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R-matrix calculation of low-energy electron collisions with phosphoric acid

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Abstract

Electron collision calculations are performed on two conformers of H_3PO_4, a weakly dipolar form with all OH groups pointing up and a strongly dipolar form where one OH group points down. Strong evidence is found for a broad shape resonance at about 7 eV for both conformers, although the precise parameters of this resonance are sensitive to the details of the target wavefunction used. Ten-state close-coupling calculations suggest the presence of very narrow Feshbach resonances in a similar energy region. Again both conformers behave similarly. Elastic and electronically inelastic cross sections are calculated for both conformers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Low-energy electrons have been shown to be a major cause of radiation damage in biological systems (Boudaïffa *et al* 2000). A number of theoretical studies have considered electron collisions with DNA (Barrios *et al* 2002, Berdys *et al* 2004b, König *et al* 2006, Pan and Sanche 2006, Pan *et al* 2003, Caron *et al* 2008, 2009) or DNA constituents (Tonzani and Greene 2006a, 2006b, Winstead *et al* 2007, Gianturco *et al* 2008, Winstead and McKoy 2008, Dora *et al* 2009). However, the backbone of DNA also contains phosphate, and as it has been suggested that electron attachment to the phosphate group (Berg *et al* 2002) also contributes to DNA strands breaks, the study of electron collisions with phosphoric acid, H_3PO_4, is also of potential importance.

Li *et al* (2003) performed calculations on a sugar-phosphate-sugar model system using the ONIOM layer method (using B3LYP/6-31+G* as the high level and AM1 as the low level) and found that the activation barrier for bond rupture of the anion's phosphate-sugar C–O bond is only 0.5 eV, indicating that very-low energy electrons can induce DNA strand breaks. Berdys *et al* (2004a) argued that electrons with kinetic energies near 0 eV cannot directly (i.e. vertically) attach to the phosphate group, but electrons with energies in the 2–3 eV range can. These attach to the phosphate's P=O π^* orbital, forming a metastable anion.

Like many large and flexible molecules, phosphoric acid can occur as several conformers which are fairly close in energy. Here we consider two possible conformers, a weakly dipolar form with C_3 point group symmetry, described below as conformer uuu, and an asymmetric, strongly dipolar form described below as conformer uud, see figure 1.

There is only limited data on electron collisions with phosphoric acid and previous studies appear each to have focussed on a single conformer. Calculations on low-energy collisions with H_3PO_4 were performed by Winstead and McKoy (2008), who studied electron collisions with conformer uuu, and Tonzani and Greene (2006b), who appear to have studied an asymmetric geometry somewhere between the uuu and uud minima. Related studies have considered electron collisions with trimethyl phosphate (TMP), $(CH_3)_3PO_4$ (Aflatooni *et al* 2006, Burrow *et al* 2008), higher substituted phosphates (König *et al* 2006) or indeed the salt NaH_2PO_4 (Pan and Sanche 2005). The focus of most of this work has been on detecting behaviour associated with low-energy resonances. The results remain somewhat inconclusive; while Winstead and McKoy (2008) and Tonzani and Greene (2006b) both reported resonances close to the ionization limit of H_3PO_4, Burrow *et al* (2008) found no evidence for resonances in TMP and, by extension, did not expect them to appear in the phosphate group of DNA.

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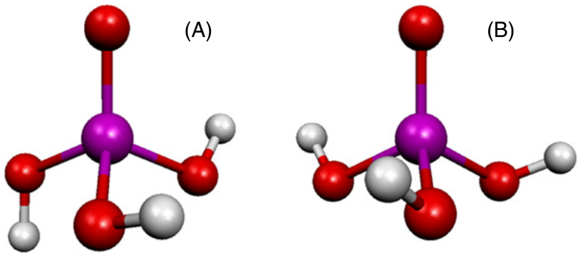

Figure 1. Conformers of phosphoric acid studied in this work: (A) uud, (B) uuu.

In this work we present *R*-matrix calculations of low-energy collisions for both the main conformers of phosphoric acid performed using a variety of models. We report cross sections for both elastic collisions and electron impact excitation, as well as results for low-lying resonances.

