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Low-energy electron collisions with formic acid

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We report differential and momentum transfer cross sections for elastic scattering of low-energy electrons by *trans* formic acid. Our calculations employed the Schwinger multichannel method with pseudopotentials and were performed in the static-exchange and in the static-exchange plus polarization approximations. We found a shape resonance around 1.9 eV belonging to the A'' symmetry of the C_s group. This result agrees with recent calculations and experiments. Our differential cross sections show good agreement with experiment, but disagree with another theoretical calculation at higher scattering angles.

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I. INTRODUCTION

Formic acid (HCOOH) is the prototype of organic molecules as it is the simplest organic acid. It can be found in insects, such as ants and bees, as a chemical defense mechanism. It can also be used as an antibacterial agent. There are two isomers of this molecule, *trans* and *cis*, the former being more stable.

The work of Boudaïffa *et al.* [1], which reported that single-stand and double-stand breaks in DNA occurs by collisions with secondary low energy electrons (with energies below 20 eV), motivated several studies concerning electron collisions with biological molecules [2]. Since formic acid is the simplest organic molecule, it can be considered as a start point towards more complicated systems, such as DNA and RNA bases.

There are recent experimental [3–6] and theoretical studies [7–9] regarding electron collisions with formic acid. On the experimental side, Pelc *et al.* [3] carried out a study on dissociative electron attachment (DEA) to formic acid. They found a resonance around 1.25 eV, and reported that it decays into $HCOO^-$ and H. In another work, Pelc *et al.* [4] determined the product anions of DEA to formic acid. They found that low energy electron collisions with formic acid generated three anions $HCOO^-$, OH^-, and O^-. Vizcaino *et al.* [5] measured differential cross sections for electron collisions with formic acid for energies ranging from 1.8 to 50 eV. They also extracted elastic integral and momentum transfer cross sections from their measured differential cross sections. Allan [6] measured absolute differential elastic and vibrational excitation cross sections at 135° for formic acid and discussed the results at the shape resonance. On the theoretical side, Gianturco and Lucchese [7] found two shape resonances for the *trans* formic acid, one located around 3.48 eV and belonging to the A'' symmetry of the C_s group, and the other located around 12.26 eV and belonging to the A' symmetry of that group. In another study [8], the same authors reported calculated differential cross sections for the *trans* and *cis* isomers of formic acid and also for the dimer. They found good agreement with the experimental data of Vizcaino *et al.* at low scattering angles, but found discrepancies at higher scattering angles. Rescigno *et al.* [9] discussed the mechanism of the dissociation of this molecule by dissociative electron attachment. In particular, they also reported the existence of the π^* shape resonance around 1.9 eV (assigned to the A'' symmetry).

In this paper we present elastic momentum transfer and differential cross sections for *trans* formic acid. Our calculations employed the Schwinger multichannel method with pseudopotentials and were carried out in the static-exchange approximation, for energies from 0.5 to 50 eV, and in the static-exchange plus polarization approximation, for energies from 0.5 to 15 eV. Our aim is to provide cross sections in reasonable agreement with experiment and with other calculations, and also to further investigate the π^* shape resonance that appears in the cross section of this molecule.

In the next section we discuss our computational procedures. We then present and discuss of our results, comparing them with available experimental data and with other theoretical results. We end this paper with a brief conclusion.

II. THEORY

To compute the elastic cross sections we employed the Schwinger multichannel method (SMC) [10–12] with pseudopotentials [13]. The SMC method has been described in detail in several publications and here we will only discuss those points that are relevant to the present calculations.

Our calculations were performed in the static exchange and in the static exchange plus polarization approximations in the C_s point group. We used the ground state equilibrium geometry of the *trans* isomer, as given in Ref. [14]. The norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter [15] were used to replace the core electrons of carbon and oxygen. The Cartesian Gaussian functions used in the bound state and in the scattering calculations for carbon and oxygen were generated according to Ref. [16], and are listed in Table I. We included extra functions at the molecular center of mass, that were used in both bound state and scattering calculations and are also shown in Table I. For hydrogen we used the same basis set quoted in Ref. [17].

To include polarization effects in the A' symmetry we considered single (virtual) excitations from the (valence) occupied orbitals to a set of polarized orbitals, as described in Refs. [18,19]. The configuration state functions (CSFs), which are $(N+1)$-particle Slater determinants used to expand the scattering wave function, were then generated by the antisymetrization of the product of this excited N-particle

TABLE I. Uncontracted Cartesian Gaussian functions used for carbon and oxygen. The extra functions located at the center of mass are also shown.

