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To cite this article: F A Gianturco and R R Lucchese 2004 New J. Phys. 6 66

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Nanoscopic models for radiobiological damage: metastable precursors of dissociative electron attachment to formic acid

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Received 16 March 2004
Published 28 June 2004
Online at http://www.njp.org/
doi:10.1088/1367-2630/6/1/066

Abstract. The HCOOH molecule represents the simplest organic acid which is also supposed to play a role in the interstellar formation of more complicated biomolecules. Its interaction with slow electrons in the gas phase is analysed in the present work with the view of providing specific structural and dynamical information on those resonant states which lead to different transient negative ions (TNIs) formation. The latter resonant states in turn guide molecular fragmentation along different pathways, forming HCOO\(^-\), O\(^-\) and OH\(^-\) fragments as experimentally observed. The present calculations, carried out at the equilibrium molecular geometry, indeed support the presence of two main resonances within the expected energy range and further indicate the presence of antibonding nodal planes in the excess electron resonant wave function features which could explain the observed fragmentation products formed during the subsequent dissociative break-up.

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1. Introduction

It is by now a fairly well-established fact that low-energy electrons are one of the main, secondary products from any type of material when irradiated by either energetic particles (e.g. in ion implantation devices) or by photons. In the case of biological media, these secondary electrons are capable of fragmenting the biomolecules in question and are considered the chief initiators of permanent radiation damage effects, which occur through the formation of highly reactive radicals and ions within the supporting medium [1]–[3]. Since the produced secondary electrons are believed to have thermalization distances of the order of 1–10 nm [4], the latter dimension helps us to define the volume along the radiation track where the initial energy deposition into the surrounding medium is expected to occur and, furthermore, can indicate the short-time effects of the secondary electrons prior to their full thermalization within the medium itself [3, 4]. It is therefore often conjectured that highly excited molecular ions and radicals could be formed under non-thermal reactions within a few femtoseconds and that the majority of such species are caused by interactions within that time scale with the secondary electrons formed along the primary radiation track [4]. It is therefore the aim of the present work to analyse in some detail the possibility of setting up a nanoscopic modelling of such initiating processes by using a quantum mechanical description of the electron-molecule dynamics under single-collision conditions in the gas phase. The latter, fairly restrictive conditions, are those which are being most frequently employed by the recent upsurge of experiments that analyse dissociative electron attachment (DEA) for biomolecules and describe the ensuing fragmentation patterns for a broad variety of relevant target species [5]–[7]. Although it is fair to note that it still remains to be seen how well the conditions of a ‘real’ biological environment (e.g. aqueous solutions and higher concentrations along the ionizing tracts) are described by the simplified operational conditions of the scattering experiments, and therefore how realistically we can consider the observations as describing the actual radioimaging processes in the ‘live’ environment, one should also remember that the very complicated situations of the latter environment often make it next to impossible to reliably extract the significant variables and to establish interpretative models of predictive value. Hence, the use of the above gas-phase experiments is beginning to provide one of the few possible paths to our understanding, at the molecular level, of the radioimaging processes in biosystems. The theoretical interpretation of such experiments is therefore our current main tool for setting up
explanatory descriptions, at the same molecular level, for more complex situations in realistic biological environments [3].

In the present paper we intend to focus on the simplest organic acid, the formic acid HCOOH, because of it having been detected in the interstellar medium [8] and therefore been suggested as one of the earliest prototypes of a catalytic centre for enzymatic activity [9] once its anionic moiety is bound to a water molecule.

Furthermore, formic acid constitutes, together with glycine, one of the simplest building blocks of more complicated biosystems [10] and therefore both molecules have been considered in experiments that study their behaviour under the action of ‘secondary’ electrons following the ionizing radiation impact on the medium [11].

The next section briefly summarizes our theoretical and computational model, while section 3 presents the results of our calculations and compares them with the available experiments. Finally, section 4 summarizes our conclusions.

