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Electron collisions with furan

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The authors report integral, differential and momentum transfer cross sections for elastic scattering of low-energy electrons by C$_4$H$_4$O (furan) molecules. Their calculations employed the Schwinger multichannel method with pseudopotentials and were performed in the static-exchange and in the static-exchange plus polarization approximations. The authors found two shape resonances located around 2.1 and 4.2 eV that belong to the $B_1$ and $A_2$ symmetries of the C$_2v$ group, respectively. The authors’ results are consistent with recent measurements of vertical electron attachment energies.


I. INTRODUCTION

Electron attachment is a common effect occurring during the process of electron-molecule collision. The continuum electron attaches to the molecule forming a temporary anion state. In other words, the incoming electron may get trapped in a so-called shape resonance, which is due to an overall potential resulted from a combination of the angular momentum barrier, static, exchange, and polarization interactions. A shape resonance can decay into different vibrational channels. One of great interest is responsible to a process known as dissociative electron attachment (DEA). Shape resonances appear as peaks in the cross sections (total, elastic, vibration excitation, etc.) and as maxima/minima in the derivative of the electronic current. Experiments usually give the location and width (in energy) of the resonance. When DEA occurs, experiments also give the resulting products of the dissociation process. Theoretical calculations of electron-molecule collision cross sections are able to predict the existence of shape resonances. These calculations can assign the shape resonances to a particular symmetry of the molecular point group, being useful to the interpretation and understanding of experimental data. In this paper we carry a theoretical search for shape resonances in $e^-$-C$_4$H$_4$O scattering.

Electron attachment by a series of molecules including furan (C$_4$H$_4$O) has been investigated by Modelli and Burrow$^1$ through electron transmission spectroscopy. In this experiment the derivative of the electron current through the gas is measured and the resonances are related to maxima and minima presented in the measured signal. The resonance energies [the vertical attachment energies (VAEs)] correspond to the midpoint energies between these maxima and minima. They observed the formation of two anion states at 1.73 and 3.15 eV. They also preformed calculations of the VAE, which is the negative of the vertical electron affinity (according to Koopman’s theorem). They employed minimal basis sets and an empirical scaling to the computed VAE in order to bring the computed VAE close to the experimental data. The theoretical values reported by Modelli and Burrow were 1.53 and 2.91 eV obtained in a MP2/6-31G$^*$ calculation and 1.64 and 2.93 eV obtained in a B3LYP/6-31$^*$ calculation. The lower VAE was characterized as a $\pi^*$($B_1$) resonance, and the higher VAE was characterized as a $\pi^*$($A_2$) shape resonance.

Recently, Sulzer et al.$^2$ investigated the dissociative electron attachment to furan, tetrahydrofuran, and fructose using crossed electron/molecular beam experiment with mass spectrometric detection of the anions. For furan, they covered energies from 0 to 12 eV. For energies below 5 eV they detected a very small signal due only to the furanyl anion. This energy range includes the energies were Modelli and Burrow reported the VAE. They found a pronounced peak located at 6 eV responsible for the generation of several anionic fragments (FN-H$^-$, C$_2$H$_5$O$^-$, C$_3$H$_3$O$^-$). They suggested that the DEA at 6 eV occurred through a core excited shape resonance based on the existence of two excited states of furan at 5.8 and at 6.04 eV which involve the two highest occupied orbitals.$^3$

In the present paper we report calculated integral, differential, and momentum transfer cross sections for elastic scattering of electrons by furan in the energy range from 0.5 to 15 eV. We employed the Schwinger multichannel cross sections to compute the scattering cross sections in the static-exchange and in the static-exchange plus polarization approximations. We aim to provide additional information concerning the shape resonances observed by the experimental studies.

In the next section we will describe the theoretical procedures used in the present calculation, followed by the presentation and discussion of our results. We end the paper with a summary of our results.

