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LETTER TO THE EDITOR

Elastic scattering of low-energy electrons by tetrahydrofuran

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Abstract. We present the results of *ab initio* calculations for elastic electron scattering by tetrahydrofuran (THF) using the complex Kohn variational method. We carried out fixed-nuclei calculations at the equilibrium geometry of the target molecule for incident electron energies up to 20 eV. The calculated momentum transfer cross sections clearly reveal the presence of broad shape resonance behavior in the 8-10 eV energy range, in agreement with recent experiments. The calculated differential cross sections at 20 eV, which include the effects of the long-range electron-dipole interaction, are also found to be in agreement with the most recent experimental findings.

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

Radiation damage to biological systems was long believed to arise predominantly from high-energy primary ionizing radiation events. But much of the energy deposited in living cells by ionizing radiation is channelled into the production of low-energy secondary electrons which are in turn responsible for most genotoxic effects. It has been demonstrated [1, 2] that slow electrons, with energies well below direct ionization thresholds, can still induce irreversible damage to DNA as well as to basic DNA components through dissociative electron attachment processes. Since electron attachment is a resonance process that generally proceeds through the formation of transient negative ions, the detection of resonances in the vibrational excitation of, or dissociative electron attachment to, biologically relevant species can play an important role in understanding the details of radiation damage to living cells. Indeed, models have been proposed [3] for studying low-energy electron-DNA scattering which take account of multiple-scattering and diffraction effects. These models require as input scattering information for the subunits that form the macromolecule, providing additional incentive for studying resonance scattering from DNA constituents.

Studies of low-energy electron collisions with tetrahydrofuran (THF: C₄H₈O) are of particular value in gaining a better understanding of the dynamics of energy deposition in DNA, because THF can be viewed as a sugar-like component of the backbone of DNA [4]. THF is also an important component of RNA [5]. For these reasons, electron interactions with THF have been widely studied experimentally. Much of this work was focused on differences in the electron spectroscopy of THF in the gas phase and in the solid phase. A study of damage induced by low-energy electrons in solid THF by Breton *et al.* [6] reports and discusses the production of aldehydes in terms of electron resonances, and lists previous investigations of both electron and photochemical interactions with gas, liquid and solid state THF. On the other hand, absolute cross section measurements for electron collisions with gaseous

THF have only recently appeared. Zecca *et al.* [7] reported total cross sections for positron and electron scattering from THF at energies below 21 eV and found a broad shape resonance in the total electron scattering cross section, peaked at ~ 7.5 eV. At the same time, Milosavljević *et al.* [8] reported the first absolute differential cross sections for elastic scattering of electrons from THF for incident electron energies between 20 and 60 eV. To the best of our knowledge, the only previous theoretical investigation of low-energy electron-THF scattering has been the R-matrix study of Bouchiha *et al.* [9], which focused primarily on excitation of low-lying electronic states. They found no shape resonances in this investigation, but reported a few core-excited resonances in the energy region spanning the first eight excited states.

In the present study, we carried out calculations of differential and momentum transfer cross sections for electronically elastic electron-THF scattering using the complex Kohn method. Details of this variational technique can be found elsewhere (see [10, 11] and the references therein). The calculations were carried out for fixed nuclear geometry and were restricted to electronically elastic processes. For this case, the trial wave function used in the complex Kohn method takes the form:

$$\Psi = \mathcal{A}[\Phi_o(\vec{r}_1 \dots \vec{r}_N)F(\vec{r}_{N+1})] + \sum_{\mu} d_{\mu} \Theta_{\mu}(\vec{r}_1 \dots \vec{r}_{N+1}) \quad (1)$$

where Φ_o is the wave function that describes the ground-state of the target molecule, \mathcal{A} antisymmetrizes the coordinates of the incident electron (\vec{r}_{N+1}) with those of the target and the sum contains square-integrable, $(N + 1)$ - electron terms that describe dynamic polarization and/or short-range target distortion effects by the incident electron. In the complex Kohn method, the scattering function $F(\vec{r}_{N+1})$ is further expanded in a combined basis of square-integrable (cartesian Gaussian) functions, ϕ_i and numerical continuum functions, j_l , and h_l^+ , that incorporate physical, outgoing-wave boundary conditions [12].

$$F(\vec{r}) = \sum_i c_i \phi_i(\vec{r}) + \sum_{lm} [j_l(kr)\delta_{l0}\delta_{mm_0} + T_{l_0mm_0} h_l^+(kr)] Y_{lm}(\hat{r})/r. \quad (2)$$

where $Y_{lm}(\hat{r})$ are spherical harmonics. Substituting the trial wave function into the stationary principle for the T -matrix,

$$T_{stat} = T_{trial} - 2 \int \Psi(H - E)\Psi \quad (3)$$

results in a set of linear equations for the coefficients c_i , d_{μ} and $T_{l_0mm_0}$. The T -matrix elements, $T_{l_0mm_0}$, are the fundamental dynamical quantities from which all fixed-nuclei cross sections are derived.

