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Electron collisions with hydrogen-bonded complexes

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We investigated elastic collisions of low-energy electrons with the hydrogen-bonded formic-acid dimer, formamide dimer, and formic-acid–formamide complex. We focused on how the π^* shape resonances of the isolated monomers are affected when bonded to another molecule. The scattering cross sections were computed with the Schwinger multichannel method with pseudopotentials in the static-exchange and static-exchange-plus-polarization approximations, for energies ranging from 1 to 6 eV. The present results support the existence of two low-lying π^* shape resonances for the formic-acid dimer, as suggested in previous theoretical and experimental studies. We also found low-lying π^* shape resonances for the formamide dimer and for the formic-acid–formamide complex. For the dimers, the presence of a center of inversion is key to understanding how these resonances arise from linear combinations of the π^* anion states of the respective monomers. For the formic-acid–formamide complex, the resonances are more localized on each unit, lying at lower energies with respect to the isolated monomers. The present results suggest that if there is no delocalization of the π^* resonances over the pair for hydrogen-bonded molecules, then their positions would lie below those of the units.

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I. INTRODUCTION

Single- and double-strand breaks in DNA can be caused by low-energy electrons, the most abundant secondary products of the interaction of ionizing radiation to the human body [1]. These electrons may occupy empty molecular orbitals forming transient negative ions (TNIs), often referred to as resonances, which in turn may dissociate along particular bonds. This process is known as dissociative electron attachment (DEA). Though it would be impractical to study electron collisions with DNA strands in a biological environment, experiments have pointed out that electron attachment is local [2], i.e., it occurs in specific sites of the DNA chain. This has motivated a series of electron-collision studies with isolated DNA constituents in the gas phase [3], and it is now well established that the formation of long-lived π^* shape resonances is fundamental in single-strand breaks [4,5] and related low-energy DEA processes.

Though gas-phase studies are invaluable to understanding the details of DEA in biomolecules, discrepancies with DNA film data have been suggested [5]. Reducing the gap between gas-phase models and condensed-phase processes is thus a very important challenge. To this end, studies of hydrogen-bonded systems would be a key step. A recent study of electron scattering by hydrated formaldehyde [6] pointed out that a single water molecule can shift the position of a π^* resonance by 0.6 eV, and the relation between TNIs and hydrogen bonds should be further investigated. It has also been suggested that the formic-acid dimer would be a good prototype to understand the effect of hydrogen bonding in chemical processes that occur in DNA [7], since it is a smaller and simpler complex with similar properties to the DNA base pairs.

In the present work, we report integral cross sections for low-energy electron scattering by the dimers of formic acid (FAD), i.e., HCOOH...HCOOH, and formamide (FD), i.e., $HCONH_2 \ldots HCONH_2$. Since the base pairs in DNA are formed by different molecules, we also study the formic-acid–formamide complex (FAFC), i.e., $HCOOH \ldots HCONH_2$. The formic-acid and formamide monomers have well known π^* shape resonances at 1.9 [8–14] and at 2.05 [15–19] eV respectively. As the characterization of TNI spectra is a key step to understanding electron-driven processes, the present calculations only address the resonant symmetries of the dimers and of the complex. Recent electron-FAD scattering calculations [20] assigned two π^* resonances in the A_u and B_g symmetries around 2.8 and 3.4 eV, respectively. Though this result would be consistent with electron energy loss (EEL) spectra [21], the resonance positions are somewhat overestimated with respect to the experimental assignments (1.40 and 1.96 eV). It is thus interesting to further investigate the resonance spectrum of FAD, as well as FD and FAFC.

II. THEORY

Scattering cross sections were calculated using the Schwinger multichannel (SMC) method, which has been described elsewhere [22,23]. Here we will only discuss the theoretical and computational aspects that are relevant to the present calculations. The SMC method is a fully *ab initio* variational approach to the scattering amplitude and allows the use of L^2 functions to describe the scattering process. Our calculations were carried out in the static-exchange (SE) and in the static-exchange-plus-polarization (SEP) approximations. The dynamical target response to the incident electron field is neglected in the former, while accounted for through virtual single excitations in the latter.

