri *et al* (2002) developed a method which combined laser ablation with rotational spectroscopy in a supersonic jet; this allowed them to obtain structural information for each individual conformers present in the adiabatic expansion. This technique is most useful for low volatility organic compounds as it avoids using of thermal heating where the amino acid may decompose thermally before reaching their melting point. Blanco *et al* (2004) using laser-ablation molecular-beam Fourier transform microwave spectroscopy (LA-MB-FTMW) studied the rotational spectrum of neutral alanine in a supersonic jet. They observed the two lowest energies conformers of alanine I and IIA. Their study failed to observed the presence of conformer IIB or any type III conformers in the supersonic jet using using Ne or He as carrier gases. Blanco *et al* suggested that collisional relaxation could convert the absent conformers in the most stable IIA and I forms because of the low-energy barriers for this process. They found the relative abundances between I and IIA conformers for post-expansion was $N_{\mathrm{I}}/N_{\mathrm{IIA}} = 4$, assuming that both conformers are in the lowest vibrational state. This finding is in good agreement with their predicted equilibrium of the relative populations at 298 K but contrasts with the population ratio obtained by Godfrey *et al* (1993) ($N_{\mathrm{I}}/N_{\mathrm{IIA}} = 8$). Balabin (2010) performed a jet-cooled Raman spectroscopic study and identified two of the missing conformers of alanine, IIB and IIIA. His relative population for $N_{\mathrm{I}}/N_{\mathrm{IIA}} = 5$ which agrees with Blanco *et al*. Balabin suggested that the detection of these two conformers in significant concentration was related to his different experimental set up and also due to selective collisional relaxation processes associated with low interconversion barriers in the jet. Feyer *et al* (2008) recorded core level x-ray photoemission spectra (XPS) and near edge x-ray absorption fine structure (NEXAFS) spectra of alanine in the gas phase measured at the carbon, nitrogen, and oxygen K edges. With the help of theoretical calculations they determined the population ratio for conformers I and II of alanine, 0.78:0.21, respectively, which are also in good agreement with previous results of Blanco *et al* and Balabin. Powis *et al* (2003) studied photoelectron spectra of gas-phase alanine using synchrotron radiation. They concluded that their results are consistent with the suggestion that conformer I is the predominant structure; when they tried to include conformers II and III in any proportion in their analysis they did not improve agreement with their experimental results. Although the I–III structures that they optimized by DFT B3LYP/6-31G** calculations had very close relative energies so that they would be expected in equal thermal population. Farrokhpour *et al* (2012) in a

combined theoretical and experimental study estimated the population ratio of the four lowest energy conformers of alanine from the experimental photoelectron spectrum supported by high level theoretical calculations. After fitting the spectra the relative population that they obtained for the conformers were I = 70%, IIA = 14%, IIB = 10% and III = 6% at 403 K.

Bazsó *et al* (2013) measured near (NIR) and mid-infrared (MIR) spectra of α-alanine isolated in matrices of Ar, Kr and N_2 at low temperature (8–14 K). Upon short irradiation with NIR laser light at the first O–H stretching overtone band of conformer I, a short-lived conformer VI was observed, which decayed by H-atom tunnelling at 12 K. The half-lives were measured for each matrix. They also observed that when conformer I is exposed to prolonged irradiation it is transformed into conformer IIa, but conformer IIb was not observed. Their observations are consistent with an extremely low barrier to interconversion of IIb $\rightarrow$ IIa and it was not expected that higher energy conformers could be isolated in a matrix at around 10 K. In contrast to glycine, they did not observed conformer IIIb because of the very low IIIb $\rightarrow$ I barrier height in alanine. Note that the nomenclature of conformers 'a' and 'b' used by Bazsó *et al* (2013) differs from the 'A' and 'B' conformer designations of Császár (1996).

The discovery that DNA molecules could be severely damaged by secondary electrons with energies less than 20 eV, has led to increased research into electron scattering by biological molecules. The DNA damage is caused when the low-energy electron is captured by an unoccupied orbital of a DNA constituent molecule creating a transient anion or resonant state which can then decay into negative and neutral fragments. Depending on what the type of DNA constituent (such as, amino acids, sugar, nucleobase, or phosphate moieties, etc) absorbs the electron, this process can lead to single or double strand brakes in the DNA molecule (Boudaïffa *et al* 2000).

