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Electron Collisions with Biomolecules

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Abstract. We report on results of recent studies of collisions of low-energy electrons with nucleobases and other DNA constituents. A particular focus of these studies has been the identification and characterization of resonances that play a role in electron attachment leading to strand breaks in DNA. Comparison of the calculated resonance positions with results of electron transmission measurements is quite encouraging. However, the higher-lying π^* resonances of the nucleobases appear to be of mixed elastic and core-excited character. Such resonant channel coupling raises the interesting possibility that the higher π^*resonances in the nucleobases may promote dissociation of DNA by providing doorway states to triplet excited states.

1. Introduction

The demonstration by Sanche and coworkers [1,2,3,4] that low-energy electrons can induce single- and double-strand breaks in DNA has stimulated significant interest in the interactions between slow electrons and the molecular constituents of DNA and RNA. Because the observed yield of strand breaks exhibits peaks as a function of incident electron energy, processes involving resonances in the electronically elastic channel are implicated, particularly resonance-enhanced dissociative attachment. Not surprisingly, there have been numerous experimental studies of dissociative attachment to the nucleobases [5,6,7,8,9], which have not only demonstrated that resonant dissociative attachment indeed occurs in these bases but have also provided the mechanistic insight that gas-phase dissociative attachment may be driven largely by vibrational Feshbach resonances built on dipole-bound temporary anions. There have also been measurements of the derivative electron-transmission spectra of the nucleobases and their halogenated derivatives that reveal the location of the low-energy scattering resonances [7,10]. Comparison between the attachment and transmission measurements on the nucleobases also indicates that the strongest resonance features in the total cross section (presumably the π^* elastic shape resonances) are not necessarily responsible for the strongest features in the dissociative-attachment cross section [3,7,11]. These experimental studies have been complemented by several calculations of electron-collision cross sections for the nucleobases [12,13,14,15,16,17].

In this contribution we review the results of our calculations of low-energy electron collisions with the nucleobases and other DNA constituents. Our studies have concentrated on the identification and characterization of low-energy shape resonances that play a role in the initial capture electrons and thus in promoting subsequent disruption of the DNA structure, as well as on examining how the resonance positions change when smaller subunits are incorporated into larger moieties. On balance, our calculations support the assignments by Burrow and coworkers [7,10] of the electron-transmission features to π^* shape resonances and thus support the interpretation of the main dissociative-attachment

peak as arising from an alternative mechanism, namely a vibrational Feshbach resonance. A consistent discrepancy between the calculated and measured positions for the third π* resonance in each nucleobase probably reflects the influence of channel-coupling effects not included in our calculations. That is, these higher-lying resonances are not pure elastic shape resonances but also have core-excited character built on the low-lying triplet excited states into which they may decay. This raises the interesting possibility that the higher π* resonances in the nucleobases may promote dissociation of DNA by providing doorways to triplet excited states. The significance of such resonant mixing is demonstrated for pyrazine, a high-symmetry analogue to the pyrimidine bases.

2. Theoretical and computational aspects

Our work employs the Schwinger multichannel (SMC) method [18]. The SMC method is a full many-electron formulation of electron-molecule collisions that is capable of treating the complications arising in low-energy collisions, including exchange, polarization, and electronic excitation. As with other high-level methods that aim to treat the full complexity of the electron-molecule collision process [19,20], the computational demands of the SMC method scale rapidly with the size of the molecule of interest and can become extreme for large polyatomic molecules. Key challenges in our work have therefore been the development of computer codes that run efficiently on parallel computers and workstation clusters [21,22] and improvements in the design of calculations that accelerate convergence and thus mitigate the scaling problem. By formulating the SMC method for massively parallel computers [21], we have been able to achieve sustained performance in the hundreds of gigaflops, making studies of electron collisions with targets such as the nucleobases and deoxynucleosides feasible.