2. Method

The basic idea of the *R*-matrix method is the division of space into two regions: a spherical inner region of radius *a*, which is designed to enclose all the charge density of the target, and an outer region, where interactions between the electron and the target can be represented by long-range moments. The major advantage of the method is that within the inner region the problem is solved independent of scattering energy. Within this region the wavefunction can be written as

$$\psi_k^{N+1} = \mathcal{A} \sum_{ij} a_{ijk} \Phi_i^N(\mathbf{x}_1 \ldots \mathbf{x}_N) u_{ij}(\mathbf{x}_{N+1}) + \sum_i b_{ik} \chi_i^{N+1}(\mathbf{x}_1 \ldots \mathbf{x}_{N+1}) , \quad (1)$$

where the target contains *N* electrons and functions are labelled as N or $N + 1$ according to whether they refer to the target or the compound scattering system, respectively. In this work all orbitals underlying the wavefunctions of equation (1) were constructed from Gaussian-type orbitals (GTOs).

In equation (1), Φ_i^N is the wavefunction of the ith target state and u_{ij} are the extra orbitals introduced to represent the scattering electron (Faure *et al* 2002). The operator $\mathcal{A}$ ensures that the product of these two terms obeys the Pauli principle. The second summation in equation (1) involves L^2 configurations which have no amplitude on the *R*-matrix boundary and where all electrons are placed in orbitals associated with the target. Such configurations, the choice of which is quite subtle (Tennyson 1996), are essential in even the simplest scattering model applied here, static exchange (SE), as they allow for relaxation of the orthogonalization between the continuum orbitals and those belonging to the target given that the continuum orbitals are forced to be orthogonal to the target ones. In the more sophisticated static exchange plus polarization (SEP) model, extra L^2 configurations are obtained by considering single excitation from the target wavefunction which allows for the effects of target polarization.

Equation (1) contains most of the physics of the problem; the three models considered below are determined by the choices made for this equation. While the SE and SEP models only consider a single target state in the first sum, usually represented by a Hartree–Fock wavefunction, the close-coupling (CC) model runs over a sum of such states which here are represented using configuration interaction (CI). One of us has recently written a comprehensive review of the *R*-matrix method for electron–molecule collisions (Tennyson 2010); the reader is referred to this for more details of the method.

All calculations were performed using the fixed nuclei approximation except for the Born correction discussed below which included treatment of rotational motion within the rigid rotor approximation.

3. Calculations

3.1. Target models

As a first step we performed a series of calculations to determine which geometries of H_3PO_4 we should consider. The three hydroxyl groups can be in up or down position with respect to the P=O group. Starting structures were created by taking into account all possible combinations of the positions of the hydroxyl groups. These were optimized with the B3LYP method (Becke 1993, Lee *et al* 1988, Vosko *et al* 1980, Stephens *et al* 1994) and the 6-31+G* basis set (Hehre *et al* 1972) using the Gaussian 03 computational package (Frisch *et al* 2003). Three stationary points were found: the first one with two hydrogens up and one hydrogen down (uud) with C_1 symmetry, the second one with three hydrogens up (uuu) with C_3 symmetry, see figure 1, and one transition state with one imaginary frequency and C_{3v} symmetry and three hydrogens down (ddd). The uuu conformer was found to have a lower electronic ground-state energy (−644.15488 Hartree) and a smaller dipole moment (0.40 D) than the uud conformer (−644.15388 Hartree, 3.34 D, respectively). These results agree with the recent CCSD(T)/aug-cc-pV(T+d)Z calculations by Yekutiel *et al* (2010), which showed that the uuu conformer is about 0.06 eV lower in energy than the uud conformer. Calculations are presented for both of these conformers below. The geometries of these minima are given as supplementary data.

Subsequent target calculations on these two conformers were performed with several different basis sets and with a variety of CI models using a mixture of MOLPRO (Werner *et al* 2006) and the less flexible target calculation facility provided in the UK molecular *R*-matrix code (Morgan *et al* 1998). Only a brief summary of target models considered is discussed here. Unless otherwise stated, calculations were performed using the cc-pVTZ target basis set; however, some differences in the results obtained with calculations performed with different target basis sets were observed and these will be noted below.