Conversely, there are relatively few works on electron collisions cross sections with alanine in the gas phase. Marinković *et al* (2008), to our knowledge, were the first to measure elastic cross sections for alanine in the range from 40 to 80 eV. In a combined theoretical and experimental study, they compared their measured data with calculated results from a corrected form of the independent-atom method, known as the Screen Corrected Additivity Rule procedure and obtained good agreement between them. They present theoretical results for electron impact energies ranging from 1 to 10 000 eV. Panosetti *et al* (2010) focused on modelling resonance fragmentation; they made a systematic study involving glycine, alanine, proline and valine. Panosetti *et al* reported the elastic integral cross sections (ICS) for these molecules at the equilibrium geometry and observed resonance near 3 eV for all the amino acids studied. These resonances are important for the dissociative electron attachment (DEA) process which is the main low-energy electron-collision destruction mechanism for neutral molecules (Aflatooni *et al* 2001, Ptasińska *et al* 2004). Fujimoto *et al* (2014) reported elastic differential cross sections (DCS) and ICS for two conformers of alanine and observed differences in the resonance positions between them.

In this paper, we report a theoretical study comparing elastic cross sections for the 9 lowest-energy conformers of α-alanine in the gas phase for the energies ranging from 1 to 10 eV. We present averaged-cross sections which take into account relative populations of different conformers. We believe that these should be more reliable results for comparison with measured data at temperatures where the gas phase molecule is experimentally accessible.

The organization of article is as follows: section 2 presents an outline of the theory and some details of the calculations are provided in section 3. Section 4 presents and discusses our calculated data; this is followed by a summary of conclusions.

2. Calculations

2.1. Geometry of conformers of α-alanine

In this work, we use the nomenclature and geometry of conformers given in table 2 of Császár (1996). Császár describes 13 geometrical structures of α-alanine corresponding to minima on the potential energy surface. We have used Császár's geometric parameters which were optimized at MP2/6-311++G** level; these parameters are given in the supplementary material.

We aim to compute cross sections that can be compared with experimental data, so we need to consider that in crossed-beam experiments α-alanine is sublimed by heating to 400–500 K, as it is solid at room temperature. Initially, we started to work with the 13 conformers of alanine given by Császár. However, below we limit our study to only the 9 lowest energy conformers, I to VB (see table 1 of Császár (1996)), because their Boltzmann population ratios indicate that they dominate the population at temperatures at which the experiment are conducted.

2.2. The R-matrix method

The *R*-matrix method used in this paper is the UKRMol implementation (Carr *et al* 2012) of the UK molecular *R*-matrix codes which is described in detail elsewhere by Gillan *et al* (1995) and Tennyson (2010). Fujimoto *et al* (2014) performed *R*-matrix calculations on two alanine conformers and present a detailed study of how this was done. Here we use the same approach to calculate cross sections for 9 conformers; the reader is referred to the previous calculation for further details.

Here we just present an brief summary of the *R*-matrix method and calculations. In this method, space is split in two regions: the inner and outer region. The inner region is a sphere of radius a around the target molecule centre-of-mass. The electronic density of the target molecule is considered, in practice, to be completely inside this region. Here a radius of $a = 10a_0$ was used. 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 wave functions of the target in the ith state and u_{ij} is the wave function of the continuum electron which is expanded in a partial wave expansion up to some maximum value of ℓ, $\ell_{\max}$; $\mathcal{A}$ is an antisymmetrization operator as the $(N+1)$-electrons are indistinguishable in the inner-region electrons. The second summation in equation (1) contains configurations χ_i^{N+1} which are included to relax the constraint of orthogonalization between scattering and target orbitals of the same symmetry, and to allow for target polarization effects. a_{ijk} and b_{ik} are the variationally optimized coefficients of expansions.