Type	Carbon exponent	Oxygen exponent	Center of mass exponent
s	12.49628	16.05878	0.16
s	2.470286	5.920242	0.04
s	0.614028	1.034907	0.01
s	0.184028	0.316843	
s	0.039982	0.065203	
p	5.228869	10.14127	0.32
p	1.592058	2.783023	0.08
p	0.568612	0.841010	0.02
p	0.210326	0.232940	
p	0.072250	0.052211	
d	1.794795	1.698024	0.64
d	0.420257	0.455259	0.16
d	0.101114	0.146894	

Slater determinant with a one-particle function. The set of the one particle functions is represented by the polarized and virtual orbitals. The total number of CSFs used in this symmetry is 7137.

The A'' symmetry presents a shape resonance and no background scattering. To include polarization in this symmetry we followed the procedure formulated by Winsted and McKoy [20]. We considered all excitations from the (valence) occupied orbitals to the virtual orbitals that preserved the symmetry of the molecular ground state. We used a single orbital, represented by a modified virtual orbital (MVO) [21], as scattering orbital. We included all singlet and triplet coupled resulting CSFs, giving a total of 2165 configurations.

Formic acid has a permanent dipole moment. The calculated value is 1.71 D, and the experimental value is 1.41 D [14]. To correct the differential cross sections at low scattering angle, we included the dipole interaction through the Born closure of the dipole potential. Our calculated polarizability is 3.4×10^{-24} cm^3. This value agrees well with the value of 3.3×10^{-24} cm^3 ($\sim 22.5a_0^3$) reported by Vizcaino *et al.* [5] and is also in perfect agreement with the experimental value given by Ref [14].

III. RESULTS AND DISCUSSION

Figure 1 shows our calculated momentum transfer cross section (MTCS) in both static-exchange (SE) and static-exchange plus polarization (SEP) approximations. For the SE approximation we show results from 0.5 to 50 eV, and for the SEP approximation we show results from 0.5 to 15 eV; above 15 eV polarization effects are no longer important, since the results obtained in both approximations agree. The SE approximation places the shape resonance, which was assigned to the A'' symmetry, around 3.5 eV. Polarization effects clearly brings the shape resonance to lower energy, locating it around 1.9 eV. This result agrees with the results reported by Allan [6] and Rescigno *et al.* [9], but disagrees with the results reported by Gianturco and Lucchese [7]. Gianturco and Lucchese reported a shape resonance around 3.48 eV, which is close to the position obtained in our SE calculation. The rise seen in the MTCS for energies below ~1.5 eV, in the SEP approximation, and below ~2.5 eV, in the SE approximation, is due to the dipolar nature of the molecule. We also show in this figure the estimated MTCS obtained by Vizcaino *et al.* [5]. Our results follow the experimental data for energies above 5 eV, but lie below them.

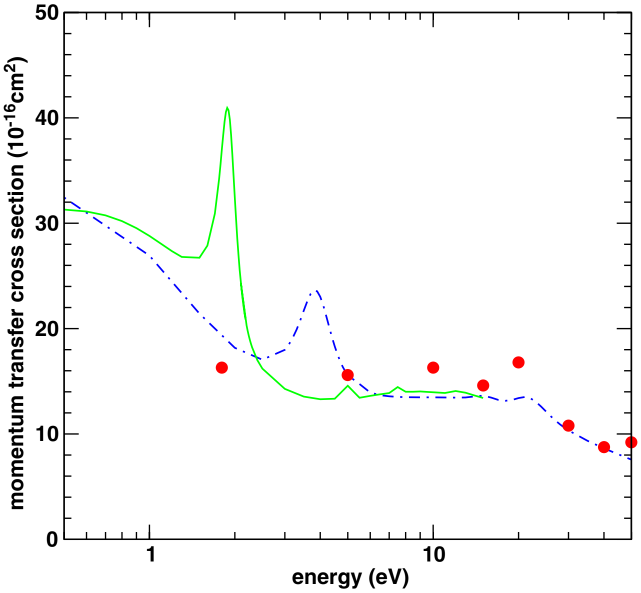

FIG. 1. (Color online) Momentum transfer cross section for HCOOH. Solid (green) line, our results in the SEP approximation; chain (blue) line, our result in the SE approximation; circles (red), experimental data of Ref. [5].

Figures 2–4 show our calculated differential cross sections (DCSs) at 5, 10, and 15 eV, computed in the SEP approximation, and at 20, 30, 40, and 50 eV, computed in the SE approximation. We also show the experimental data of Vizcaino *et al.* [5] and the theoretical results of Gianturco and Lucchese [8]. In general there is good agreement between our results and the experiment, specially at 15 eV.

The present results agree better with the experiment than the results of Gianturco and Lucchese for scattering angles above ~30°. This indicates that the static, exchange and polarization interactions used in the present calculations are better described than theirs. However, the results of Gianturco and Lucchese show better agreement with the experiment than those obtained in the present calculations for scattering angles below ~30°. This indicates that the long range interaction is better described by the calculations of Gianturco and Lucchese than by the present calculations. In fact, Gianturco and Lucchese attributed the disagreement between their results and the experiment at higher scattering angles to their treatment of correlation-polarization interactions in the intermediate and short range distances.