Restricted Hartree–Fock (RHF) wavefunctions were used for the SE and SEP calculations presented below. The CC calculations used a complete active space CI (CAS-CI) model. In this model, 36 ‘core’ electrons were frozen in their RHF orbitals whereas the remaining 14 ‘active’ electrons were distributed over ten orbitals. A variety of different orbital sets were tested; all CAS-CI results presented here are based

Table 1. The $X\,^1$A ground-state energy (in Hartree), vertical excitation energies (in eV) for singlet and triplet electronic states for the two conformers of phosphoric acid considered. Ground-state dipole moments are also given.

	uuu			uud		
State	6-31G	cc-pVDZ	cc-pVTZ	6-31G	cc-pVDZ	cc-pVTZ
X^1A	−641.750 14	−642.073 14	−642.213 34	−641.752 39	−642.074 20	−642.227 51
1^3A	8.01	8.51	7.46	7.86	8.43	7.84
2^3A	8.05	8.54	7.51	7.98	8.55	7.96
2^1A	8.75	9.13	7.82	8.63	9.10	8.35
3^1A	8.81	9.17	7.87	8.69	9.15	8.42
3^3A	9.30	9.52	8.76	9.25	9.55	9.17
4^3A	9.76	10.02	9.05	9.58	9.97	9.50
4^1A	10.04	10.31	9.22	9.77	10.19	9.70
5^3A	9.85	10.11	9.63	10.09	10.34	10.01
5^1A	10.24	10.50	9.53	10.29	10.66	10.20
μ / D	1.35	0.39	0.35	3.31	2.96	3.08

on the use of state-averaged CASSCF orbitals obtained for the lowest five singlet and triplet electronic states.

Our CAS-CI model gives 4950 singlet configurations and 6930 triplet configurations for both conformers. We note that none of the codes we used in this study are able to explicitly treat the C_3 symmetry of the uuu conformer, so no symmetry was used in any of our calculations. The results of the CAS-CI models are summarized in table 1. The CAS-CI results show lower energies for the uud than for the uuu conformer, in apparent disagreement with the B3LYP results. However, in our state-averaged CASSCF calculations the orbitals were optimized for an average of ten states, and these calculations therefore do not yield accurate ground-state energies. We note that the lowest two triplet states and the lowest two excited singlet states occur as quasi-degenerate pairs for the uuu conformer which almost certainly correspond to ^{3}E and ^{1}E states, respectively. For the lower symmetry uud conformer, the corresponding states lie close to each other but with an increased splitting. All higher states appear to be non-degenerate and therefore correspond to A states in C_3 symmetry.

3.2. Scattering

A variety of calculations were performed to test both the numerical stability of our models and their convergence with respect to various parameters. These tests showed that an R-matrix box of radius at least $a = 15\ a_0$ was required to get realistic results: calculations with $a = 10\ a_0$ gave eigenphase sums which were clearly unphysical, while calculations with $a = 13\ a_0$ appeared physically correct but gave resonance structures that disappeared when a was increased. In all cases, GTO continuum basis sets were used which followed the prescription of Faure *et al* (2002).

A second key parameter was found to be the number of virtual orbitals retained in the calculation. These unoccupied target orbitals can be thought of as providing low-lying unoccupied orbitals which temporarily trap the electron in resonance states as well as compensating the truncation of the angular part of the continuum basis by providing high angular momentum functions in the region of the nuclear singularities. It is well known that the representation of low-lying resonances depends critically on these orbitals (Winstead and McKoy 2006, Dora *et al* 2009). Tests showed that to get converged results it was necessary to retain at least 15 virtual orbitals in all calculations and the results presented here were performed on this basis. Calculations which retained a larger set of virtual orbitals were essentially indistinguishable from the ones presented here and, in particular, showed no new resonance structures. For the CC calculations, the ten lowest electronic states, as listed in table 1, were retained in the CC expansion.

Molecules with dipole moments have cross sections that become very large at low scattering energies and low scattering angles. These cross sections are difficult to determine experimentally and require special treatment theoretically (Zhang *et al* 2009). Here allowance was made for the contribution due to high ($l > 4$) partial waves using the Born approximation and code BORNCROSS (Baluja *et al* 2000); this treatment also includes the effects of target rotational motion which acts to reduce the effects of the asymptotic dipole potential. Rotational constants were calculated from the conformer geometries and only motions about the A-axis were considered. In practice the uuu conformer is very close to being a spherical top and the uud conformer is only slightly further from this high symmetry limit. Given the significant difference between the polarity of the two conformers considered here, inclusion of this effect will be important for evaluating any relative properties.

