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Interaction of slow electrons with methyl phosphate esters

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ABSTRACT

We report computed cross sections for low-energy elastic collisions of electrons with the methyl esters of phosphoric acid, monomethyl, dimethyl, and trimethyl phosphate, and with phosphoric acid itself. For phosporic acid and monomethyl phosphate, polarization effects are included in the calculation, while the two larger molecules are treated in the static-exchange approximation, that is, with polarization neglected. The integral elastic cross sections exhibit broad shape resonances above 5 eV that give rise to strong variations in the differential cross section with energy. However, no shape resonances are evident below 5 eV. We compare our results to previous calculations and measurements and discuss their relevance to electron-induced damage to the DNA backbone.

1. Introduction

Much attention has been devoted to investigating the mechanisms by which slow electrons break DNA strands (for a recent review, see [1]). Though the site of breakage appears to be quite specific, namely the phosphoesteric bonds connecting C 3′ or C 5′ of deoxyribose to the phosphate group [2], the initial site of electron capture may nonetheless be elsewhere. In the model advanced by Simons and co-workers [3–6], electrons are initially trapped in empty π^* orbitals of the nucleobases to form metastable anions (elastic shape resonances, in scattering terminology) and then undergo intramolecular transfer to the backbone, where they localize in a C 5′–O σ^* orbital and thus lead to bond breaking at that site. This model has received implicit support from work that shows a correlation between nucleobase shape-resonance energies and the observed pattern of single-strand breaks in thin-film DNA [9]. However, in light of the limited information so far available, direct attachment of electrons to the DNA backbone has also been suggested [7,8] and is by no means ruled out as a competing, if not the primary, mechanism of strand breaking. Several recent studies have, therefore, addressed the possibility of direct electron attachment to the DNA backbone. Among these, we mention in particular the experiments of Illenberger and coworkers, who have studied gas-phase dissociative attachment (DA) to deoxyribose analogues [10–12] and to the phosphoric acid esters dibutyl phosphate and triethyl phosphate [13]. In the latter study, DA to dibutyl phosphate was observed to produce a number of phosphorous-containing anionic fragments, as well as one in which an entire neutral butyl group had been removed. Such processes, if operable in DNA itself, would lead to strand breaks.

In the present work, we use first-principles computational methods to study the interaction of slow electrons with three simple model compounds containing phosphoesteric bonds, (mono)methyl phosphate (hereafter MMP), dimethyl phosphate (DMP), and trimethyl phosphate (TMP), as well as with their parent compound, phosphoric acid, H_3PO_4. We are particularly interested in identifying any shape resonances that may be present in the elastic electron-scattering cross sections, because temporary trapping in such resonances may promote DA and other energy-deposition processes. Although no electron-collision data for MMP or DMP are, to our knowledge, available, recently Aflatooni et al. [14] have reported DA measurements for TMP, while Burrow et al. [15] have reported electron transmission measurements for TMP. Our results may also be compared to the DA measurements on dibutyl and triethyl phosphate mentioned above [13], as well as to elastic cross section calculations on H_3PO_4 [16] and DA measurements on thin films of the salt NaH_2PO_4 [17].

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2. Computational details

We optimized the geometries of H_3PO_4, MMP, DMP, and TMP at the level of second-order Möller-Plesset perturbation theory in the 6-31 G(d) basis set using GAMESS [18]. Because various conformers appear plausible, we tested several different starting geometries for H_3PO_4 and MMP in an effort to locate the respective global minima. Our lowest energy results were geometries in which the hydroxy and methoxy groups are all *gauche* to the phosphoryl bond, and these structures were used in the electron-scattering calculations. We likewise used all-*gauche* geometries for DMP and TMP. The conformers adopted for H_3PO_4 and TMP have C_3 point-group symmetry, while those used for MMP and DMP have C_1 (i.e., no) symmetry. Other conformers of H_3PO_4 and MMP were nearly as low in energy as the all-*gauche* forms (within ≈ 2 millihartree), and it is likely all four molecules exist in the gas phase as mixtures of conformers. Although the forward scattering may be significantly affected by the molecular conformation, inasmuch as the net static electric dipole moment is quite sensitive to the orientation of the hydroxyl and esteric bonds, we do not expect the precise molecular conformation to strongly affect the resonance structure of the cross sections that is our main interest.