3. Results

Over the past few years, we have employed the parallel implementation of the SMC method to carry out all-electron calculations of the collisions of low-energy electrons with the 5 nucleobases as well as with deoxynucleosides and the deoxynucleotide deoxyadenosine 5′-monophosphate [14,15,16]. In these calculations, exchange effects were treated explicitly and polarization effects were included through virtual excitations of the molecule (closed channels) when computing the π* resonance energies. Though the nucleobases are not quite planar, each molecule was treated in C_s symmetry. Imposing a planar geometry on these molecules facilitates the computations and their analysis by allowing us to separate the orbitals and electronic states into either the $^2A''$ representation or $^2A'$ representation; in particular, the π* resonances fall into the $^2A''$ representation where they can be more readily distinguished from the large $^2A'$ background. However, distorting the molecular geometry may shift resonance positions, as we recently found, for example, in tetrahydrofuran [23], but these shifts are expected to be small for the nucleobases. In fact, calculations of the static-exchange cross sections at the C_s and undistorted (C_1) geometries for the purine base guanine determined that the π* resonances are shifted up by about 0.2 eV in the planar configuration. Furthermore, the nucleobases are all polar, and long-range scattering of electrons by the dipole potential leads to strong forward scattering that can be difficult for methods that rely on finite basis sets, such as the SMC method, to capture. Though there are procedures for correcting the calculated cross sections to account for this long-range scattering, we have neglected such corrections because they are not expected to significantly affect the π* resonance energies of interest here.

Fig. 1 shows our computed $^2A''$ cross section for the purine base adenine [15], displaying the low-energy resonances associated with temporary trapping of the electron in vacant π* orbitals. We show results only up to 5 eV because of pseudoresonances at higher energy which make it difficult to determine the actual location of the fourth resonance. Our computed resonance energies of 1.1, 1.8, and 4.1 eV compare reasonably well with the resonances observed at 0.54, 1.36, and 2.17 eV in transmission measurements [10]. The agreement between the computed resonance positions and the transmission measurements for the other nucleobases, uracil [14[, thymine and cytosine [16], and

guanine [15], is quite similar to that seen here for adenine, and we may conclude that our calculations support the assignment of the observed electron-transmission resonances [7,10] as π* resonances. In contrast, other scattering calculations [12,13,17] place the π* resonances considerably higher in energy, requiring either empirical shifts [13] or the association of the first calculated π* resonance with the second resonance observed in the transmission spectra [12,24]. The calculations of Tonzani and Greene employ local approximations to both the exchange and polarizations potentials, and, while both approximations may introduce errors, errors due to the approximation to exchange are probably responsible for much of the error in the resonance energies, because comparable errors are seen when comparing a static-exchange calculation for CO_2 using the same procedure [25] with all-electron static-exchange calculations.

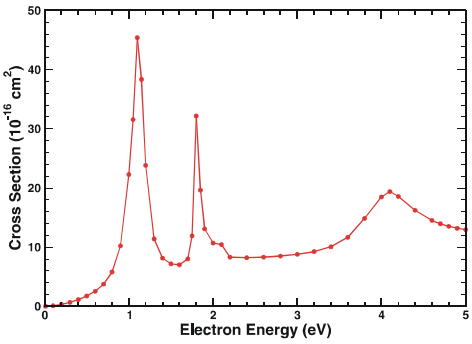

Figure 1. A'' component of the integral elastic cross section for electron scattering by adenine as computed in the static–exchange plus polarization approximation. The three prominent peaks are due to π* resonances.

The error of the order of 2 eV between our computed position for the third π* resonance in adenine and the electron-transmission measurement is much less satisfactory than for the two lowest-energy π* resonances where the errors are about half an eV. We have observed this pattern consistently in our calculations on the nucleobases [14,15,16] where the calculated positions of the two lowest and narrowest resonances agree quite well with the measurements but the computed locations of the third and broadest resonance are consistently too high. While these discrepancies may partly

arise from limitations of our treatment of polarization, it was surprising that the error is largest for the highest-energy and broadest resonance, because polarization effects are expected to be less important as the collision time decreases. In [15] we surmised that this larger discrepancy was due to some underlying difference in the physical character of the higher-lying π* resonances from that of the lower resonances that was not being captured by our choice of configurations describing polarization effects.

In our calculations of electron collisions with nucleobases polarization effects were represented by including terms built on singlet virtual excitations of the molecule in the scattering wavefunction. Such excitations describe the relaxation of the molecular charge density and account for the long-rang polarization interactions as well as shorter-range electron correlation effects. By excluding configurations built on triplet excited states of the molecule, we precluded the possibility of coupling between the elastic-channel shape resonances and core-excited resonances built on low-lying triplet states of the nucleobases. Such resonant channel coupling might be expected to be more important for the higher-lying resonances than for those lying well below the lowest triplet excitation threshold and could account for the trend we observed in our calculated π* resonance positions in the nucleobases. Moreover, because such mixed resonances can decay not only into the elastic channel but also into triplet states, they may play a role in promoting DNA damage by slow electrons.