2. The quantum modelling

To begin to set up a possible physical picture, at the molecular level, of the initial effects of slow-electron impact on the isolated molecule, we need to know first the interaction potentials which will act during that event and then use them within a quantum formulation of the scattering process. To this effect, we have drawn on our previous, and extensive experience [12] in treating electron scattering processes off polyatomic targets in the gas phase. We therefore provide here only a brief outline of our theoretical models, referring the reader to the previous literature for further details [11].

2.1. The scattering equations

Within the Born–Oppenheimer (BO) scheme the total wave function of a continuum electron that scatters from an $N$-electron molecular target is an antisymmetrized product of one-electron orbitals that parametrically depend on the nuclear coordinates. Our present treatment of the scattering process is limited here to an analysis of the elastic channels and no excitations will be considered for either the bound electrons or the bound nuclei. In fact, we will describe the scattering within the fixed-nuclei (FN) approximation [12], which neglects any dynamics involving the nuclear motion, whereas the bound electrons will be taken to be in the ground electronic state of the target at its optimized nuclear geometry. The initial description of that state will be given as a single-determinant of near-Hartree–Fock molecular orbitals (MOs) describing the $N$-bound electrons. To obtain our scattering equations we then expand both the bound MOs and the continuum electron in a single-centre expansion (SCE) around the centre of mass of the target by employing symmetry-adapted angular functions for each of the irreducible representations (IRs) that belong to the molecular point-group at the chosen geometry of its nuclei. Any arbitrary three-dimensional single-electron function is thus represented on a spherical-polar coordinate grid centred in the body-fixed (BF) molecular frame of reference:

$$F^{\mu\nu}(r, \hat{r}| R) = \sum_{l, h} r^{-1} f^{\mu\nu}_{lh}(r| R) X^{\mu\nu}_{lh}(\hat{r}).$$  \hspace{1cm} (1)

The indices refer to the $\mu$th element of the $p$th IR of the point group of the molecule at the nuclear geometry $R$. The angular functions $X^{\mu\nu}_{lh}(\hat{r})$ are symmetry-adapted functions given by the
The proper combination of spherical harmonics $Y_{lm}(\hat{r})$:

$$X_{lh}^{p\mu}(\hat{r}) = \sum_{m} b_{lmh}^{p\mu} Y_{lm}(\hat{r}).$$  \hfill (2)

The coefficients $b_{lmh}^{p\mu}$ are discussed in the literature and can be obtained from a knowledge of the character tables of the relevant molecular point group [13].

The coupled partial integro-differential scattering equations are

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2(E - \epsilon_{\alpha}) \right] f_{lh}^{p\mu}(r|R) = 2 \sum_{l'h'h'} \int dr' V_{lh,l'h'}^{p\mu\alpha,p\mu'\beta}(r, r'|R) f_{l'h'}^{p\mu'\beta}(r'|R),$$  \hfill (3)

where $E$ is the collision energy and $\epsilon_{\alpha}$ the electronic eigenvalue for the target ground state so that $(E - \epsilon_{\alpha}) = k^2/2$, where $k$ is the asymptotic momentum of the scattered electron. The $(p, \mu)$ indices, equation (3), now label the specific $\mu$th component of the $p$th IR that characterizes the continuum that belongs to the $\alpha$th electronic target state (initial state) coupled with the excited states labelled by $\beta$ with the corresponding continuum symmetry labelled by $(p', \mu')$. Equation (3) contains the kernel of the integral operator $V$, a sum of diagonal and non-diagonal terms that in principle fully describe the electron–molecule interaction during the collision. If one now further truncates the sum on the right-hand side of equation (3) to a single state only, one obtains the exact-static-exchange (ESE) representation of the electron–molecule interaction for the ground state at the geometry $R$. With the assumption of having only a local $e^−$–molecule interaction (as we shall discuss below) one can further write the scattering equations as

