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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 H₃PO₄, 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. 10-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.

1. Introduction

Low-energy electrons have been shown to be a major cause of radiation damage in biological systems (Boudaiffa et al. 2000). A number of theoretical studies have considered electron collisions with DNA (Caron et al. 2008, Caron et al. 2009) or DNA constituents (Tonzani & Greene 2006*a*, Tonzani & Greene 2006*b*, Winstead et al. 2007, Gianturco et al. 2008, Winstead & 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, H₃PO₄, 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. (2004*a*) 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 Fig. 1.

There is only limited data on electron collisions with phosphoric acid and previous studies appear each to have focussed on a single conformer. Calculation on low-energy collisions with H_3PO_4 were performed by Winstead & McKoy (2008), who studied electron collisions with conformer *uuu*, and Tonzani & Greene (2006*b*), 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, Kopyra, Bald & Illnberger 2006) or indeed the salt NaH_2PO_4 (Pan & 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 & McKoy (2008) and Tonzani & Greene (2006*b*) both reported resonances close to the ionisation 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.

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:

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

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 wave functions of eq. (1) were constructed from Gaussian Type Orbitals (GTOs).

In eq. (1), Φ_i^N is the wave function of the i^{th} target state. 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 eq. (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.

Eq. (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 optimised 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 Yekutieli 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 configuration interaction (CI) models using a mixture of MOLPRO (Werner et al. 2006) and the less flexible target calculation

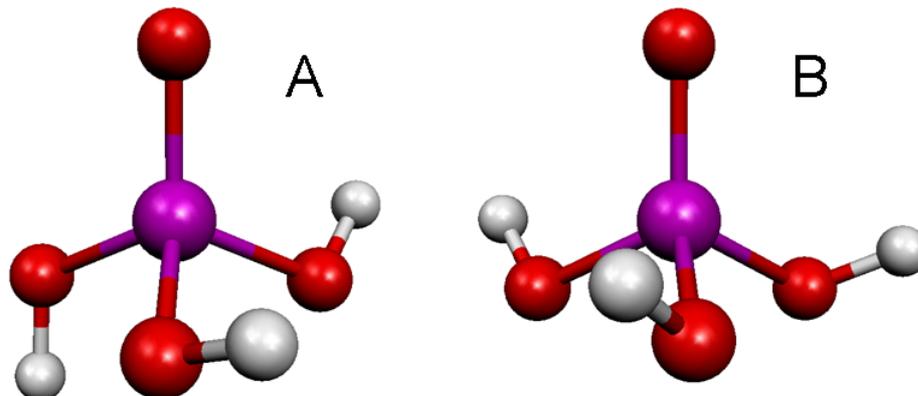


Figure 1. Conformers of phosphoric acid studied in this work: (A) uud, (B) uuu.

facility provided in the UK molecular R-matrix code (Morgan et al. 1998). Only a brief summary of target models considered are 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 10 orbitals. A variety of different orbital sets were tested; all CAS-CI results presented here are based on the use of state-averaged CASSCF orbitals obtained for the lowest 5 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 summarised 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-

Table 1. The X^1A 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.

State	uuu			uud		
	6-31G	cc-pVDZ	cc-pVTZ	6-31G	cc-pVDZ	cc-pVTZ
X^1A	-641.75014	-642.07314	-642.21334	-641.75239	-642.07420	-642.22751
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

averaged CASSCF calculations the orbitals were optimised for an average of 10 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 3E and 1E 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

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.