4. Results

4.1. Resonances

An important part of this study is the identification of any possible resonance features. For this we used the automatic resonance detection program RESON (Tennyson and Noble 1984) and visual inspection of the eigenphase sums. Figure 2 gives the eigenphase sums as a function of model for a target calculation with the cc-pVTZ basis. The eigenphases plotted show a feature in the region above 6 eV. For the SE and SEP models, a broad resonance feature is shown; for the CC model this broad feature is disrupted by the opening

Table 2. Positions (and widths), both in eV, of low-lying shape resonances found for phosphoric acid using the SE and SEP models for several target basis sets.

6-31G		cc-pVDZ		cc-pVTZ		
SE	SEP	SE	SEP	SE	SEP	CC
		Conformer uuu				
6.90 (1.12)	5.71 (0.81)	8.59 (1.63)	7.31 (1.11)	8.55 (1.64)	7.54 (1.26)	7.21 (0.021) 7.26 (0.017) 7.85 (0.040) 7.87 (0.0007)
		Conformer uud				
7.07 (1.52)	5.75 (1.07)	8.71 (1.77)	7.39 (1.26)	8.64 (1.83)	7.51 (1.42)	7.74 (0.019) 7.88 (0.014)

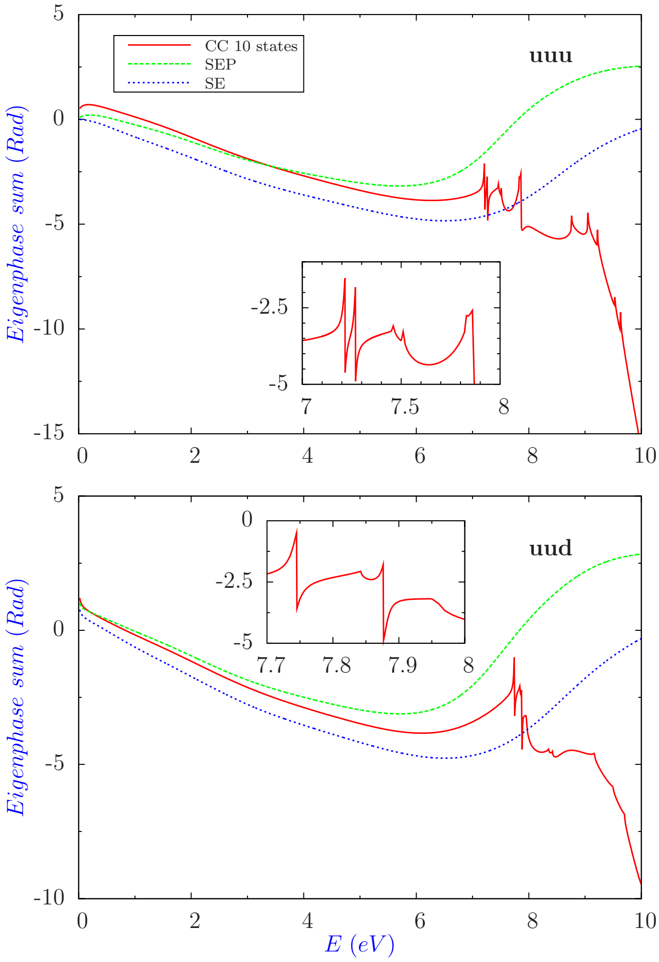

Figure 2. Eigenphase sums for electron scattering from phosphoric acid as a function of model (see the text for details): upper panel uuu conformer, lower panel uud conformer. The insets show the narrow Feshbach resonances in the CC calculation.