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \right] f_{i}^{p\mu}(r|R) = \sum_{j} V_{ij}^{p\mu}(r|R) f_{j}^{p\mu}(r|R),$$  \hfill (4)

where the indexes $i$ and $j$ represent the ‘angular channel’ $(l, h)$ and the potential coupling elements are

$$V_{ij}^{p\mu}(r|R) = \langle X_{i}^{p\mu}(\hat{r})|V(r|R)|X_{j}^{p\mu}(\hat{r}) \rangle = \int d\hat{r} X_{i}^{p\mu}(\hat{r}) V(r|R) X_{j}^{p\mu}(\hat{r}).$$  \hfill (5)

We have also replaced the exact operator of equation (3) with an energy-dependent local exchange potential [14]

$$V_{\text{ex}}^{\text{FEGE}}(r) = \frac{2}{\pi} k_F(r) \left( \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right),$$  \hfill (6)

where $\eta(r) = (k^2 + 2I_p + k_F(r))^{1/2}/k_F(r)$, $k_F(r) = (3\pi^2 \rho(r))^{1/3}$ is the local Fermi momentum and $I_p$ is the ionization potential of the molecular target.

When one restricts the summation in equation (3) to a single state the effects of static and dynamic electron–electron correlation are neglected. The latter effects asymptotically produce the long-range multipolar polarization contributions and are of prime importance for low-energy electron scattering processes. We therefore include here a modelling of the dynamical short-range correlation through the addition of a local energy-independent potential $V_{\text{corr}}$ [15, 16]. The short-range potential $V_{\text{corr}}$ is obtained by defining an average dynamical correlation
energy of a single electron within the formalism of the Kohn and Sham variational scheme (see also [15, 16] for details). The functional derivative of such a quantity with respect to the SCF $N$-electron density of the molecular target provides a density functional description of the required short-range correlation term, this being an analytic function of the target ground-state electron density. When studying the full scattering problem, we usually correct the large $r$ behaviour of $V_{\text{corr}}$ so that it agrees with the known static polarizability of the target molecule [17]. However, in the present study, where we are only interested in the resonant states of the system, the latter are confined to the region of the molecular framework and are thus not greatly affected by the asymptotic behaviour of $V_{\text{corr}}$.

2.2. The adiabatic potential model

Since we now wish to examine in some detail the mechanism and qualitative characteristics of low-energy, one-electron resonances, we require a model simple enough to be computationally attractive but with sufficient details of the full scattering problem to reproduce the essential features of the realistic cases. Thus, we employ a simple, purely local model potential we have called the static model exchange correlation (SMEC) potential, $V_{\text{SMEC}}$ [18]. The excellent qualitative agreement we have found between results obtained using an exact exchange and those given by the present local model exchange potentials (see e.g. [19, 20]) gives us confidence that the resonant trapping mechanism is probably the same for both potentials, although quantitative features may be different.

To facilitate the analysis of scattering resonances we have used a different but equivalent form of the scattering equations based on an adiabatic representation of the electron–molecule interaction potential. We start by noting that the standard, symmetry-adapted angular momentum eigenstates, $X_{lh}^{p\mu}$, do not form the most compact angular set for the electron–molecule scattering problem: an alternative expansion basis is provided by diagonalizing the angular Hamiltonian at each radius $r$. These new angular eigenstates are the adiabatic angular functions (AAFs) $Z_{k}^{p\mu}(\theta, \phi, r)$ which are $r$-dependent, linear combinations of the symmetry-adapted ‘asymptotic’ harmonics

$$Z_{k}^{p\mu}(\theta, \phi, r) = \sum_{lh} X_{lh}^{p\mu}(\theta, \phi) C_{lh,k}(r),$$

where the expansion coefficients come from the matrix eigenvalue equation

$$\sum_{lh} V_{l'k',lh}(r) C_{lh,k}(r) = C_{l'k',k}(r) V^{A}_{k}(r).$$

The eigenvalues $V^{A}_{k}(r)$ now form an adiabatic radial potential for each index value $k$ over the selected range of the $e^{-}$–molecule distance.