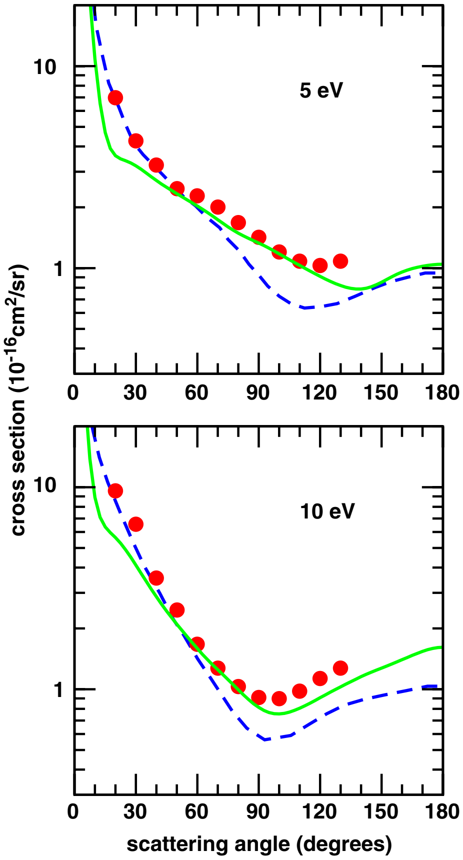

FIG. 2. (Color online) Differential cross section for HCOOH at 5 and 10 eV. Solid (green) line, our results in the SEP approximation; dashed (blue) line, results of Ref. [8]; circles (red), experimental data of Ref. [5].

For polar molecules, there is a competition between the polarization and dipole interactions at low scattering angles. For molecules with large dipole moment, as formic acid, the dipole interaction becomes more important than the polarization interaction. This is the reason because our results agree better with experiment for scattering angles above ~30° and disagree near forward scattering. As discussed above, only the DCSs at 5, 10, and 15 eV were computed including polarization effects. Although the DCSs at 20, 30, 40, and 50 eV were obtained at the static-exchange approximation, they also disagree with the experiment and with the calculations of Gianturco and Lucchese near forward scattering, indicating that the dipole interaction dominates the forward scattering.

Our DCSs present a shoulder below 30°. We believe that this shoulder is an artifact of the Born closure employed to compute the dipole interaction. In our calculations the dipole interaction is computed using the usual Born closure as follows: the partial wave expansion of the scattering amplitude obtained with the SMC method was done up to $l=10$. This value gives converged results for the energies considered in this paper except near the forward scattering. To include the Born partial waves, the partial wave expansion of the SMC scattering amplitude is truncated at some l_{SMC} and the Born partial waves are included from $l_{\mathrm{SMC}}+1$ to ∞. The value of l_{SMC} was chosen so that the DCS obtained with the Born closure agrees with the DCS obtained with the SMC for scattering angles above ~30°; the correction for the DCS at small scattering angles comes from the Born partial waves. The problem here is that the dipole of HCOOH is large, and since the SMC method deals only with square integrable functions, the higher partial waves are not properly described by it; the range of the potential is determined by the range of the Cartesian Gaussians used as basis functions. In fact, the SMC method works well near the molecule, where the scattering is short ranged and it fails when the scattering is long ranged. As a consequence our calculated DCSs at the small angles region do not increase sufficiently in order to match

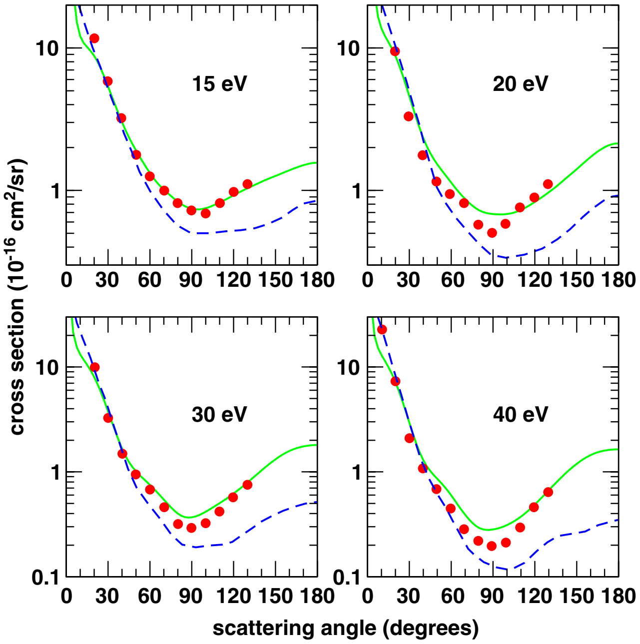

FIG. 3. (Color online) As in Fig. 2 at 15, 20, 30, and 40 eV. At 20, 30, and 40 eV our results were obtained in the SE approximation.