Bound-state and scattering calculations were performed at the optimized equilibrium geometry of the target, shown in Fig. 1. For all target molecules, geometry optimizations were carried out with second-order Møller-Plesset (MP2) perturbation potentials and the augmented correlation-consistent basis sets (aug-cc-PVDZ) built into the GAMESS [31] computer code. The FAD and FD were treated as C_{2h} molecules and the

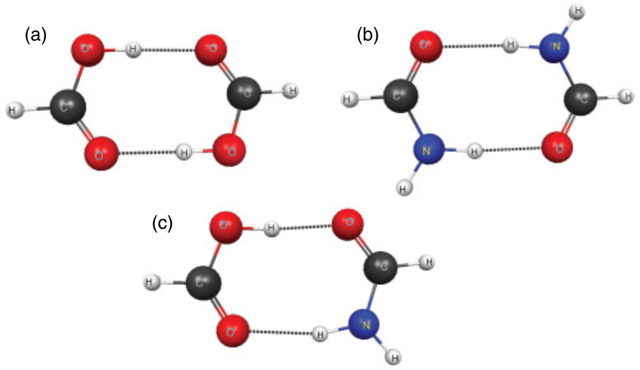

FIG. 1. (Color online) Geometric structures of (a) FAD, (b) FD, and (c) FAFC (generated using MACMOLPLT [24]).

FAFC was treated as a C_s molecule. The $1s$ core electrons of carbon, nitrogen, and oxygen atoms were replaced by the norm-conserving pseudopotentials of Bachelet *et al.* [25], and the Cartesian Gaussian functions used to represent bound and scattering orbitals of valence electrons included $5s4p2d$ on each heavy atom (these were generated according to Ref. [26]). For hydrogen atoms, a Dunning basis set [27] was augmented with one p-type function with exponent 0.75. The symmetric combinations of the d-type Cartesian Gaussian functions [namely, $(x^2 + y^2 + z^2)\exp(-\alpha r^2)$] were not included in the calculations to avoid numerical linear dependency.

Modified virtual orbitals (MVOs) [28] obtained from cationic Fock operators with charge +8 were employed to represent the particle and scattering orbitals in the SEP calculations. We considered the 18 (valence) occupied orbitals as hole orbitals and the 50 first MVOs as particle and scattering orbitals, and only singlet coupled excitations. We kept only doublet configuration state functions (CSFs) in the scattering calculations, as described in [29], resulting in 5294 CSFs for each one of the A_u and B_g symmetries for FAD, 5295 CSFs for each one of the A_u and B_g symmetries for FD, and 10 589 CSFs for the A'' symmetry of FAFC.

III. RESULTS

In Fig. 2, we show the calculated elastic integral cross section for the A_u and B_g symmetries of FAD obtained in the SE and SEP approximations, along with the results of Gianturco *et al.* [20]. The A_u symmetry displays a π^* shape resonance around 3.2 eV in the SE calculations and the inclusion of polarization effects shifts it down to 1.62 eV. The $\pi^*(A_u)$ resonance reported by Gianturco *et al.* lies at a considerably higher energy (2.8 eV), close to the present SE results (a similar discrepancy was also found for the π^* resonance of formamide [30]). The B_g symmetry also displays a π^* shape resonance around 3.9 and 1.93 eV in the SE and SEP calculations, respectively. The most significant discrepancy between the two theoretical results is in the position of the resonances, although the present results are in agreement with the EEL data of 1.40 (A_u) and 1.96 eV (B_g) by Allan [21].