One drawback to the adiabatic potential approach is that the non-adiabatic radial coupling introduces additional terms in the radial differential equations for which the standard integration method is not directly applicable [18]. To avoid the non-adiabatic coupling terms, we actually employ a piecewise diabatic (PD) representation for the potential [17]–[19], where the radial coordinate is divided into many regions so that sector $i$ is defined as $r_{i-1} < r < r_{i}$, with $r_{0} = 0$. In each region, we average the coupling potential $V_{l'k',lh}(r)$ over $r$ and the resulting averaged potential is diagonalized as in equation (8) to yield a set of angular functions $Z_{k,i}^{p\mu}(\theta, \phi)$. Then in
region $i$ the scattering potential is transformed into the new representation in which it is nearly diagonal. The resulting equations are then solved using the full scattering potential in each region with the further approximation of ignoring the off-diagonal couplings within each of the regions. If they are small enough this turns out to be a rather good approximation.

To solve the radial equations using the PD approach requires matching of the radial functions and their derivatives at the boundary between radial regions. The transformation of the radial functions from one region to the next is given by the transformation matrix $U_{k,k'}^{(i+1 \leftarrow i)}$ defined by

$$U_{k,k'}^{(i+1 \leftarrow i)} = \sum_{lh} C_{lh,k}^{(i+1)} C_{lh,k'}^{(i)}.$$

When the size of the angular momentum eigenfunction basis used is larger than the size of the diabatic angular basis set, the transformation matrix $U_{k,k'}$ is not in general unitary. We accomplish the unitarization of $U_{k,k'}^{(i+1 \leftarrow i)}$ using simple Gram–Schmidt orthonormalization on the columns of $U_{k,k'}^{(i+1 \leftarrow i)}$.

The scattering was then solved within the reduced basis of the effective diabatic potential terms and the corresponding poles of the $S$ matrix have been obtained using a very narrow grid of values that however span the energy range of experimental interest, i.e. from threshold to about 15 eV.

3. Results and discussion

3.1. Computational details

In the present study we wish to analyse the possible presence of low-energy TNIs for electrons scattered from gas-phase formic acid. The latter geometry appears in cis and trans forms and we have carried out calculations for both configurations, taking the equilibrium geometries from [21]. The basis set expansion employed to generate the target wave functions was the (aug-cc-pvtz) and the corresponding Hartree–Fock (HF) energies obtained were $-188.844823$ a.u. for the trans configuration and $-188.837946$ a.u. for the cis configuration. The local, energy-dependent exchange model potential of equation (6) was evaluated at one fixed energy value of 5.0 eV and it changed very little over the whole range of examined collision energies. The ionization potential of equation (6) was taken from the Koopmans’ theorem estimate given by our present HF calculations of the cis form (12.8 eV).

The radial integration region employed for the PD representation of the total, model interaction included 90 regions of diabatization and the integration extended out to $11.6 \text{ a.u.}$ The angular representation of the anisotropic potential went up to a maximum value of 80 for the angular momenta of the angular coefficients in equation (2), while the scattering wave function of equation (1) went up to $l_{\text{max}} = 40$. No asymptotic polarizability was employed to extend the $V_{\text{corr}}$ potential beyond the matching range since we are chiefly interested in obtaining the resonant wave functions that are dominated by exchange and correlation effects [22] and not in producing realistic total elastic cross-sections for the present processes.

The employed IRs pertaining to the molecular point group were $A'$ and $A''$. For each of them we obtained converged $S$-matrix values by including up to $l = 10$ for the PD potentials and therefore we employed 66 adiabatic functions for the $A'$ symmetry and 55 for the $A''$ one to describe the resonant states. The results given in figure 1 report the positions of the computed
Figure 1. Computed pole positions of the $S$ matrix in the complex energy plane. The filled triangles are for the $A''$ symmetry, while the filled circles refer to the $A'$ symmetry.