SE	6-31G		cc-pVDZ		cc-pVTZ		CC
	SEP	SE	SEP	SE	SEP	SE	
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)

these orbitals (Winstead & 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 10 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 was 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 the present study is the identification of any possible resonance features. For this we used the automatic resonance detection program RESON (Tennyson & Noble 1984) and visual inspection of the eigenphase sums. Fig. 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 of channels associated with excited target electronic states which also show associated narrow resonance features (see insets). For the other target basis sets a broad resonance is found for both conformers in the 6 to 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 & McKoy 2008, Tonzani & Greene 2006*b*) also identified broad resonances in this region. Tonzani & Greene (2006*b*) found a resonance at 7.70 eV with a width of about 2.0 eV; Winstead & 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 & McKoy (2008) used their cross sections to identify two further, higher-energy resonances. Our cross sections (Fig. 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 isomerisation.

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 characterised by CC calculations in which the “parent” state is included in the close-coupling expansion. Table 2 summarises 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.

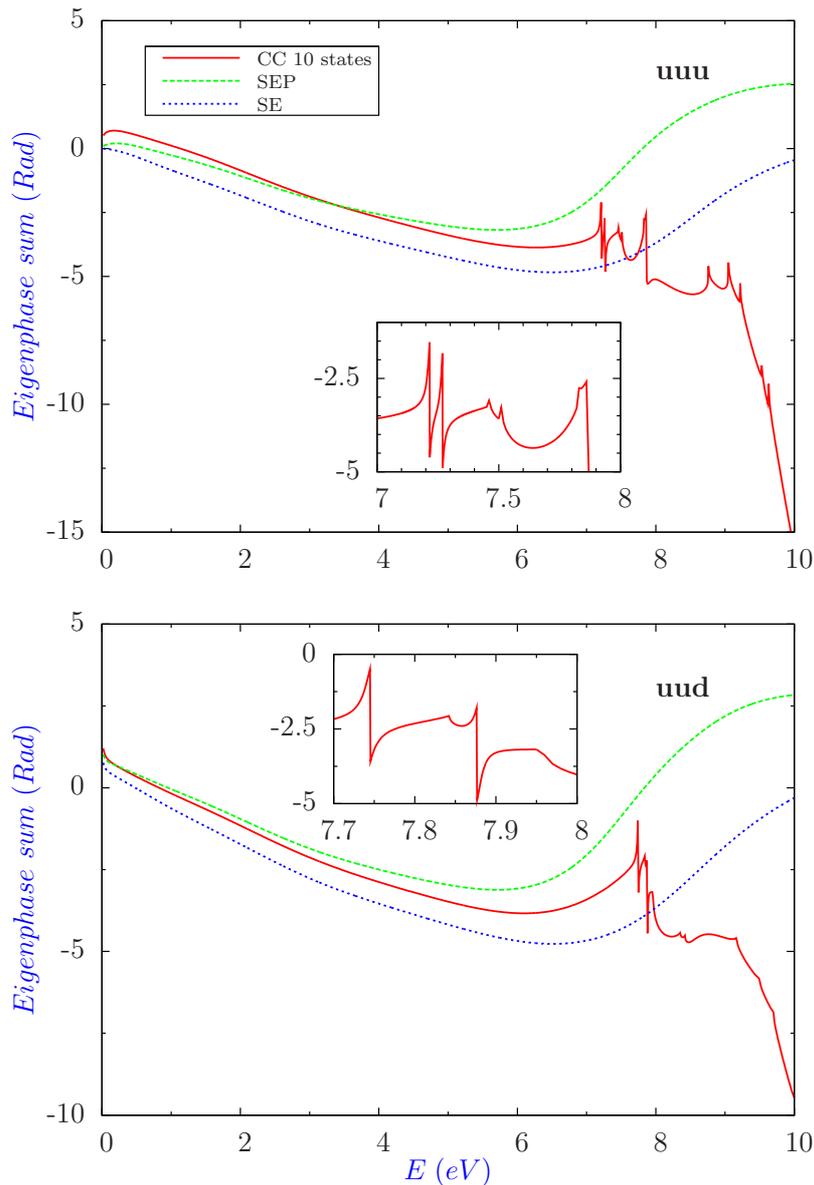


Figure 2. Eigenphase sums for electron scattering from phosphoric acid as a function of model (see text for details): Upper panel uuu conformer, lower panel uud conformer. The insets show the narrow Feshbach resonances in the CC calculation.