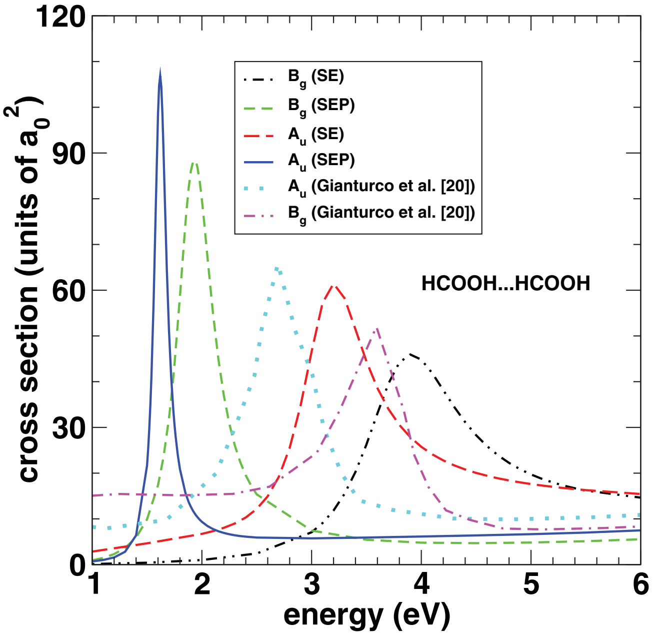

FIG. 2. (Color online) Integral cross sections for the A_u and B_g symmetries of FAD in the SE and SEP approximations. The results from Ref. [20] are also shown. Cross sections are in units of a_0^2, where a_0 is the Bohr radius and $1a_0 = 0.52918 \times 10^{-10}$ m.

Figure 3 shows the cross sections for the FD in the SE and SEP approximations. The A_u and B_g resonances appear at around 3.9 and 4.8 eV, respectively, in the SE approximation, and move to 2.21 and 2.98 eV with the inclusion of polarization effects.

SE and SEP results for the FAFC are shown in Fig. 4, along with the SEP calculations for the monomers [14,18]. The FAFC belongs to the C_s group and therefore both resonances appear in the A'' symmetry. In the SE approximation, the resonances almost overlap and are located at around 3.6 and

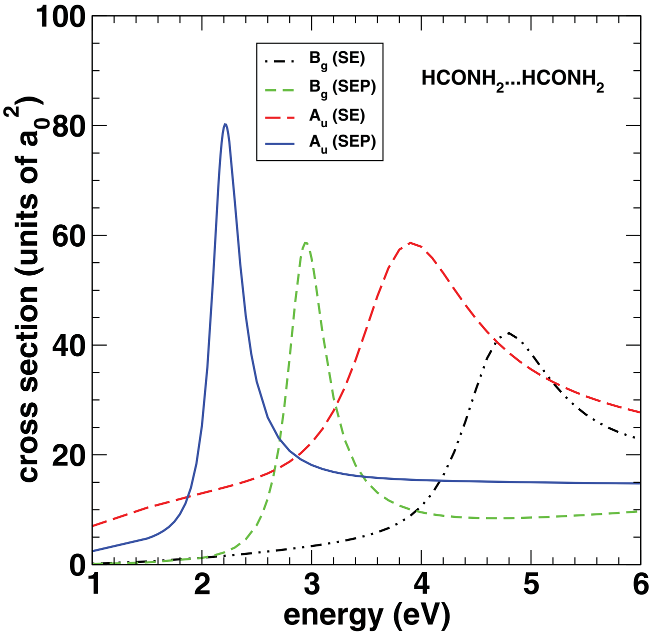

FIG. 3. (Color online) Integral cross sections for the A_u and B_g symmetries of FD in the SE and SEP approximations. Cross sections are in units of a_0^2, where a_0 is the Bohr radius and $1a_0 = 0.52918 \times 10^{-10}$ m.