Table 1. Computed resonance positions and widths for both cis- and trans-formic acid configurations. All values are in eV.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$A''$</th>
<th>$A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_R$</td>
<td>$\Gamma$</td>
</tr>
<tr>
<td>Cis</td>
<td>3.49</td>
<td>0.93</td>
</tr>
<tr>
<td>Trans</td>
<td>3.48</td>
<td>0.95</td>
</tr>
</tbody>
</table>

S-matrix poles in the complex energy plane, where the complex energy values provide the corresponding resonance widths, $\Gamma$, as $|E_I| = \Gamma/2$. The triangles indicate resonances of $A''$ symmetry, and the solid circles indicate those of $A'$ symmetry.

We clearly see that the calculations show a fairly large number of ‘resonances’, although their corresponding widths tell us that only a very small number of them exhibit lifetimes of physical significance. The examples of the figure, in fact, indicate only two resonances to carry width values corresponding to lifetimes larger than a vibrational period ($\sim 10^{-14}$ s), whereas the third one is too close to the threshold to be experimentally detected. We summarize the resonance positions and widths from the present calculations in table 1.

From the results reported in the table we see that both configurations show very similar behaviour, with their corresponding resonance positions and widths appearing to be rather close to each other. We further see from the data in the table the presence of one distinct resonance at lower energies (and with narrower widths) in the $A''$ symmetry with a resonance of $A'$ symmetry appearing at much higher collision energies and exhibiting a shorter lifetime.
To try and gain further understanding of the trapping mechanisms which act for these two TNI species, we report in figure 2, and for the trans configuration only, the radial shapes of the PD model potential components which most significantly contribute to the scattering process. The upper panel in the figure shows that only up to $l_{\text{max}} = 4$, we see contributions which allow...
Figure 3. Dominant radial components for the two scattering resonant states of trans-formic acid. Upper panel: $A''$ symmetry; lower panel: dominant components for the $A'$ resonant wave function.

significant interaction between the scattered electron and the molecular (electrons + nuclei) network: the distances are measured from the target centre-of-mass, with the oxygen atoms located at about 2.0 a.u. from it. One should therefore expect that the resonant electron trapping by the centrifugal potential should be mainly caused by one of the lower-$l$ values reported in the figure. To confirm this conjecture, we therefore report in figure 3 the squared module of the
real parts of the scattering wave functions: the upper panel shows the dominant ones for the lower-energy resonance of $A''$ symmetry, whereas the lower panel reports the main components for the higher-energy resonance of $A'$ symmetry. Both examples refer to the calculations for the trans configuration of the formic acid.

The results for the wave function that is antisymmetric with respect to reflection in the plane of the molecule (upper panel) reveal that the $l = 3$ component exhibits clear decaying shape in the outer radial region, thus resembling a bound-type state at that positive energy location: coupling with the lower channel of $l = 2$ therefore provides the dominant 'leak-out' mechanism of the multichannel resonant state. For the broader resonance at higher energy, on the other hand, the lower panel in the same figure shows a more complicated coupling behaviour: the trapping occurs behind the $l = 4$ component but decaying is now strongly coupled to both $l = 2$ and $l = 0$ channels. The more efficient 'leak-out' process therefore affords the markedly broader feature of this TNI state.

In conclusion, our calculations indicate the presence of two marked resonances due to potential-barrier trapping but within a multichannel picture, i.e. with the additional presence of resonance decay mechanisms related to the relative strengths of the interchannel couplings exhibited by the TNI state formed by the formic acid. Furthermore, our calculations show two, very distinct energy regions where such resonances could be detected and further suggest that their relative lifetimes are very different from one another. In the next section we carry out a comparison with recent experimental findings [11] to see how much of them could be understood from the findings of our calculations.