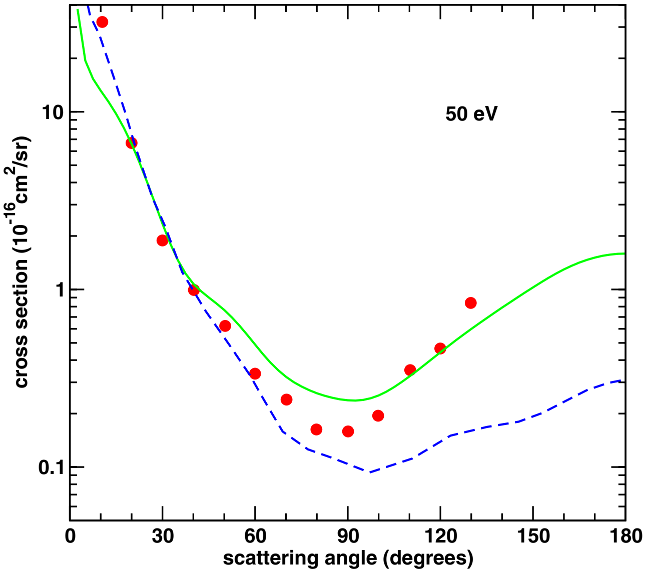

FIG. 4. (Color online) As in Fig. 3 at 50 eV.

the higher partial waves of the Born closure. Although not shown here, our results also agree with the computed MTCS and DCSs of Trevisan *et al.*, obtained using the complex Kohn variational method [22].

IV. CONCLUSIONS

We presented differential and momentum transfer cross sections for elastic scattering of electrons by *trans* formic acid. We found a π^* shape resonance located around 1.9 eV and belonging to the A'' symmetry, in agreement with previous experiments and calculations. Our calculated differential cross sections also agree reasonably well with the experiment and another calculations.

Although our calculated DCSs show a shoulder near forward scattering due to a mismatch between the dipole Born approximation and the SMC method, it is important to note that they show relatively good agreement with the experiment for scattering angles above ~30°. Smooth DCSs near forward scattering would not change this agreement neither the presence nor the location of the π^* shape resonance visible in the MTCS. The results presented in this study could be helpful for comparisons by future theoretical calculations and experiments.

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[1] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science **287**, 1658 (2000).
[2] L. Sanche, Eur. Phys. J. D **35**, 367 (2005).
[3] A. Pelc, W. Sailer, P. Scheier, M. Probst, N. J. Mason, E. Illenberger, and T. D. Märk, Chem. Phys. Lett. **361**, 277 (2002).
[4] A. Pelc, W. Sailer, P. Scheier, N. J. Mason, and T. D. Märk, Eur. Phys. J. D **20**, 441 (2002).
[5] V. Vizcaino, M. Jelisavcic, J. P. Sullivan, and S. J. Buckman, New J. Phys. **8**, 85 (2006).
[6] M. Allan, J. Phys. B **39**, 2939 (2006).
[7] F. A. Gianturco and R. R. Lucchese, New J. Phys. **6**, 66 (2004).
[8] F. A. Gianturco and R. R. Lucchese, Eur. Phys. J. D **39**, 399 (2006).
[9] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, Phys. Rev. Lett. **96**, 213201 (2006).
[10] K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981).
[11] K. Takatsuka and V. McKoy, Phys. Rev. A **30**, 1734 (1984).
[12] M. A. P. Lima, L. M. Brescansin, A. J. R. da Silva, C. Winstead, and V. McKoy, Phys. Rev. A **41**, 327 (1990).
[13] M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **47**, 1111 (1993).
[14] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide, 79th ed. (CRC, Boca Raton, 1998).
[15] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[16] M. H. F. Bettega, A. P. P. Natalense, M. A. P. Lima, and L. G. Ferreira, Int. J. Quantum Chem. **60**, 821 (1996).
[17] A. R. Lopes, M. H. F. Bettega, M. T. do N. Varella, and M. A. P. Lima, Eur. Phys. J. D **37**, 385 (2006).
[18] W. Sun, C. W. McCurdy, and B. H. Legsfield III, J. Chem. Phys. **97**, 5480 (1992).
[19] T. N. Rescigno, A. E. Orel, and C. W. McCurdy, Phys. Rev. A **56**, 2855 (1997).
[20] C. Winstead and V. McKoy, Phys. Rev. A **57**, 3589 (1998).
[21] C. W. Bauschlicher, J. Chem. Phys. **72**, 880 (1980).
[22] As quoted in Ref. [5].