The polarization effects, which are related to the distortion of target electronic density, are calculated when χ_i^{N+1} configurations are included to allow the relaxation of target bonded orbitals. This level of calculation is called SEP (static-exchange-polarization). SEP calculations are known to provide a good practical method of converging polarisation effects in low-energy electron molecule collisions and, in particular, of providing reliable predictions of resonance parameters in this region (Vizcaino *et al* 2008, Fujimoto *et al* 2012). Following tests by Fujimoto *et al* (2014), 30 virtual orbitals are used to generate χ_i^{N+1} configurations.

The outer region, we solve a coupled second-order differential equation for the continuum electron, it is a one-particle problem. The *R*-matrix matches the inner and outer solutions, propagate to large r and then uses the K-matrix to calculate scattering observables. The partial wave expansion includes partial waves explicitly up to $\ell_{\max}$ ($\ell_{\max} = 4$) and is then completed using a Born closure procedure (Padial *et al* 1981, Gianturco and Jain 1986, Morrison 1988). This takes into account the long-range dipole interactions as all of alanine conformers have permanent dipole moment. The code POLYDCS (Sanna and Gianturco 1998) is employed to calculate rotational transitions and the rotational constants used for each conformers are reported in supplementary material. The rotationally unresolved elastic differential cross sections is obtained by the sum over rotational transitions until the convergence. Here we limit our partial wave expansion to $\ell_{\max} \leqslant 4$; our previous study on alanine (Fujimoto *et al* 2014) tested adding the $\ell_{\max} = 5$ partial wave. However, once the Born closure (which allows for the contribution of many partial waves particularly at low angles) is performed, the results were essentially unchanged except that the $\ell_{\max} \leqslant 5$ calculations showed unphysical behaviour in the DCS for angles higher than 150° when Born closure procedure was used.

3. Results and discussion

In this section, we present our results including eigenphase sums, resonance positions, DCS and ICS for elastic electron collisions with alanine molecules in the range of 1–10 eV. All the results were calculated in SEP level with 30 virtual orbitals.

3.1. Target properties and population

All our target wave functions for the 9 conformers are described at the RHF/6-311+G* level and the relative energies compared with conformer I are around only 0.1 eV. Table 1 reports key data on target conformers which are important for the calculations below. Target wave functions and molecular properties were obtained using the MOLPRO Quantum Chemistry package (Werner *et al* 2012).

Table 1 gives our relative energy and dipole moment calculated at the RHF/6-311+G* level for all 9 conformers using geometries from Császár (1996) optimized at MP2/6-311++G** level. The Boltzmann relative populations are presented for two levels of theory: RHF (where our RHF relative energies are used), CCSD(T) (where relative energies calculated with CCSD(T) method by Császár (1996) are used) and a set of experimental relative population deduced by Farrokhpour *et al* (2012).

Experimental studies of processes including DEA, photoelectron spectra and elastic electron scattering require alanine to vaporized. In these gas phase studies the temperature, in general, ranges from about 400–500 K. We observe that for a given level of theory, RHF or CCSD(T), the relative population is not significantly affected over this range of temperatures, however the CCSD(T) population ratio is very different for conformers IIA and IIB, compared with that calculated at the RHF level. A detailed discussion of the difference in the total energies of α-alanine conformers at various levels of theory is given by Császár (1996), who commented that RHF calculations overestimate the relative energies compared to conformer I and fails to predict them reliably. According to Császár, when the electron correlation is included it stabilizes all conformers relative to conformer I, but not uniformly. As can be seen from table 1, the CCSD(T) relative population for conformer IIA, IIB and IIIB are very different compared to those predicted at the RHF level. The set of experimental relative population we considered were deduced by Farrokhpour *et al* (2012) from the measured photoelectron spectra. Their analysis found that it was only necessary to consider 4 conformers (I, IIA, IIB and IIIA) in the molecular beam to fit their observations. Comparing the CCSD(T) population ratio with the experimental set, we find good agreement for IIA, IIB and IIIA, but a larger discrepancy for conformer I. However we note that our analysis suggests that about 30% of the population should be in conformers not considered by Farrokhpour *et al* and, given, that all populations are normalised, this leads to their population of conformer I being larger than our predicted one. The discrepancies and the absence of some conformers may well be related to the conversion from one conformer to another due to the very low barrier heights involved (Blanco *et al* 2004) or decay by H-atom tunnelling (Bazsó *et al* 2013).