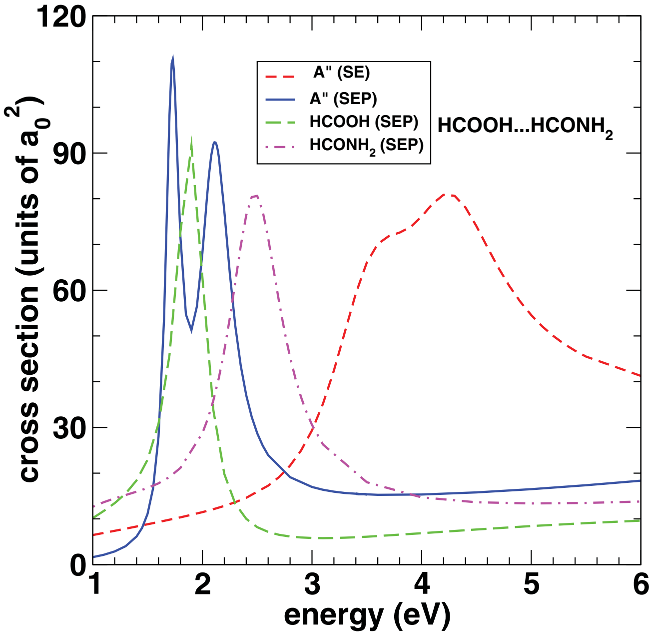

FIG. 4. (Color online) Integral cross sections for the A'' symmetry of FAFC in the SE and SEP approximations. We also show the results from Refs. [14,18] for the formic-acid and formamide monomers, respectively. Cross sections are in units of a_0^2, where a_0 is the Bohr radius and $1a_0 = 0.52918 \times 10^{-10}$ m.

4.2 eV. Two clear peaks appear when polarization effects are taken into account, at 1.72 and 2.11 eV. These resonances are lower when compared with the resonances of the formic-acid and formamide monomers, which are located at 1.9 and 2.5 eV, respectively.

IV. DISCUSSION

To gain some insight into the relation between the π^* shape resonances of the complexes (FAD, FD, and FAFC) and those of the monomers (formic acid and formamide), we inspected the a_u and b_g MVOs of FAD (although not shown here, the MVOs of FD are very similar). These were obtained at the Hartree-Fock (HF) level employing the aug-cc-PVDZ basis set as implemented in GAMESS [31] from a cationic Fock operator with charge +8. The MVOs are considered as resonance orbitals since they are compact, valencelike, and localized near the molecule [32]. The two lowest-lying MVOs were used as scattering orbitals in the CSFs accounting for target distortion is SEP calculations; the anion states can thus be viewed as formed by attaching electrons to the π^* MVOs of the relaxed target molecules. As discussed elsewhere [18,33], both monomers have their lowest unoccupied orbitals mostly located on the O–C=O moiety. The lowest-lying MVOs of FAD are shown in Figs. 5, and can be viewed as arising from even (+) and odd (–) combinations of the orbitals located on each unit. In view of the inversion symmetry, the even combinations give rise to *ungerade* dimer orbitals (a_u) and would favor constructive interference between monomer orbitals. The odd combinations would in turn favor destructive interference, giving rise to *gerade* dimer orbitals (b_g). Drawing an analogy with molecular orbital theory (MOT), this situation would be similar to the formation of bonding and antibonding orbitals in homonuclear diatomic molecules. The A_u and B_g anion states of the dimers would thus be expected to lie below and above the π^* resonances of the monomers. This is, indeed, the case, as summarized in Table I.

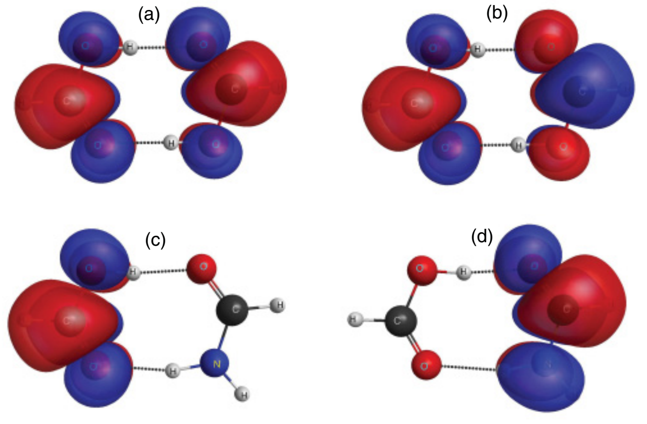

FIG. 5. (Color online) MVO plots for FAD (top) and FAFC (bottom). Panels (a) and (b) show the two lowest-lying MVOs having a_u and b_g symmetries (FAD). Panels (c) and (d) show the two lowest-lying MVOs having a'' symmetry (FAFC) (generated using MACMOLPLT [24]). Although not shown here, the low-lying a_u and b_g MVOs of FD are very similar to those of FAD. See text for discussion.

