

Role of a short-lived σ^* resonance in formic-acid O—H bond breaking

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We review briefly the recent work on dissociative electron attachment (DEA) to formic acid. Using Feshbach resonance theory we present results calculating the forces on various atoms during resonance processes that can arise at different electron impact energies. The conclusion is that DEA to formic acid happens through a short-lived σ^* resonance with minimal involvement from π - σ symmetry breaking as suggested elsewhere. We conclude that rehybridization on a C atom caused by the π - σ mixing is too far from the O—H bond to detect its effect on the DEA cross section. A recent experimental confirmation is also reported.

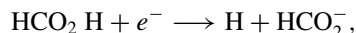
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I. INTRODUCTION

Several papers have appeared in the past few years treating the mechanism for the dissociative electron attachment (DEA) to HCO_2H . Formic acid is the simplest of the carboxylic acids and is a prototype for that class of substances. In addition the —COOH group is also present in the biologically important amino acids. Since the work of Boudaïffa *et al.* [1] and Sanche [2] it is now known that low energy electrons can cause bond breaking in all sorts of biologically important molecules through the mechanism of DEA, which frequently operates through interactions of the electron and antibonding virtual orbitals in the molecule. This motivates a careful examination of DEA in the simplest of organic acids, formic acid.

In HCO_2H DEA results in the breaking of the O—H bond,



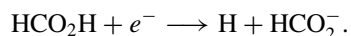
which in a planar geometry is a “ σ ” bond. In the 1970s several experimental and theoretical works were published showing that in some molecules DEA to a molecule resulting in a broken “ σ ” bond might occur with the intervention of a π resonance. It was realized that this must happen through a geometry distortion that destroyed the “ π - σ ” separation [3,4].

In the following decades, however, it became clear through the work of Domcke and co-workers [5], that such π - σ interactions were unnecessary for DEA breaking of σ bonds. This was clear since many of these new studies involved diatomic molecules where π - σ symmetry breaking cannot happen. Nevertheless, it was also clear that the symmetry breaking, where possible, could enhance cross sections substantially.

In light of this history, Rescigno *et al.* [6] reported on the behavior of the C=O shape resonance in formic acid with a fixed nucleus approximation (FNA) method at a number of discrete arbitrary geometries. (We return to the specifics of these geometries in Sec. V.) The energies and lifetimes of molecular resonances are important ingredients in any rigorous theory of DEA, which, unfortunately for polyatomic molecules, is beyond the development of current theory. Nevertheless, knowing the behavior of resonances as a function of geometry, i.e., knowing the complex Born-Oppenheimer surface (BOS) associated with a resonance, can lead to considerable certainty

about the likelihood of DEA caused by that resonance. It can go only so far; a full-fledged multiatom treatment is required to yield an accurate cross section, of course.

On the other hand, there are many parallels in DEA to formic acid compared with DEA to HCl, in that a single H atom leaves a stable negative ion. Following up on this idea, Gallup *et al.* [7] gave a treatment of DEA to formic acid approximated as a diatomic system. Using a correct complex nonlocal nuclear potential, this gave cross sections with a peak shape and size in reasonable agreement with experiment, but based on the O—H σ resonance as the driving force, unlike the procedure of Rescigno *et al.* This new work also applied the diatomic method to glycine with even better results. In short course a Comment [8] and Rely [9] were published, raising a debate concerning the detailed mechanism of the DEA process in formic acid,



The principal controversy is thus between two pictures of DEA to formic acid, a model involving an out-of-plane motion of the C—H hydrogen and the C=O resonance posited by Rescigno *et al.*, and a completely planar model involving the O—H resonance used by Gallup *et al.* Rescigno *et al.* also suggested that the substitution, C—H \longrightarrow C—D, should, according to their model, reduce the cross section for DEA because of the greater mass of the deuterium nucleus. Recently, Janečková *et al.* [10] have tested this notion experimentally and have found no detectable (within experimental error) influence on the cross section from the isotopic substitution in apposition to the conclusion of Rescigno *et al.*

Nevertheless, the cross-section calculations of Gallup *et al.* did use a diatomic model. More realistically, the H atom can recede from the ion in several directions. So in this article we examine a broader range of motions, still within the FNA and, thus, obtain more information about the complex BOS associated with the O—H antibonding orbital and the forces of the atom due to a resonance. For completeness we also make Feshbach calculations for the C=O resonance to study the forces on the atoms for the C=O resonance.

II. GENERAL COMPUTATIONAL DETAILS

We use Feshbach resonance theory [11–13] to determine portions of the complex BOS in the FNA at the neutral geometry and at a number of distorted geometries, and we

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use these results to make certain predictions concerning DEA to HCO_2H .

The finite element discrete model (FEDM) approximation has been used to solve the Feshbach equations, and its use is thoroughly described by Nesbet [14] and the current author [15,16]. In line with our standard procedure, we use the conventional Pople 6-31G(d) Gaussian basis set and standard MP2 techniques to represent the Feshbach quasibound state (QBS) and its energy.

The FEDM involves a set of pseudocontinuum (PC) orbitals to provide the singly occupied molecular orbitals (SOMOs) for the PC states required in the theory. Details concerning these will be given in the sections devoted to the O—H and C=O antibonding orbitals discussed.