The relative energies and dipole moments presented in table 1 are calculated in RHF level are slightly different from

Table 1. Relative energy (RE), dipole moment and relative population in % of molecules for 9 α-alanine conformers at two temperatures, 403 and 500 K.

			Relative population, %				
			RHF[a]		CCSD(T)[b]		Expt[c]
Conformer	RE[a] (cm^{-1})	Dipole (D)	403 K	500 K	403 K	500 K	403 K
I	0	1.35	50.2	42.0	35.7	30.0	70.0
IIA	1126	6.10	0.9	1.6	16.1	15.8	14.0
IIB	1156	6.15	0.8	1.5	16.9	16.4	10.0
IIIA	584	1.77	6.2	7.8	6.7	7.8	6.0
IIIB	214	1.55	23.3	22.6	7.5	8.5	
IVA	594	2.36	6.0	7.6	6.1	7.3	
IVB	633	2.32	5.2	6.8	5.1	6.2	
VA	666	2.66	4.7	6.2	3.9	5.1	
VB	832	2.88	2.6	3.8	2.0	2.9	

[a] Our relative energies calculated at the RHF level.
[b] Relative energies from CCSD(T) calculations by Császár (1996).
[c] Experimental data from Farrokhpour *et al* (2012).

those reported by Császár for his RHF/6-311++G** level calculations (Császár 1996) because we used geometries optimized by Császár in MP2 level and a 6-311+G* basis set. Despite these small differences we can expect similar results. Comparing our total energies against the results (not shown) of Császár (1996) for each conformer, the differences are around 0.03%. The maximum relative difference between our calculated dipole moments and those of Császár is 10.8% for conformer IIIB and about 9% for conformers IIA and IIB. The difference in dipole moment for conformer I is 3.8% (1.4D) compared with Császár and 25, 2% (1.8D) compared with the experimental results of Godfrey *et al* (1993). Conformer IIB has a dipole moment 18% higher than experimental results (5.13 D) (Godfrey *et al* 1993).

3.2. Eigenphase sums and resonances

Figure 2 shows the eigenphase sums for 9 conformers of α-alanine. In all cases there is a sharp structure around 2.8 eV that is related to the electron capture at π^* unoccupied orbital of the carboxyl group as discussed previously (Aflatooni *et al* 2001, Ptasińska *et al* 2004). A more detailed discussion of these resonances is given by Fujimoto *et al* (2014) and the references cited therein. Table 2 presents our resonance positions and widths which are fitted by Breit–Wigner formula made by an automated fitting procedure (Tennyson and Noble 1984). As found by Fujimoto *et al*, our fits give a sharp lower-energy and a broad higher-energy resonance. Table 2 shows that there is a spread in the resonance positions and widths. The positions of lower-energy resonance vary from near 2.6 eV up to 3.1 eV and the widths vary from 0.3 to 0.5 eV. We would expect the positions of these lower-energy resonance to be well described by our SEP model; the resonance is formed by electron captured by the unoccupied π^* orbitals of carboxyl group which is relatively straightforward to model. The formation mechanism for the higher-energy resonance is not well-established: it has been suggested that is a core-excited resonance (Tashiro 2008) or a shape resonance

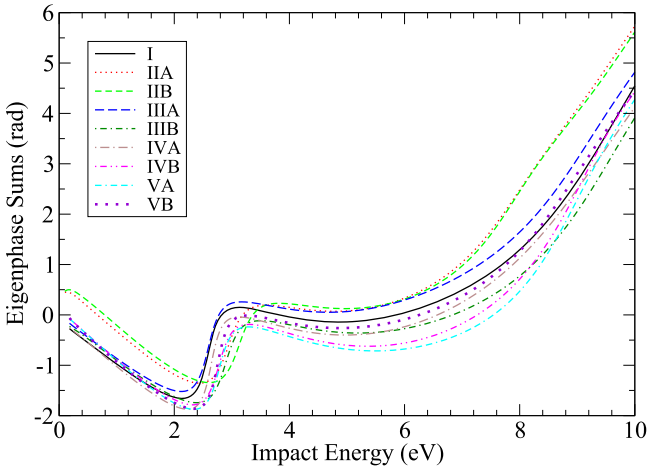

Figure 2. Eigenphase sums for 9 conformers of α-alanine computed in the SEP level.