The lowest MVOs of FAFC are also shown in Fig. 5. Though an analogy could be made with the formation of bonding and antibonding orbitals in heteronuclear diatomics, the MVO plots suggest strong localization on the units. In fact, while simple MOT arguments would indicate that the π^* resonances of the FAFC would lie below the π^* resonance of formic acid and above the π^* resonance of formamide, we find both complex anion states lying below the respective anion states of the units (see Table I). The localization of virtual orbitals and the downshift of both resonances indicate that effects other than orbital superposition would prevail.

Along the same lines of a previous study on water-formaldehyde complexes [6], we surveyed the interaction polarizability in FAFC that accounts for a mutual polarization between the molecules. It was defined by Maroulis [34] in studies of water dimers and was used in studies of water complexes by Fileti *et al.* [35]. Here the average polarizabilities were computed at the HF/MP2 level employing the aug-cc-PVDZ basis set built into the GAMESS [31] package. The calculated values for formic acid (22.73 a_0^3), formamide (28.23 a_0^3), and FAFC (51.05 a_0^3) are in good agreement with the experimental values [36] of 22.40 a_0^3 and

TABLE I. Calculated π^* resonance peak positions (E_r) for formic acid (FA), formamide (F), formic-acid dimer (FAD), formamide dimer (FD), and formic-acid–formamide complex (FAFC). Symmetry assignments are also indicated.

	FA	FAD	F	FD	FAFD
E_r (eV)	1.9 (A'')	1.62 (A_u) 1.96 (B_g)	2.5 (A'')	2.21 (A_u) 2.98 (B_g)	1.72 (A'') 2.11 (A'')

27.53 a_0^3, respectively. The corresponding interaction polarizability [$\alpha(\text{inter}) = \alpha(\text{FAFC}) - \alpha(\text{HCOOH}) - \alpha(\text{HCONH}_2)$] of 0.08 a_0^3 is smaller than the result obtained in [6], which is consistent with the smaller resonance downshifts obtained in the present work. Based on the results discussed above, we would expect that the anion states of hydrogen-bonded DNA pairs would lie below the parent π^* resonances of the isolated bases, i.e., resonance stabilization would arise from the interaction polarizability.

V. CONCLUSIONS

In this work, we reported elastic cross sections for the H-bonded systems FAD, FD, and FAFC. The calculations indicate two π^* shape resonances for each system. For the FAD and FD, the resonances belong to the A_u and B_g symmetries and arise from linear combinations of the well-known π^* (A'') anion state of the formic-acid and formamide monomers. For the FAFC, the resonances belong to the A'' symmetry and are lower in energy than the corresponding π^* resonances of the formic-acid and formamide monomers. The character of these resonances could be understood from the low-lying MVOs of the molecule. To date, most of the calculations have focused on electron collision with single molecules, as DNA building blocks. However, this work shows that the environment substantially affects the location of the π^* resonances. Furthermore, the results reported in this paper suggest that if the π^* resonances do not delocalize over the pair for hydrogen-bonded molecules, their positions would lie below those of the units.

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[1] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science **287**, 1658 (2000).

[2] See, for example, G. Hanel, B. Gstir, S. Denifl, P. Scheier, M. Probst, B. Farizon, M. Farizon, E. Illenberger, and T. D. Märk, Phys. Rev. Lett. **90**, 188104 (2003); S. Denfil, S. Ptasinska, M. Cingel, S. Matejcik, P. Scheier, and T. D. Märk, Chem. Phys. Lett. **377**, 74 (2003); H. Abdoul-Carime, S. Gohlke, and E. Illenberger, Phys. Rev. Lett. **92**, 168103 (2004).

[3] See, for instance, C. Winstead and V. McKoy, J. Chem. Phys. **125**, 074302 (2006); **125**, 244302 (2006); C. Winstead, V. McKoy, and S. d'A. Sanchez, *ibid.* **127**, 085105 (2007); J. D. Gorfinkel, L. G. Caron, and L. Sanche, J. Phys. B **39**, 975 (2006); E. M. de Oliveira, M. A. P. Lima, M. H. F. Bettega, S. d'A. Sanchez, R. F. da Costa, and M. T. do N. Varella, J. Chem. Phys. **132**, 204301 (2010), and references therein.