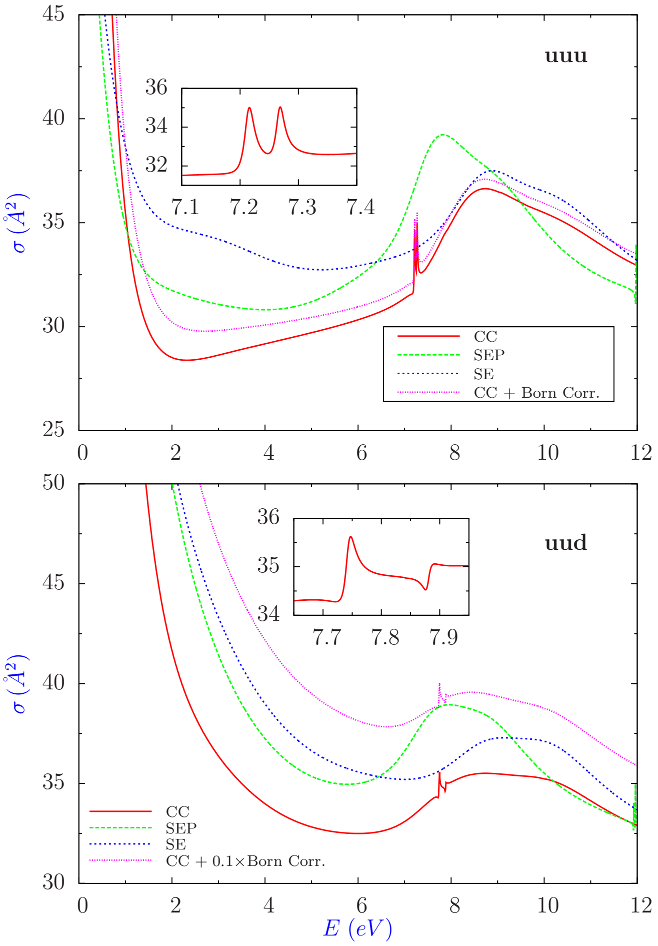

Figure 3. Total electron impact cross sections for phosphoric acid as a function of model (see the text for details): upper panel uuu conformer, lower panel uud conformer. The insets illustrate the influence of the narrow Feshbach resonances in the CC calculations without Born correction.

of channels associated with excited target electronic states which also show associated narrow resonance features (see the insets). For the other target basis sets, a broad resonance is found for both conformers in the 6–9 eV region. The predicted position of this resonance appears to vary little between the two conformers but to be sensitive to the target basis and model chosen, see table 2.

Previous studies (Winstead and McKoy 2008, Tonzani and Greene 2006b) also identified broad resonances in this region. Tonzani and Greene (2006b) found a resonance at 7.70 eV with a width of about 2.0 eV; Winstead and McKoy (2008) identify broad resonances directly from peaks in the integral cross sections. They find a peak at about 8.5 eV for the SE model and 7 eV for SEP. These results are very similar to ours obtained with the cc-pVDZ target basis. Winstead and McKoy (2008) used their cross sections to identify two further, higher energy resonances. Our cross sections (figure 3) show some structure, although the strong dipole-scattering background cross section tends to obscure these. We are however cautious about assigning resonances on the basis of features in the cross section alone. Our conclusion is that H_3PO_4 does indeed show a broad resonance (-like) feature at about 7 eV. This feature appears to be approximately the same for both conformers which can be understood from the fact that the two lowest unoccupied molecular orbitals (LUMOs) in the system are associated with P–O bonds and are therefore, presumably, not very sensitive to the isomerization.

Some of our SEP calculations also showed rather narrow, higher energy resonances not shown in the corresponding SE studies. Such resonances, which are likely to be Feshbach in nature, are better characterized by CC calculations in which the 'parent' state is included in the close-coupling expansion. Table 2 summarizes the Feshbach resonances found below 10 eV for each conformer in the CC calculations. These resonances are all extremely narrow. For the uuu conformer the lowest two (quasi-) degenerate resonances are associated with the two (quasi-) degenerate triplet excited states at 7.5 eV, while the next two, also (quasi)-degenerate, resonances lie almost on top of the (quasi-) degenerate singlet excited states at 7.85 eV. The two uud conformer resonances can also be associated with the two lowest triplet states. The increased separation between these target states is reflected in an increased splitting between the resonances. For uud, RESON did not find a pair of resonances associated with the two lowest singlet excited states. However, given the likely proximity of these resonances to the target state, it is entirely possible that the fit missed them or, indeed, that the resonances have become unbound.

4.2. *Cross sections*

Figure 3 presents our total cross sections, which are essentially elastic cross sections, for the two conformers considered as a function of the different models used. Both conformers show cross sections which increase rapidly at low energy which is the characteristic of electron collisions from targets with large permanent dipole moments. As could be anticipated, the Born correction significantly increases the resulting cross sections; for simplicity this correction is only shown augmenting the CC calculations, but a very similar correction could be applied to the other models. While both conformers show an increased low-energy cross section when the Born correction is added, this is very much larger for the strongly polar uud conformer (note the 10% scaling of this curve in the figure).

Our uuu cross sections are about 10% larger than those of Tonzani and Greene (2006b) and show similar structures at lower energies. Below 5 eV, both cross sections are significantly larger than those calculated by Winstead and McKoy (2008); it is unclear why Winstead and McKoy's results do not show the low-energy peak characteristic of polar molecules.