To explore such channel mixing [26,27] we chose pyrazine, a close analogue of the pyrimidine bases, because of its high symmetry (D_{2h}) and the experimental data available on the positions of its three low-energy resonances [28]. Calculations [26,27] reveal that the two lowest resonances are nearly pure single-channel resonances but the third is, indeed, as long suspected [28], heavily mixed with core-excited resonances built on triplet $\pi \rightarrow \pi^*$ excited states. In fact, Nenner and Schulz [28] posited that the higher-lying shape resonances they had observed in benzene and azabenzenes were probably mixed with core-excited shape or Feshbach resonances associated with low-lying excited states of the molecule. Though such mixing was confirmed by subsequent observation in benzene of the decay of the higher π^* resonance into both the elastic channel and a triplet excited state [29], it had not been previously accounted for in calculations on elastic electron-molecule collisions nor had its potential to produce a large and selective effect on resonance energies been generally appreciated.

To make a closer connection between our results and DNA itself, we have also studied collisions of slow electrons with the purine and pyrimidine nucleosides and the deoxynucleotide 2′-deoxyadenosine 5′-monophosphate [15,16]. For these systems, higher-level calculations including polarization effects are not yet feasible with the current versions of our computer codes, and they were therefore studied at the static-exchange level. Though the static-exchange cannot be expected to yield correct resonance positions, it is fairly reliable above 10 eV, where polarization effects are small, and provides upper bounds to resonance energies because the omitted polarization interaction is attractive. Moreover, by comparing resonance positions obtained with and without polarization on the nucleobases, we can make informed estimates of the actual resonance positions in the deoxynucleosides and deoxynucleotides.

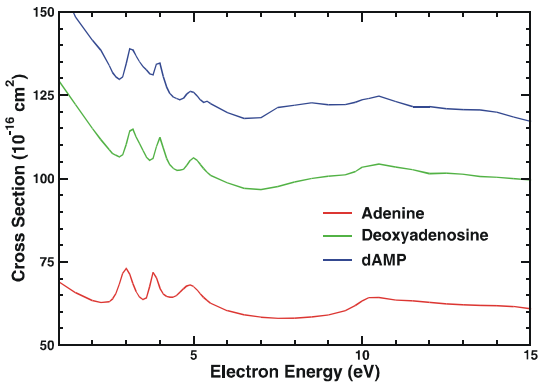

Figure 2. Integral elastic cross sections for electron scattering by adenine (bottom, red), 2-deoxyadenosine (middle, green), and 2-deoxyadenosine 5-monophosphate (top, blue), computed in the static--exchange approximation.

Fig. 2 shows our calculated integral elastic cross sections for collisions of low-energy electrons with adenine, its nucleoside, deoxyadenosine, and its nucleotide 2′-deoxyadenosine 5′-monophosphate (dAMP). For comparison, the adenine cross sections in this figure were also obtained at the static-exchange level which neglects polarization effects. The significant upward shift in the π^* resonance positions in the nucleobase in comparison to the results of Fig. 1 reflects the importance of polarization effects. Details of the calculations, including the assumed nuclear geometries, can be found in [15]. Because of the lack of symmetry in the larger molecules, we can no longer separate the π^* resonances cleanly from the background, as we could in adenine, but their positions are still evident. There is clearly a close correlation between the low-energy resonances of the nucleoside and those of the nucleobase, the main difference being a slight upward shift of the resonances in deoxyadenosine relative to adenine. The positions of the π^* resonances, however, are virtually unchanged going from the nucleoside to the nucleotide (dAMP).

4. Summary

We have reviewed results of first-principles calculations of the collisions of slow electrons with the nucleobases of DNA and RNA as well as with the nucleosides and nucleotides of the DNA bases [14,15,16]. Our studies have emphasized the characterization of the π* resonances in the nucleobases and our calculated positions for these resonances support the assignments proposed by Burrow and coworkers [7,10] on the basis of electron transmission measurements. In the course of our studies of the nucleobases, we uncovered an interesting difference between the lowest-energy π* resonances and those at higher energy. Exploring this difference in the high-symmetry model compound pyrazine, a close analogue of the pyrimidine bases, we found that the third π* resonance actually has mixed character: it is partly an elastic channel shape resonance and partly a core-excited resonance built on low-lying triplet excited states, and inclusion of this resonant channel coupling is essential to obtaining the correct resonance energies. This result raises the interesting possibility that the higher π* resonances (and perhaps other high-energy shape-resonances) in the nucleobases may promote dissociation of DNA by providing doorways to triplet excited states.

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