An all-electron, first-principles scattering calculation on a molecule of this size is computationally challenging and therefore some simplifying assumptions were made in order to keep the problem tractable. For the equilibrium geometry, we used a C_{2v} structure, taken from Cadioli *et al.* [13], with the oxygen and four carbon atoms lying in a single plane. In fact, there are lower-symmetry, twisted (C_2) and envelope (C_s) structures that have lower absolute energies. However, as shown by large-scale calculations [13, 14], the energy differences between the various structures are small (< 0.2 eV) and the bond distances and angles are quite similar, so using the C_{2v} structure for the equilibrium geometry is not expected to introduce any significant errors.

The Gaussian basis sets employed in these calculations, for determining both the target self-consistent field (SCF) wave function as well as the Kohn trial function, were

based on the [9s,5p,1d] sets for carbon and oxygen, and the [4s,1p] set for hydrogen given by Dunning [15]. We also included one additional diffuse p-function on the oxygen ($\alpha = 0.059$). Most of the calculations we report used Dunning’s triple-zeta contraction of these basis sets (TZP), which give a total of 151 molecular orbitals. We also performed calculations with the smaller double-zeta contraction of the basis (DZP), which gives 123 molecular orbitals. As we will show below, the differences we found in the computed cross sections using the DZP and TZP sets were not very large. For the scattering calculations, which were carried out in C_{2v} symmetry, the variational trial functions included numerical continuum functions up to and including $l = |m| = 7$. Higher partial-wave contributions were included perturbatively, as described below. The target was described by an SCF wave function. The augmented TZP basis gave an SCF ground-state energy of -231.0285 Hartree and a dipole moment of 0.834 atomic units, the latter being somewhat larger than the experimental value of 0.641 atomic units [16].

A preliminary set of calculations was carried out at the static-exchange level using the DZP basis. These calculations showed broad shape resonances in both A_1 and B_2 (in plane) symmetry, while in A_2 and B_1 symmetry, where the wave functions vanish in the plane containing the carbon-oxygen ring, there was no sign of any resonance behavior. Since shape resonances can be sensitive to the effects of target distortion by the incident electron, we decided to carry out more extensive calculations in A_1 and B_2 symmetry which incorporated relaxation effects through single excitations of the occupied target orbitals.

As first noted by Schneider and Collins [17] in their study of electron- N_2 scattering, and subsequently confirmed by numerous studies of negative ion shape resonances for a number of closed-shell molecules, target response in resonant symmetries is most reliably described by “radial correlation” effects, that is, by including only single-excitations of target orbitals into unoccupied orbitals of the same symmetry (in THF, $a_1 \rightarrow a_1$, $a_2 \rightarrow a_2$, $b_1 \rightarrow b_1$, and $b_2 \rightarrow b_2$ excitations). This prescription in turn calls for the inclusion of two-particle, one-hole configurations in the $(N + 1)$ -electron trial wave function of the form $(p\gamma \rightarrow q\gamma)n\delta$, where $p\gamma$ is an occupied orbital, $q\gamma$ is a virtual orbital of the same symmetry and the set $[n\delta]$ includes virtual orbitals of the overall symmetry being considered. The number of configurations generated in this “relaxed-SCF” model grows rapidly with the complexity of the target. In the present case, for example, in overall A_1 symmetry with the 10 core electrons (carbon and oxygen 1s) kept frozen, the relaxed-SCF model with the TZP basis generates over 60,000 $(N + 1)$ -electron terms. Winstead and McKoy [18] have suggested a less demanding procedure for including target relaxation in resonant symmetries. Instead of including all symmetry-preserving correlation terms, they include only terms of the form $(p\gamma \rightarrow q\gamma)\delta^*$, where δ^* is valencelike virtual orbital that gives an approximate representation of the local part of the resonance orbital. With this model, the same example of an A_1 calculation with the TZP basis requires ~ 1000 correlation terms. To obtain reference valencelike orbitals of a_1 or b_2 symmetry, we used the so-called Improved Virtual Orbital (IVO) procedure [19], in which the virtual orbitals are obtained by diagonalizing a V_{N-1} Fock operator in the subspace of SCF unoccupied orbitals. We found that including orbital relaxation produced only small changes in the resonance positions and widths, so that more extensive treatments of correlation were not really warranted in this case.

With polar molecules such as THF, there are aspects of the low-energy electron scattering that are dominated by the underlying long-range electron-dipole interaction.