Figure 4 presents electron impact electronic excitation to the two lowest singlet and triplet excited states of each conformer. For the singlet states, a Born correction has been added to the cross section based on our calculated transition dipole; however, this correction is small in all cases. As we found for uracil (Dora *et al* 2009), the electronic excitation cross sections are fairly small compared to the elastic cross section. The cross sections show near-threshold structure, albeit weakly except for excitation of the uuu triplet states whose structures can be attributed to the broad, near-threshold shape-resonance-like feature discussed above.

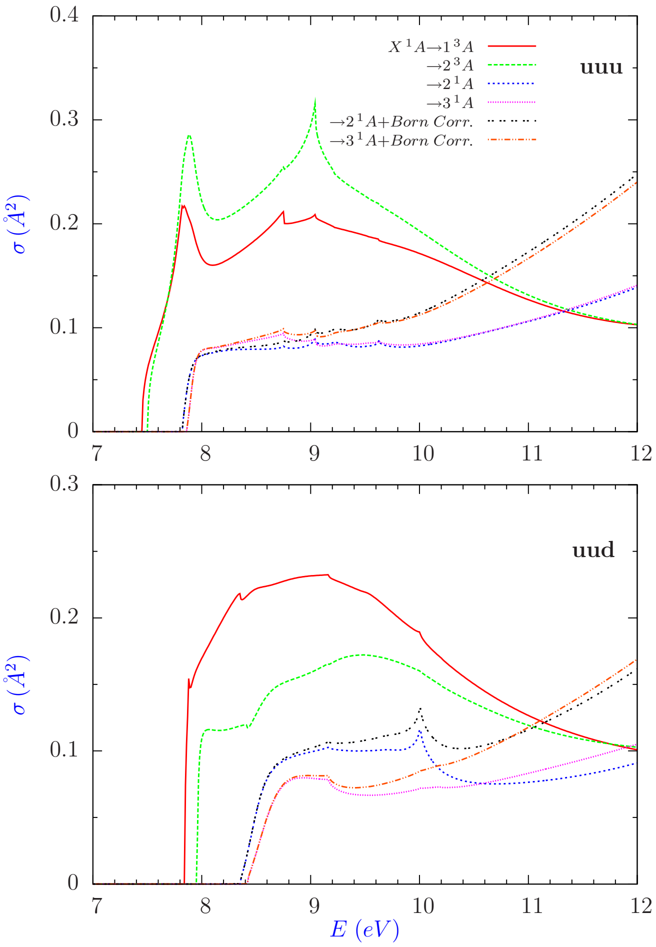

Figure 4. Electron impact excitation cross sections for excitation of the lowest two singlet and two triplet excited states of phosphoric acid; calculations were performed using the close-coupling (CC) model; the upper curves have a Born correction: upper panel uuu conformer, lower panel uud conformer.

5. Conclusions

We have performed electron collision calculations on the two main conformers of phosphoric acid. Both conformers display a broad feature at about 7 eV which may be associated with a shape resonance, as well as some very much narrower Feshbach resonances. The broad feature had been found in previous static exchange plus polarization studies (Winstead and McKoy 2008, Tonzani and Greene 2006b); the Feshbach resonances are a feature of a close-coupling treatment and appear not to have been identified previously. In common with the other electron scattering calculations on isolated H_3PO_4 molecules, we found no evidence for very low resonances or zero-energy states that could be the key to DNA strand breaks due to collisions with very low energy electrons. We note that our calculations do not give a definitive, converged value for the resonance positions since these are very sensitive to the treatment of polarization in the calculation. The molecular *R*-matrix with pseudo-states method (Gorfinkiel and Tennyson 2004, 2005) gives a systematic procedure for addressing this issue but, due to computational considerations, has yet to be applied to a molecule as large as phosphoric acid.

In general, the behaviour of the two conformers is notably similar to resonance positions close to each other and cross sections that match quite closely. This suggests that calculations on either conformer would be appropriate input for modelling the phosphate group in studies of low-energy collisions with DNA and related biological molecules. However, one area where the electron scattering between the two conformers may differ is that the uuu conformer is actually chiral. Scattering of spin-polarized electrons from chiral systems can lead to enantiomer-dependent scattering (Blum and Thompson 1998), an effect known as electron circular dichroism.

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