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II. THEORY

To compute the elastic cross sections we employed the Schwinger multichannel method\textsuperscript{4–6} (SMC) with pseudopotentials.\textsuperscript{7} Since the details of the SMC method has been described in several publications, here we will only focus on those points concerned with the present calculations.

The ground state of furan was described in the Hartree-Fock approximation at the ground state equilibrium geometry given by Ref. 8. We worked within the $C_{2v}$ point group. The geometrical structure of furan is shown in Fig. 1. Our scattering calculations were carried out in the static-exchange and in the static-exchange plus polarization approximations. In the bound state and scattering calculations we employed the norm-conserving pseudopotentials of Bachelet et al.\textsuperscript{9} to replace the core electrons of carbon and oxygen atoms. The Cartesian Gaussian functions used for carbon and oxygen in both calculations are from Ref. 10 and were generated according to Ref. 11. For the hydrogen atom we used the same basis set quoted in Ref. 12.

The calculated dipole moment for furan was 0.85 D which is in relative agreement with the experimental value of 0.66 D. Since this dipole moment is relatively small ($<1$ D), we will omit in our calculations the contribution of the higher partial waves of the dipole potential (we are considering partial waves up to $\ell = 10$ in our calculations), except for the differential cross sections at 5 and 7.5 eV, as discussed below. The differential cross sections obtained from the truncated scattering amplitude will be finite in the forward direction, but the conclusions regarding the shape resonances are not going to be affected by truncating the scattering amplitude. To illustrate this point, we computed the differential cross sections at 5 and 7.5 eV using the usual Born closure of the dipole potential in order to account for the higher partial waves. The inclusion of the higher partial waves through the Born closure affects angles smaller than $10^\circ$ at these energies. In general, the changes in the momentum transfer will be small (since there is the $(1-\cos \theta)$ factor in the integral which excludes the forward direction).

$A_1$ is a nonresonant symmetry and $B_2$ is a resonant symmetry with a background scattering. To compute polarization effects for these symmetries we considered single excitations from the occupied orbitals to a set of polarized orbitals, as described in Refs. 13 and 14. The configuration state functions (CSFs) $(N+1)$-particle Slater determinants used to expand the scattering wave function were constructed by antisymmetrizing the product of the excited $N$-particle Slater determinant and a one-particle function. The set of one-particle functions used as scattering orbitals is represented by polarized and virtual orbitals. The total number of CSFs used in $A_1$ is 5594 and in $B_2$ is 5640.

The other two symmetries, namely, $A_2$ and $B_1$, are resonant symmetries with small background scattering. To compute polarization effects at these symmetries we considered all excitations from the occupied orbitals to the virtual orbitals that preserved the spatial and spin symmetries of the molecular ground state $(^1A_1)$. To represent the scattering orbital we used a single orbital for each symmetry, represented by a modified virtual orbital.\textsuperscript{15} We included all singlet and triplet coupled resulting CSFs, giving a total of 1832 CSFs for $A_2$ and 1834 CSFs for $B_1$. This procedure was proposed by Wineland and McKoy\textsuperscript{15} and was developed in order to provide a balanced description between the target, described in the Hartree-Fock level of approximation, and the temporary anion (thus avoiding the overcorrelation); it gives the resonance position in very good agreement with the experiment.\textsuperscript{16}

III. RESULTS AND DISCUSSION

In Fig. 2 we present our calculated integral cross section in both the static-exchange (SE) and static-exchange plus polarization (SEP) approximations. Both cross sections show three structures.

To assign these structures to the corresponding symmetries of the $C_{2v}$ group, we show in Fig. 3 the symmetry decomposition of the integral cross section for both SE and...
SEP approximations. With the help of Fig. 3, we can assign the first structure of Fig. 2 to a shape resonance belonging to the $B_1$ symmetry. This structure appears at around 4 eV in the SE approximation and at 2.1 eV in the SEP approximation. The second structure in Fig. 2 corresponds to a shape resonance belonging to the $A_2$ symmetry. It is located around 6 eV in the SE approximation and at 4.2 eV in the SEP approximation. The third structure belongs to the $B_2$ symmetry and corresponds to a broad shape resonance located around 11 eV in the SE approximation and around 9 eV in the SEP approximation. The cross section of the $B_2$ symmetry obtained in the SEP approximation presents a small peak located around 6.5 eV. Additional calculations indicate that this is a spurious peak due to some sort of linear dependency/numerical instability. Above 9 eV the cross sections for $A_1$ and $A_2$ symmetries obtained in the SEP approximation show some pseudoresonances, which are due to the existence of closed channels that should be open at the corresponding energies.