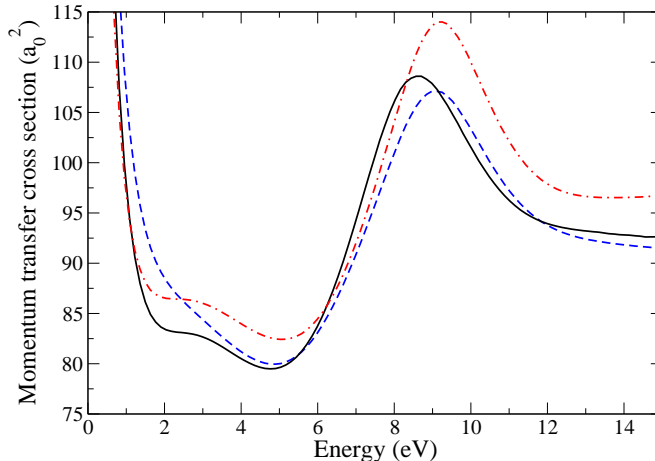


Figure 1. Electron scattering from THF: momentum transfer cross sections. Dash curve: static-exchange approximation employing the TZP basis. Chain curve: static-exchange approximation employing the DZP basis. Solid curve: relaxed calculation using the TZP basis. Cross sections are in atomic units ($a_0^2 = 2.8002852 \times 10^{-21} \text{ m}^2$). Energies are in units of $\text{eV} = 1.6021765 \times 10^{-19} \text{ J}$.

The characteristic strong forward peak in the differential elastic cross sections of polar molecules is the result of the large number of partial waves that contribute to the scattering amplitude at small scattering angles. To compute converged cross sections at small angles, however, it is neither practical nor necessary to carry out variational calculations for the high partial waves T-matrix elements that are required. Because of the centrifugal barrier, high partial-wave components of the scattering wave function do not penetrate the target and hence the corresponding high angular momentum components of the T-matrix are insensitive to the form of the interaction potential inside the molecular charge cloud and rapidly approach the values given by the first-Born approximation for a pure dipole potential. We can therefore employ a simple closure procedure to include all partial-wave contributions in the Born approximation beyond the number calculated variationally. This procedure is detailed in the work of Rescigno and Lengsfeld [20].

The fixed-nuclei approximation for polar molecules gives differential elastic cross section that diverge at zero scattering angle and, consequently, infinite total scattering cross sections. This problem can be remedied by explicitly including the rotational motion of the target when applying the closure procedure. The total cross sections will then properly depend on the initial rotational state of the target and are sensitive to the details of the representation of the rotational states employed. The fixed-nuclei treatment, on the other hand, is perfectly adequate for treating differential scattering out of the forward direction and for calculating momentum transfer cross sections which are insensitive to the form of the DCS near 0° and, since they are not dominated by the dipole interaction, display resonance features more prominently than do the total cross sections.

Figure 1 shows momentum transfer cross sections for THF. The figure shows static-exchange results computed using the TZP basis (dashed curve) and the smaller DZP basis (chained curve). Both basis sets show a broad resonance feature centered

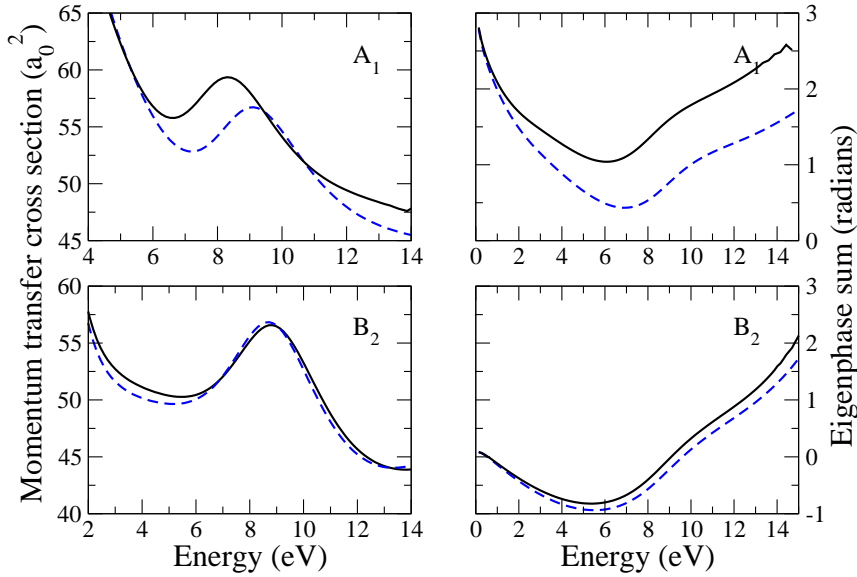


Figure 2. Electron scattering from THF: A_1 and B_2 symmetry contributions to the momentum transfer cross sections and eigenphase sums. Dash curves: static-exchange approximation with TZP basis. Solid curves: relaxed calculation using the TZP basis. Cross sections are in atomic units and energies are in units of eV.