Scattering calculations were carried out using the Schwinger multichannel (SMC) method [19,20] as implemented for parallel computers [21]. A description of the SMC method may be found in the indicated references; here we give only details specific to the present calculations. For all four molecules, we carried out static-exchange (SE) calculations, that is, calculations in which we neglected the response of the molecular charge density to the presence of the projectile electron ("polarization"). These SE calculations used the TZV (triple-zeta valence) basis set contained in GAMESS together with a (1s1p3d,1s2p) supplement. The $(x^2 + y^2 + z^2)$ linear combination of Gaussian d orbitals was excluded, and GAMESS default values were used for all exponents and splitting factors. The target molecule was described at the Hartree–Fock level, and all virtual orbitals were antisymmetrized with the N-electron target wavefunction to form an $(N + 1)$-electron doublet variational space for the scattering calculation.

For the smaller molecules, H_3PO_4 and MMP, we also carried out static-exchange plus polarization (SEP) calculations. The SEP calculation on H_3PO_4 employed the aug-cc-pVDZ basis set as contained in GAMESS, while the MMP SEP calculation employed the the DZV (double-zeta valence) basis set contained in GAMESS with a 1s1p2d supplement of diffuse and polarization functions on the heavy atoms and a 1s1p supplement on the hydrogens, again using default exponents and splitting factors; in both cases the "3s" combinations of d Gaussians were excluded. To represent polarization effects, the $(N + 1)$-electron variational space was expanded to include doublet configurations built on singlet-coupled single excitations from valence orbitals to low-lying modified virtual orbitals (MVOs) [22] that were formed using a $+6$ cationic core. Because such MVOs are compact and valence-like, their use as particle orbitals accelerates the convergence of the configuration expansion. For H_3PO_4 we included singlet excitations from the 6 outermost occupied orbitals into the 15 lowest MVOs, each antisymmetrized with one of the 100 lowest energy MVOs to form a doublet configuration state function (CSF), as well as singlet excitations from the next 6 more tightly bound occupied orbitals into the 10 lowest MVOs, antisymmetrized with the 50 lowest MVOs to form doublet CSFs. This resulted in a variational space of dimension 11,226 for the SEP calculation. For MMP, we included singlet excitations from the 15 outermost occupied orbitals into the 12 lowest MVOs, antisymmetrized with the 80 lowest energy MVOs. The resulting variational space was of dimension 13,558. As a diagnostic, we extracted SE cross sections from the SEP calculations by solving the sub-problems in which all target-excited configurations were discarded and verified that they agreed well with the TZV-basis SE results.

All of the molecules studied here are polar, and their electron scattering cross sections will consequently be affected, especially at near-forward angles, by long-range interactions of the projectile electron with the field of the permanent electric dipole. We applied a Born completion procedure described elsewhere [23] to the SEP

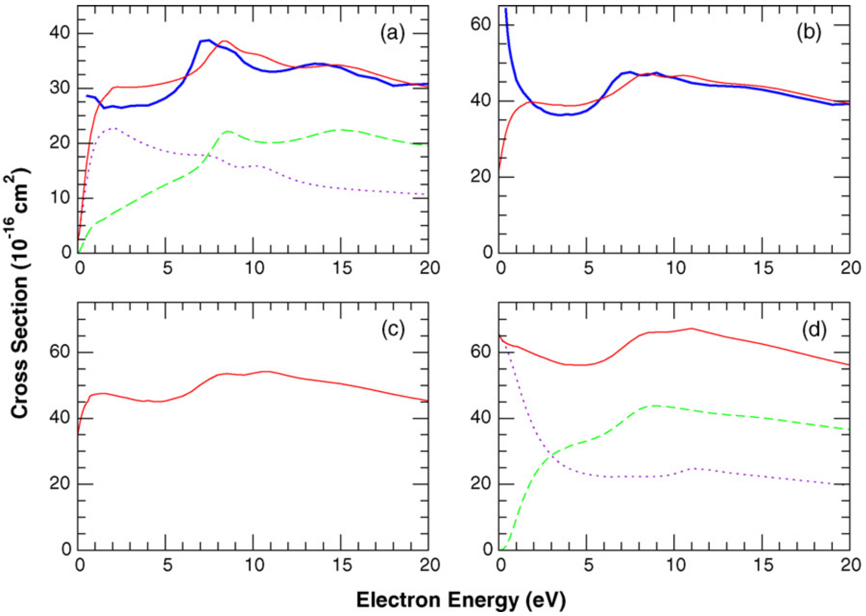

Fig. 1. Integral elastic cross sections for electron collisions with (a) H_3PO_4, (b) monomethyl phosphate, (c) dimethyl phosphate, and (d) trimethylphosphate. The heavy solid blue lines in panels (a) and (b) are computed in the SEP approximation and include the Born-dipole correction. The solid red lines are computed in the static-exchange approximation. For the molecules possessing C_3 symmetry, the static-exchange cross section is decomposed into contributions from ^{2}A (dotted violet lines) and ^{2}E (dashed green lines).