3.2. Comparison with experiments

As discussed in the experimental work [11] the measurements were carried out on a molecular beam of formic acid, where no traces of hydrogen-bonded dimer species were detected, thereby indicating that the experiments were conducted on a beam predominantly composed of monomers. Hence, our present calculations only include electron scattering from the isolated HCOOH molecule. The experiments of the DEA process [11] observed a strong, fairly narrow peak centred around 1.8 eV and with an intensity distribution covering about 1.0 eV; a further, much broader peak centred around 7.8 eV and another broad peak centred around 9 eV, covering a broad range of more than 2 eV. It is also interesting to note that earlier electron transmission (ET) experiments [23] had found a fairly symmetric resonance structure in the range between ~0.9 and ~3.0 eV, with a maximum located at 1.8 eV. The mass spectrometric detection of the DEA experiments associated that peak with the formation of the HCOO$^-$ fragment, with an energy threshold of about 1.37 eV [11]. In the experimental work, the authors also carried out ab initio calculations for the electron density of HCOOH and examined its virtual molecular orbitals (MOs) in the range 0–2 eV to qualitatively mimic the resonant state formation. They found four virtual orbitals in that energy range that described remarkably diffuse single-particle states without any particular valence character. Furthermore, all their calculations predicted that (HCOOH)$^-$ cannot bind an extra electron and therefore gaseous formic acid possesses a negative adiabatic electron affinity [11]. Finally, the structures seen in the experiments for the lower peak were attributed there to the formation of vibrationally excited states of (HCOO)$^-$. To analyse the nature of our computed resonant states, we have generated spatial density maps, over the molecular nuclear frame, of the scattering states of table 1 produced by our present quantum treatment of the dynamics. In figure 4, we present all of them, each covering a region...
of about 30 a.u.\(^2\) of area over the molecular structures: the solid curves correspond to positive constant values of the wave function and the corresponding dashed curves correspond to negative values of the wave function. The top two panels report our computed low-energy TNIs of \(A''\) symmetry and for both the trans (left) and cis (right) conformations. The wave functions exhibit a nodal plane at the molecular position and we have therefore drawn them about 0.75 a.u. above that plane. One could qualitatively consider them as \(\pi^*-\)type resonances, although our scattering calculations clearly indicate a more complex picture:

(1) the dominance of the \(l = 3\) trapping channel for this resonance (see figure 3) indicates the presence of three nodal planes, i.e. two additional ones are seen in the top two panels, orthogonal to the molecular plane and cutting the two C–O bonds of the nuclear framework;

(2) no extra electron density is present on the hydrogen atom bound to one of the oxygen atom, i.e. the general strengthening of the bonds provided by the temporarily trapped electron does not extend to that specific H atom.
One should not be too disappointed by the energy mismatch that we see between our shape resonance location and that found by experiments, since several approximations were introduced both in the interaction potential we employed and in the quantum dynamics without couplings to nuclear motion that generates the molecular TNI: we think, however, that the qualitative accord and the features of our resonant excess electron are already indicative of the existence of a precursor state which leads to the DEA fragmentation path into $(\text{HCOO})^-$ observed in the low-energy experimental channels. The nodal structure of our computed resonant state wave function further classifies it as a $\pi^*$ intermediate and confirms the excess electron valence features that show it to be entirely localized on the HCOO molecular framework. The present findings also show that the simpler use of bound-state electronic calculations via virtual orbital analysis [11] is not sufficient to catch the fundamentally valence-type, molecular features of the resonant state that is clearly indicated by our scattering calculations. In the experiment [11], there is also some indication that there is vibrational structure in the dissociative attachment cross-section that reflects the presence of an appreciable lifetime for the resonant negative ion states. This observation is consistent with our hypothesis that the low-energy $\pi^*$ resonance does not lead to direct dissociation. Rather, this resonance must lead to dissociation through vibrational energy redistribution from the $\text{C=O}$ and $\text{C−OH}$ vibrational modes, which are initially excited, to the dissociative $\text{O−H}$ stretching mode.