near 9.2 eV with a width of ~ 3 eV. The DZP basis gives cross sections that are $\sim 5\%$ smaller than the TZP results. Also shown in Figure 1 are the results of calculations using the TZP basis that include relaxation effects in A_1 and B_2 symmetry. The principal effect of including target distortion is to lower the resonance peak to ~ 8.6 eV while the overall width of the feature remains about the same. The position and width of this resonance feature are consistent with the total cross section measurements of Zecca *et al.* [7] and the gas phase THF excitation functions for the CH_2 stretching modes measured by Lepage *et al.* [4].

Figure 2 shows eigenphase sums for A_1 and B_2 symmetry as well as the individual components of the momentum transfer cross section in these symmetries. It is clear from this figure that the broad resonance feature seen in the momentum transfer cross section is the result of two overlapping shape resonances of A_1 and B_2 symmetry, respectively. It is also interesting to note that the A_1 resonance, which has contributions from s-waves which effectively penetrate the target, is most sensitive to target distortion, while target relaxation effects on the B_2 resonance are relatively small.

Differential cross sections for several incident electron energies are plotted in Figure 3. As explained above, contributions from partial waves higher than $l = |m| = 7$ were included in the first-Born approximation using a closure procedure, while the lower partial waves were treated variationally. These results again came from calculations in the TZP basis and include target relaxation. The cross sections show

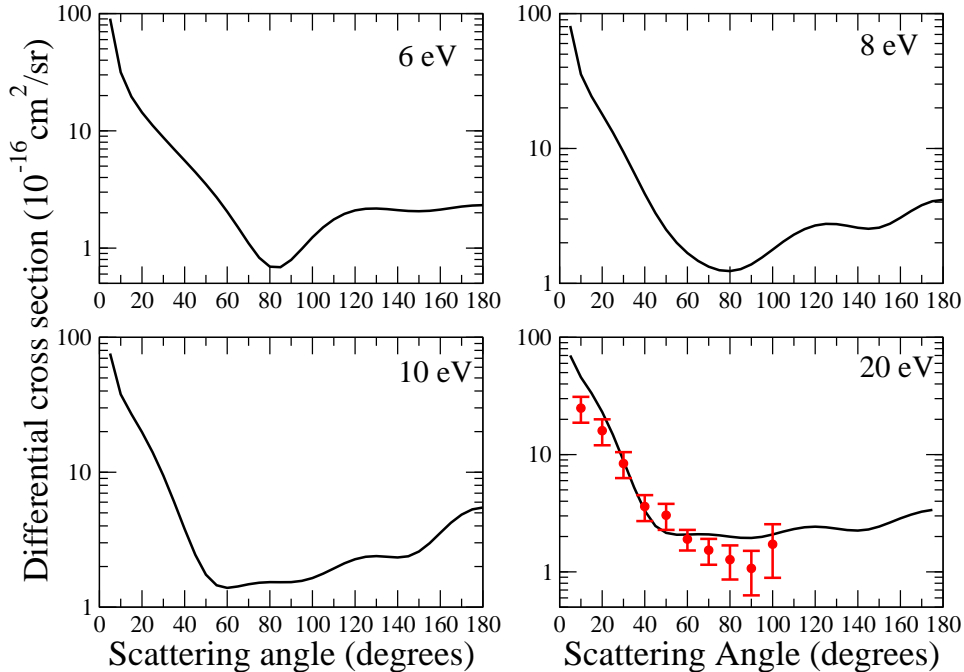


Figure 3. Electron scattering from THF: angular differential cross sections for different incident electron energies. Experimental data at 20 eV is from Milosavljević *et al.* [8].

the strong forward peaking characteristic of polar targets. At 20 eV, the lowest energy for which absolute differential cross sections have been reported, our calculations agree reasonably well with the results of Milosavljević *et al.* [8].

This preliminary study was undertaken to demonstrate the feasibility of carrying out first-principles studies of low-energy electron scattering from biologically relevant molecules. We have focused our attention on electronically elastic collisions, since the first experimental measurements of absolute cross sections for this process have recently been reported [7, 8]. Our calculations support the experimental observation of shape resonance behavior near 8 eV collision energy, in contrast to the only other theoretical study on electron-THF scattering which found no shape resonances [9], and identify the structure as coming from two broad resonances of A_1 and B_2 (in plane) symmetry.

Acknowledgments

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