Table 2. Resonance parameters for 9 α-alanine conformers: positions (widths) in eV.

Conformer	Resonances: position (width)		
I	2.59(0.35)		9.70(2.19)
IIA	2.95(0.50)	8.16(2.18)	9.60(2.65)
IIB	3.14(0.52)	8.03(1.80)	9.77(2.41)
IIIA	2.59(0.38)		9.32(2.32)
IIIB	2.90(0.46)		9.67(2.16)
IVA	2.64(0.31)		9.74(3.60)
IVB	2.78(0.42)		9.10(1.58)
VA	2.78(0.39)		9.06(1.76)
VB	2.76(0.32)		9.12(2.39)

associated with the σ^* unoccupied orbital of OH group (Scheer *et al* 2007). 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.

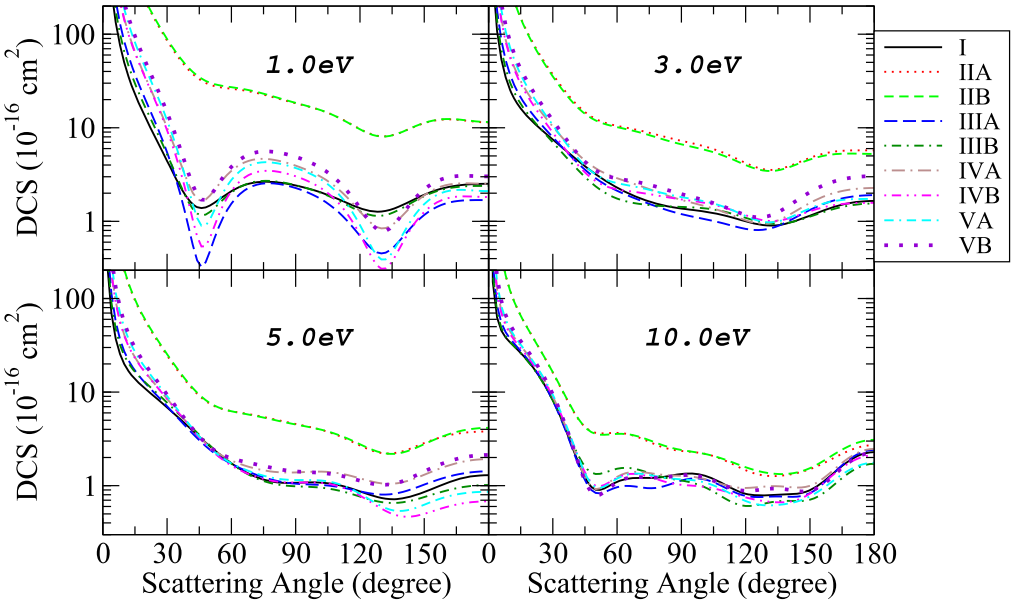

Figure 3. Elastic DCS for electron collision with α-alanine conformers for impact energies of 1, 3, 5 and 10 eV. Results for SEP calculations including a Born correction.