Both conformers show cross sections which increase rapidly at low energy which is 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).

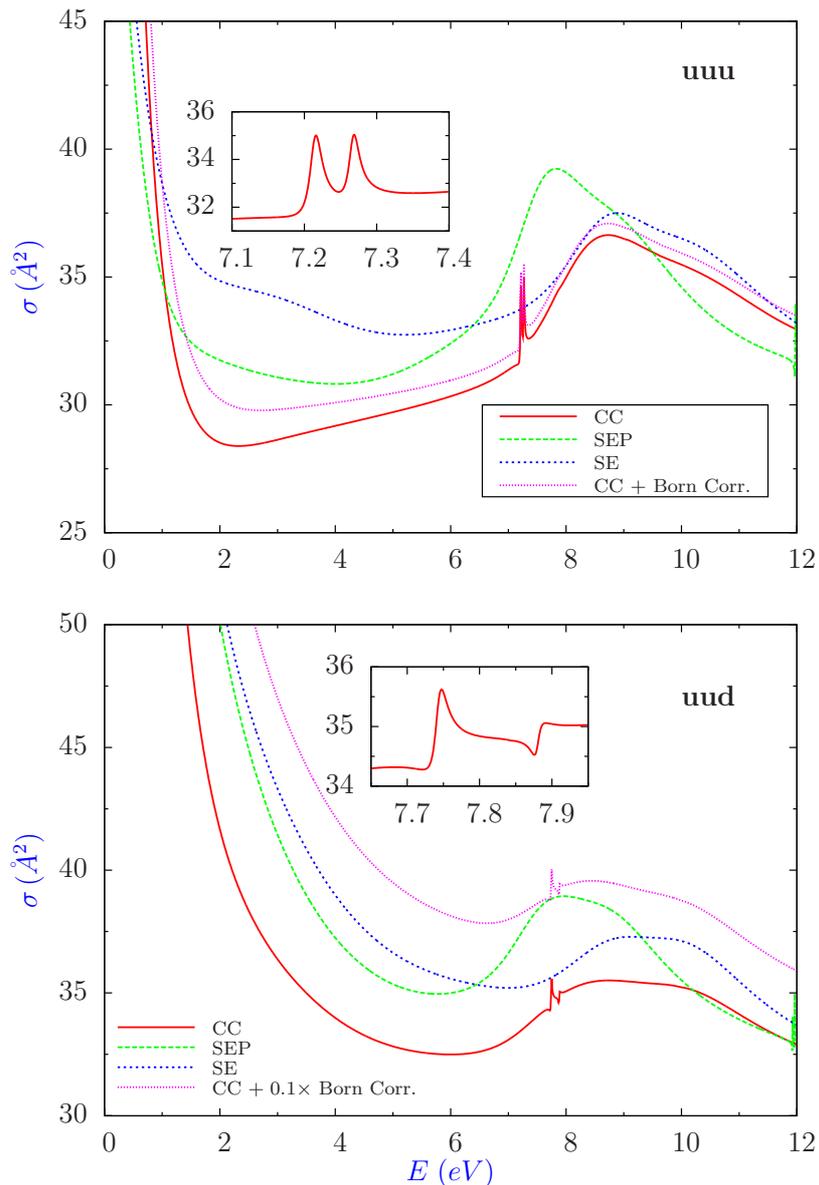


Figure 3. Total electron impact cross sections for phosphoric acid as a function of model (see text for details): Upper panel uuu conformer, lower panel uud conformer. The insets illustrate the influence of the narrow Feshbach resonances in the CC calculations without Born correction.