If we now turn to the second, higher-energy, TNI seen by our calculations, we notice that its $A'$ symmetry locates the excess electron wave function in the molecular plane, where no nodal plane exists. However, we have seen from the data of figure 3 that the dominant trapping of this resonance occurs for the $l = 4$ component, hence suggesting the presence of four nodal surfaces. The lower two panels of figure 4 clearly show that a marked antibonding character of the excess electron wave function is visible across the $\text{C−OH}$ bond, with substantial charge density being now localized on the OH fragment. It therefore stands to reason to associate this computed TNI as the probable precursor for the broad (OH)$^-$ fragment peak, centred in the experiments around 8 eV. In other words, while considering again the assignment as being only qualitatively close to existing measurements, we suggest that the second, broad TNI resonance produced by our calculations provides the precursor state for the DEA fragmentation pattern along a specific dissociative path on the potential energy surface that involves the $\text{C−OH}$ bonding region and which produces (OH)$^-$ anions. The latter fragmentation path is favoured, according to our calculations, by the antibonding features along the $\text{C−OH}$ bond which are exhibited by the resonant excess electron localized on the molecular nuclear framework.

The experiments further observed [11] the presence of the $\text{O}^-$ fragment appearing above $\sim9\,\text{eV}$ and exhibiting a very broad peak. Our calculations reveal in the higher computed resonance (see the lower two panels of figure 4) the presence of excess electron density on the carbonyl oxygen atom in the in-plane $\pi^*$-type local orbitals. Furthermore, the nodal structure of this resonance shows antibonding character across the $\text{C=O}$ bond. Thus, one could suggest that the $\text{O}^-$ fragmentation may take place from the high-energy tail of our second resonance. An alternative explanation may be that this high-energy process may proceed through a Feshbach-type resonance involving an excitation of the target. Such a process is not included in the model used in the present study of electron–molecule scattering.

In other words, we suggest that our computed TNI resonant wave functions for the two precursor states are caused by shape resonances and can account for at least two of the three observed features in ET [17] and DEA [11] experiments. We can indeed relate their fragmentation peaks to specific features of our computed excess electron wave functions over the spatial region.
of the molecular nuclei described by the initial, equilibrium configurations of the target. Our present calculations can also qualitatively suggest alternative molecular mechanisms for the fragmentation experimentally observed at the highest energy.

4. Conclusions

In the present work we have analysed the experiments on electron transmission and dissociative electron attachment processes [11, 23] for the monomer formic acid in the gas phase. We have carried out calculations for locating resonant states of the formic acid in the low-energy region sampled by experiments and have found that the elastic scattering $S$-matrix analysis at the nuclear equilibrium geometries clearly shows the presence of two distinct resonances, one around 3 eV and the other around 12 eV, produced by open-channel trapping of the impinging electron.

The use of an equivalent formulation of the scattering problem, via the definition of a piecewise diabatic (PD) model potential form, allows us to further analyse the excess electron resonant scattering wave functions in terms of dominant angular momentum components. The latter states show in turn, in a rather transparent way, the presence of specific nodal planes cutting across some of the molecular bonds and therefore help us to suggest that their corresponding antibonding character along specific cuts of the multidimensional potential energy surfaces control the motion of the network of the nuclei and are indicative of preferred fragmentation pathways during the DEA process.

In conclusion, our present analysis of the quantum dynamics, in spite of the strong simplifications introduced when setting up the interaction potentials and the scattering equations, allows us to obtain a fairly realistic classification of the probable precursor states for the metastable (HCOOH)$^-$ species that will decay into the observed fragmentation channels. The next computational step will regard both the explicit introduction of the dynamical couplings of the scattered electron with the bound molecular nuclei and also the effects on the same scattering observables of the formation of hydrogen bonds of the formic acid within its stable dimers.

Acknowledgments

This work was supported by the Italian Ministry for Research (MUIR), the Research Committee of the University of Rome ‘La Sapienza,’ the NATO program for collaborative research grants, the Welch Foundation (grant A-1020), the European V Framework through the EPIC project. We are grateful to Eugen Illenberger for several stimulating discussions and for making us aware of this very interesting system as a biomolecular prototype.

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