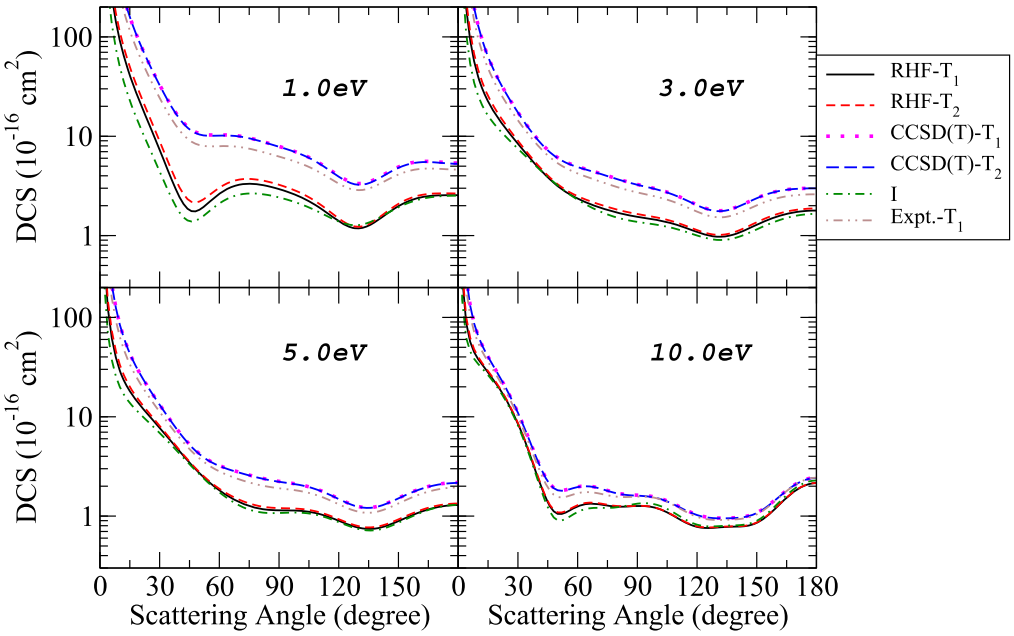

Figure 4. Comparison between averaged Born-corrected DCS using different sets of population ratio calculated with energies in RHF level, CCSD(T) level for temperature of $T_1 = 403$ K and $T_2 = 500$ K and a set estimated from experimental data (Farrokhpour *et al* 2012) for $T_1 = 403$ K. The results are presented for impact energies of 1, 3, 5 and 10 eV; a comparison with conformer I is also presented.

3.3. Cross sections

Figure 3 presents our DCS for 9 conformers of α-alanine including polarization and completed with a Born correction for collision energies 1, 3, 5, and 10 eV. Results calculated with steps of 1 eV from 1 to 10 eV are given in the supplementary material. The DCS of all of conformers show similar behaviour and magnitudes between them with the exception of two conformers: IIA and IIB. Table 1 shows that the main reason for the huge increase in the DCS of conformers IIA and IIB is due to their large dipole moments: 6.10 D and 6.15 D, respectively. The calculations are supplemented with Born corrections to take into account higher partial waves beyond of $\ell_{max} = 4$ which corresponds with including the long-range dipole interactions. This corrections depends on the square of the permanent dipole moment. This means that in the case of conformers IIA and IIB the long-range interactions contribute at least an order of magnitude more to the cross sections than for the other conformers studied here.

Figure 4 compares averaged DCSs calculated with the three different sets of Boltzmann population ratio given in

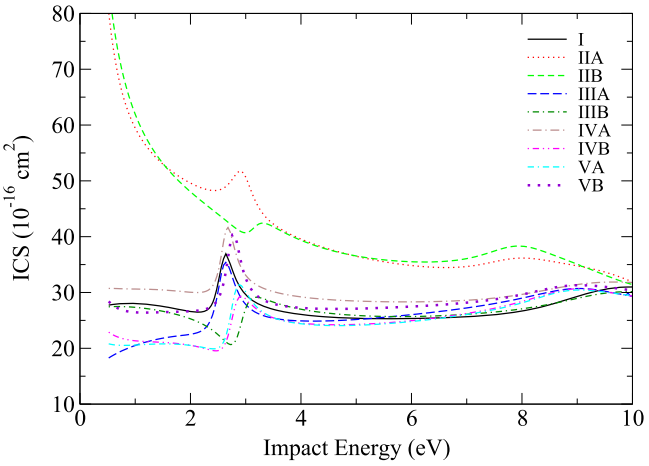

Figure 5. ICS for elastic electron scattering by 9 α-alanine conformers in a SEP model not corrected with Born closure. For impact energies from 1 to 10 eV. The resonance features are shown.