The experimental values of the VAE reported by Modelli and Burrow are 1.73 eV for $B_1$ and 3.15 eV for $A_2$. Our calculated resonance positions of 2.1 eV for $B_1$ and 4.2 eV for $A_2$ are in relative close agreement with the experimental values.

We carried out a partial wave decomposition of the cross sections for $B_1$ and $A_2$ symmetries in order to extract the leading $\ell$ of the respective shape resonances. For an electron with incoming angular momentum $\ell$ and outgoing angular momentum $\ell'$, the contribution for $B_1$ comes from $\ell,\ell'=2$ and $3, m,m'=1$ and 3 and for $A_2$ the contribution comes from $\ell,\ell'=3, m,m'=2$. From the partial wave decomposition we fitted the resulting cross sections for $B_1$ and $A_2$ using a Breit-Wigner profile (fixing the magnitude and the energy of each resonance) and obtained the width of the resonances: $\Delta E=0.48$ eV for $B_1$ and $\Delta E=0.86$ eV for $A_2$. The corresponding computed lifetimes ($\tau=h/\Delta E$) are $1.37 \times 10^{-15}$ s and $7.66 \times 10^{-16}$ s, respectively.

Sulzer et al. suggested in Ref. 2 that their observed DEA resonance at 6 eV was due to a core excited shape resonance related to singlet states parent that open at 5.8 and 6.04 eV. We found no resonances at this energy in our single channel calculation (that includes only the elastic one), which may be an indication that the experimental data is, in fact, related to a core-excited resonance. If so, it is more probable that they are related to the triplet state parents that open up at lower energies at 3.99 and 5.15 eV (Ref. 3) than to the reported singlet states.

We found another shape resonance in our integral cross section located at 9 eV, which according to Fig. 2 belongs to $B_2$. This resonance is located about 3 eV above the experimental result, and therefore cannot be responsible for the dissociation at 6 eV. This may indicate that the DEA observed experimentally indeed occurs through a core excited shape resonance, as suggested by the authors. Besides, this resonance does not correspond to the calculated VAE of 7.170 eV reported by Modelli and Burrow, which is for an orbital of $A_1$ symmetry; the calculated VAE for $B_2$ is 8.158 eV [obtained using GAMESS (Ref. 18) with MP2/6-31G*]. Although these calculations using minimal basis set are limited, they provide results which help in the interpretation and understanding of the measured and/or computed resonances, e.g., assigning a resonance to a particular (empty) molecular orbital and giving the approximate location of a resonance.

In Fig. 4 we show a comparison of the differential cross sections (DCSs) obtained at both approximations at 5, 7.5, 10, and 12 eV. There are noticeable differences between the DCSs at 5 and 7.5 eV. At 12 eV both SE and SEP approximations essentially give the same results. Unfortunately
there are no available theoretical nor experimental results for comparison. Figure 5 shows our calculated momentum transfer cross section at both SE and SEP approximation.

IV. CONCLUSIONS

We presented differential and momentum transfer cross sections for elastic scattering of electrons by furan. We found two shape resonances located around 2.1 and 4.2 eV that belong to the $B_1$ and $A_2$ symmetries, in agreement with recent experiments. We also found another resonance located around 9 eV that belong to $B_2$ symmetry. This resonance is about 3 eV above a resonance observed by the experiment and responsible for the molecule dissociation. This indicates that this shape resonance, which is related to elastic scattering, is not responsible for the dissociation.

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