[4] A. M. Scheer, K. Aflatooni, G. A. Gallup, and P. D. Burrow, Phys. Rev. Lett. **92**, 068102 (2004).

[5] F. Martin, P. D. Burrow, Z. Cai, P. Cloutier, D. Hunting, and L. Sanche, Phys. Rev. Lett. **93**, 068101 (2004).

[6] T. C. Freitas, M. A. P. Lima, S. Canuto, and M. H. F. Bettega, Phys. Rev. A **80**, 062710 (2009).

[7] R. A. Bachorz, M. Harańczyk, I. Dabkowska, J. Rak, and M. Gutowski, J. Chem. Phys. **122**, 204304 (2005).

[8] V. Vizcaino, M. Jelisavcic, J. P. Sullivan, and S. J. Buckman, New J. Phys. **8**, 85 (2006).

[9] M. Allan, J. Phys. B **39**, 2939 (2006).

[10] F. A. Gianturco and R. R. Lucchese, New J. Phys. **6**, 66 (2004).

[11] F. A. Gianturco and R. R. Lucchese, Eur. Phys. J. D **39**, 399 (2006).

[12] T. N. Rescigno, C. S. Trevisan, and A. E. Orel, Phys. Rev. Lett. **96**, 213201 (2006).

[13] C. S. Trevisan, A. E. Orel, and T. N. Rescigno, Phys. Rev. A **74**, 042716 (2006).

[14] M. H. F. Bettega, Phys. Rev. A **74**, 054701 (2006).

[15] M. Seydou, A. Modelli, B. Lucas, K. Konate, C. Desfrancois, and J. P. Schermann, Eur. Phys. J. D **35**, 199 (2005).

[16] P. Cloutier, C. Sicard-Roselli, E. Escher, and L. Sanche, J. Phys. Chem. B **111**, 1620 (2007).

[17] T. P. M. Goumans, F. A. Gianturco, F. Sebastianelli, I. Baccarelli, and J. L. Rivail, J. Chem. Theory Comp. **5**, 217 (2009).

[18] M. H. F. Bettega, Phys. Rev. A **81**, 062717 (2010).

[19] T. Hamann, A. Edtbauer, F. Ferreira da Silva, S. Denifl, P. Scheier, and P. Swiderek, Phys. Chem. Chem. Phys. **13**, 12305 (2011).

[20] F. A. Gianturco, R. R. Luchese, J. Langer, I. Martin, M. Stano, G. Karwasz, and E. Illenberg, Eur. Phys. J. D **35**, 417 (2005).

[21] M. Allan, Phys. Rev. Lett. **98**, 123201 (2007).

[22] K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981); **30**, 1734 (1984).

[23] M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **47**, 1111 (1993).

[24] B. M. Bode and M. S. Gordon, J. Mol. Graphics Model. **16**, 133 (1998).

[25] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[26] M. H. F. Bettega, A. P. P. Natalense, M. A. P. Lima, and L. G. Ferreira, Int. J. Quantum Chem. **60**, 821 (1996).

[27] T. H. Dunning Jr., J. Chem. Phys. **53**, 2823 (1970).

[28] C. W. Bauschlicher, J. Chem. Phys. **72**, 880 (1980).

[29] R. F. da Costa, F. J. da Paixão, and M. A. P. Lima, J. Phys. B **37**, L129 (2004); *ibid.* **38**, 4363 (2005).

[30] M. H. F. Bettega, Phys. Rev. A **81**, 062717 (2010).

[31] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).

[32] C. Winstead and V. McKoy, Phys. Rev. A **57**, 3589 (1998).

[33] T. C. Freitas, M. T. do N. Varella, R. F. da Costa, M. A. P. Lima, and M. H. F. Bettega, Phys. Rev. A **79**, 022706 (2009).

[34] G. Maroulis, J. Chem. Phys. **113**, 1813 (2000).

[35] E. E. Fileti, R. Rivelino, and S. Canuto, J. Phys. B **36**, 399 (2003).

[36] M. Dory, J. Delhalle, J. G. Fripiat, and J. M. Andre, Int. J. Quantum Chem. **14**, 085 (1987).