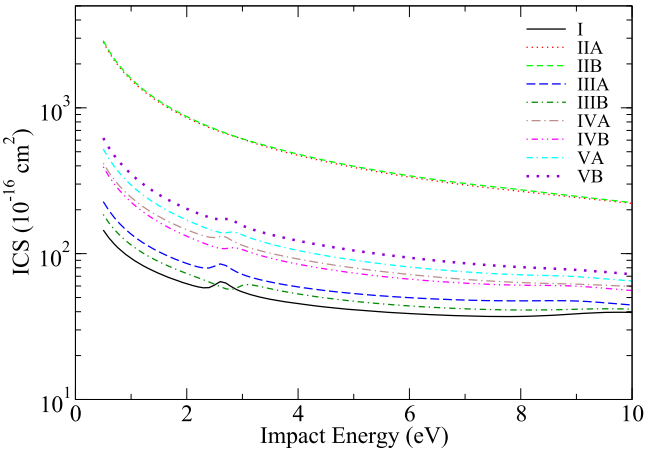

Figure 6. ICS for elastic electron scattering by 9 α-alanine conformers calculated using a SEP model including Born correction.

table 1. The averaged DCS were calculated by the sum of individual DCS weighted by population ratio, given by

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

where the $c_i(T)$ are the temperature-dependent population ratios and $(\mathrm{DCS})_i$ is the SEP DCS of conformer i.

Table 1 shows that for temperatures in the range 403–500 K, the population ratio does not change significantly. The consequence of this can be seen in figure 4 which compares the averaged-DCS calculated with population ratios computed using the same model but for different temperatures. The differences are not particularly distinct. Considering the RHF population ratios, the averaged cross section in figure 4 for temperature of 403 and 500 K are fairly similar. At the RHF level the averaged DCS are closer to the DCS of lowest-energy conformer, conformer I, than the averaged-DCS calculated using the CCSD(T) population ratio. In the CCSD(T) case, the temperature again almost does not affect the average because the cross sections of conformers IIA and IIB, whose populations do not change significantly in the temperature range considered, are dominant.

The averaged DCS calculated with CCSD(T) population ratios are larger at all angles than the RHF ones. This is because the CCSD(T) ratios lead to much larger populations of conformers IIA and IIB which have much bigger cross sections due to their large permanent dipoles: the combined CCSD(T) population of these conformers is over 30% compared with around 2.5% for the RHF ratios. This shows that the thermally averaged DCS, and by analogy other cross sections, can be very different from the DCS of the lowest-energy conformer I. Figure 4 also shows the averaged DCS based on the experimental population ratio reported by Farrokhpour *et al*. Comparing all results we infer that if we want to compared theoretical cross sections of very flexible molecules, such as, some amino acids, with correspondent measured cross sections, we should calculate cross sections for those conformers that are populated at temperatures at which the experiment is conducted, and then evaluate the averaged cross section.

Figure 5 shows the ICS without including the Born closure correction as we want to highlight the resonance features. The lower-energy resonance peak can be seen for all conformers at around 2.8 eV. Another broad resonance peak around 8 and 9 eV can also be seen. The ICS for conformers IIA and IIB are greater in magnitude by around 40% above impact energies of 3.5 eV compared to all of the others conformers; this is again due to the large dipole moments of these conformers. If the long-range interactions are suppressed, because the Born closure procedure is not considered, the ICS at energies around 10 eV are very similar for all conformers, indicating that at this electron scattering energy the differences between the geometries of the conformers are not so important in terms of the short-range contribution to the ICS.

Figure 6 shows the ICS computed at the SEP level including a Born closure correction. The cross sections fall into three separate groups: one consisting of conformers I, IIIA and IIIB whose dipole moments vary from 1.35 to 1.77 D. Another group is composed of conformers VI-A,B and V-A,B whose dipoles range from 2.36 to 2.88 D. The third group is formed by conformers IIA and IIB which dipoles are around 6 D. Furthermore, these long-range interactions effects dominate polarization effects for all conformers, and for conformers IIA and IIB the resonance peak in the ICS are completely washed out.