Our uuu cross sections are about 10 % larger than those of Tonzani & Greene (2006*b*) and show similar structures at lower energies. Below 5 eV, both cross sections are significantly larger than those calculated by (Winstead & 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

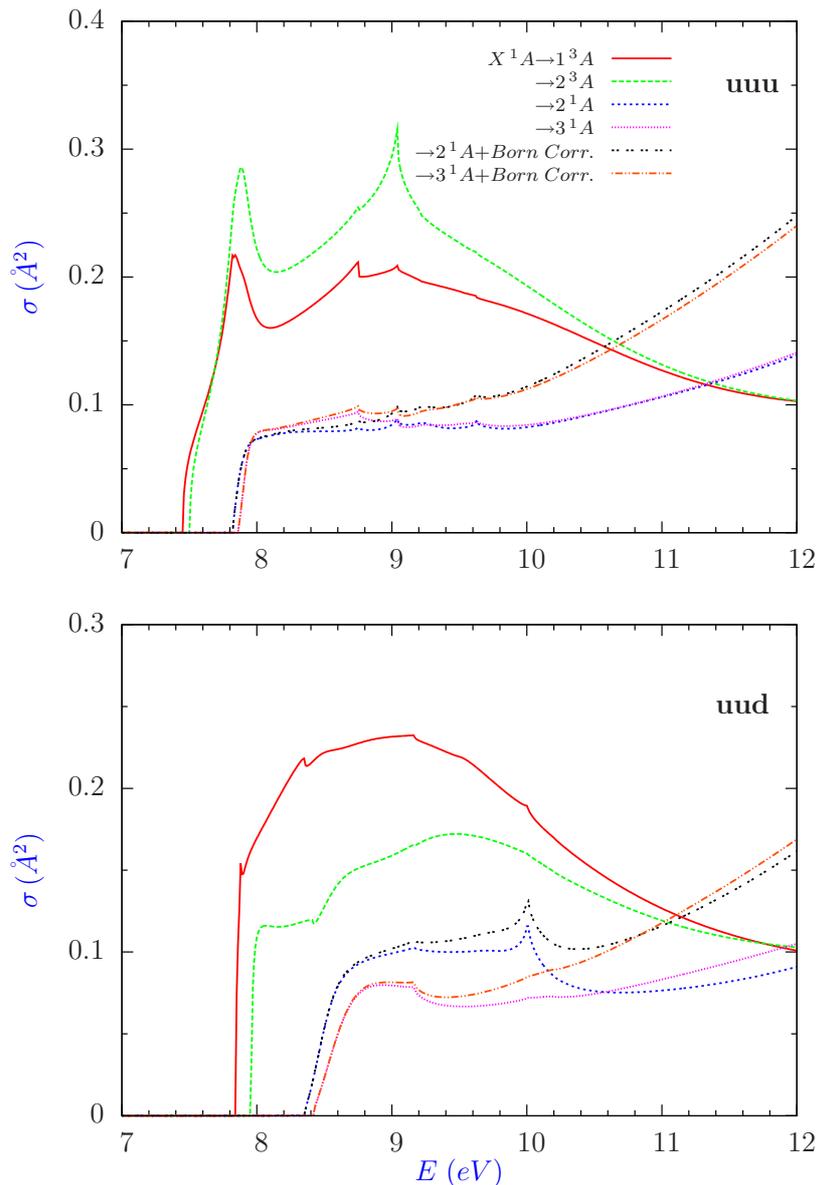


Figure 4. Electron impact excitation cross sections for excitation of the lowest two singlet and two triplet excited states of phosphoric acid; calculations were performed using the close-coupling (CC) model; the upper curves have a Born correction: Upper panel uuu conformer, lower panel uud conformer.

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.

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 & McKoy 2008, Tonzani & Greene 2006*b*); 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 H₃PO₄ 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 polarisation in the calculation. The molecular R-matrix with pseudo-states method (Gorfinkiel & Tennyson 2004, Gorfinkiel & Tennyson 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 with 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 & Thompson 1998), an effect known as electron circular dichroism.

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