Figure 7 reports the averaged ICS computed using SEP and the Born closure correction for different population ratios (RHF, CCSD(T) and experimental), and at temperatures of 403 and 500 K. These are compared with ICS for conformer I. The averaged ICS calculated with the RHF populations at 500 K shows a bigger ICS compared to 403 K, as expected as the relative contributions of conformers with energies above conformer I increases for higher temperatures, and, in particular the cross sections of conformers IIA and IIB contribute increases the average ICS. Even though the difference between the two temperatures is not large, the increase is

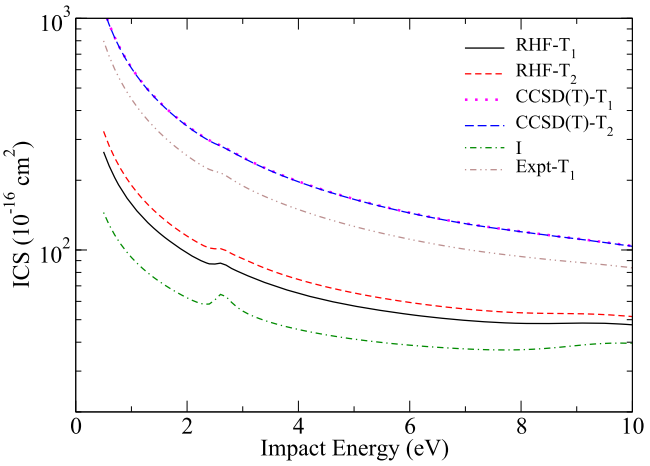

Figure 7. Averaged elastic ICS for electron scattering by α-alanine conformers. Comparison of between different sets of population ratio: RHF, CCSDT(CC) and experimental (Farrokhpour *et al* 2012) at temperatures of $T_1 = 403$ K and $T_2 = 500$ K. A comparison with conformer I is also presented.

around 14%. The ICS calculated with RHF populations is fairly similar to the ICS of conformer I because the contributions due to conformers IIA and IIB are relatively small. The averaged ICS calculated with the CCSD(T) population ratio are bigger than that one calculated at the RHF level, as the relative contributions of IIA and IIB conformers increase. The averaged ICS weighted with the experimental population ratios are closer to our averaged ICS calculated with the CCSD(T) populations. We note Császár (1996) affirmed that RHF fails to predict the relative energies of α-alanine correctly. Therefore the ICS given by the CCSD(T) or experimental populations represent our best predictions of the thermally averaged ICS.

4. Conclusions

In this work we report a theoretical study of elastic cross sections for electron collisions with nine gas-phase alanine conformers, computed at the SEP level, in the range of 1–10 eV. The results show that the low-lying shape resonance parameters are relatively unaffected by changes in conformer; similar results have been obtained before for other systems with multiple minima (Varambhia and Tennyson 2007, Bryjko *et al* 2010). However this is not true for the differential or integral cross sections where differences in dipole moments lead to large differences in the computed cross sections between conformers. This suggests that measured cross sections should depend on the relative population of the conformers and temperature.

Our results show that temperatures ranging from 400 to 500 K do not affect significantly the magnitude of cross sections. For this range of temperature, considering relative energies from the lowest-energy conformer I, the Boltzmann statistics suggest that 9 conformers should be significantly populated in the gas phase. With flexible molecules, such as some amino acids, computed cross sections should be averaged over all conformers weighted by the expected population ratio before comparing with the measured data. Our results show that the averaged cross sections can be very different from those calculated for just the most stable conformer I. This means that averaged cross sections should give a more reliable to comparison with measurements. In particular, if some conformer has a particularly large cross section because, for example, it has a large dipole moment, its contribution to the total cross sections will be very dependent on its relative population, which will vary with temperature. Furthermore, the population ratios calculated using two levels of theory, RHF and CCSD(T), to give the conformer energies are significantly different. The RHF calculations fail to predict the relative energies correctly, especially for those molecules which have intramolecular hydrogen bond, as is the case for amino acids. The population ratio calculated using higher levels of theory which include electron correlation, such as CCSD(T), give different population ratios and consequently a different averaged cross section. In this case the predicted population ratios for conformer IIA, IIB and IIIA appear to be in good agreement with those deduced from experimental.

In conclusion, as the cross sections depend on the geometry of the conformer or conformers considered, we recommend that authors who publish theoretical cross sections for large and flexible molecules, such as amino acids, both specify which geometry was used for their calculation, otherwise their results will not be reproducible, and consider the effect of thermal averaging when comparing with experiment results.

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