III. TIME DELAY AND FORCES ON THE NUCLEI

A basic idea of the Feshbach resonance theory is splitting the continuum space of a scattering problem into a finite-dimensional part, spanned by L^2 functions, and its orthogonal complement. Taking the case where the L^2 part is one dimensional, let the L^2 function be denoted ϕ . We then construct the projections

$$Q = |\phi\rangle\langle\phi|, \quad (1)$$

$$P = I - Q, \quad (2)$$

and

$$\Psi = Q\Psi + P\Psi, \quad (3)$$

where

$$H\Psi = E\Psi. \quad (4)$$

Ψ is an outgoing wave, steady-state solution to the scattering problem. As such, $|\Psi|^2$ may be interpreted as a flux density. Consider a finite volume sphere, S_C , with center at C and the integral,

$$F_C(E) = (1/V) \int_{S_C} |\Psi|^2 dV, \quad (5)$$

which gives the average flux density for the volume in the sphere centered at C and at the energy, E . If all points in S_C are at great distance from the scattering center, $F_C(E)$ is independent of the position of C .

If ϕ is now chosen as a QBS function for the current Feshbach-FEDM procedure, the quantity $\langle\Psi|Q|\Psi\rangle/F_C(E)$ is a measure of a possible relative electron probability buildup at the scattering center compared to that in the asymptotic region. This is the time-independent picture of the time delay phenomenon discussed in connection with time-dependent scattering descriptions [17]. The probability amplitude in the FNA at the scattering center is

$$\frac{Q\Psi}{\sqrt{F_C(E)}} = a(E)\phi, \quad (6)$$

where $a(E)$ is a function of E with the expected “bell shape” absolute value. If an appropriately placed spherical integral

$$[1/F_C(E)] \int_{S_C'} |P\Psi|^2 dV$$

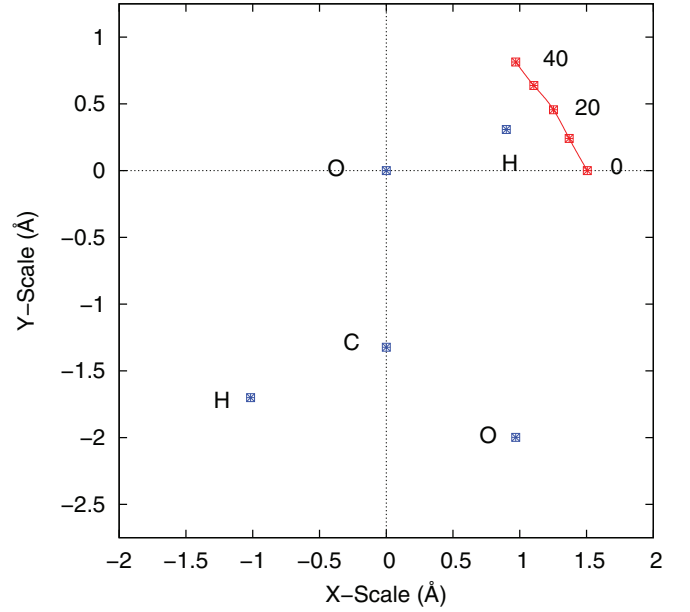


FIG. 1. (Color online) The intersection with the xy plane of the ion stability surface for the O—H resonance in formic acid. The blue squares show the equilibrium positions of the atoms, and the red squares with the connecting line shows the intersection. The numbers beside the intersection show the angle in degrees between the O—H line and the x axis.

is small at the resonance center, then one is assured that $Q\Psi$ alone is a good representation of the relative wave function at that E .

When this argument is generalized to the multielectron wave function, we can say

In the FNA at the neutral molecule geometry, the forces on the nuclei near the resonance center are determined only by the SOMO of the scattering wave function. If, on the other hand, we are treating a distorted geometry, the differences between the ion and neutral forces must be taken.

We show these forces graphically in each of the separate sections on the two antibonding orbitals.

IV. ION STABILITY POINTS FOR THE O—H RESONANCE

As the O—H distance increases during a geometry distortion the complex energy of the resonance changes with the real part decreasing and the imaginary part decreasing in magnitude. At some point the imaginary part becomes zero and, at greater distances, remains zero. We will call this the *ion stability point*, and the surface of these points is expected to be somewhat “umbrella” shaped around the original O—H line. Figure 1 shows, in relation to the atoms in the molecule, a graph of the intersection of this surface with the xy plane.

These calculations used 60 PC orbitals consisting of ten each s , p_x , and p_y atomic orbitals (AOs) at each nucleus of the O—H bond. The p_z is not involved in the A' symmetry. The expectation values of the kinetic energy range from 0.05 to ≈ 20 eV for these AOs. Figure 2 gives an orbital picture of the QBS SOMO. We call attention to the node

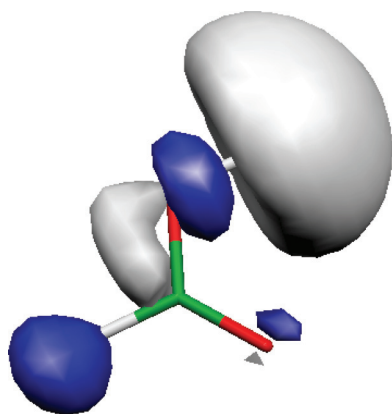


FIG. 2. (Color online) The probability amplitude of the O—H QBS function. The node in the middle of the O—H bond is clearly visible.

between the C- and H-atom positions, providing the basic driving force for the DEA. Nevertheless, the orbital is quite asymmetric about the middle and will have a sizable “s” character with respect to the node’s position. This results in the “short-lived” characterization of this resonance by Gallup *et al.* [7]. Relative to the neutral energy minimum (no zero-point energy), the complex energy at the equilibrium geometry is $(3.386 - 4.827i)$ eV. This translates into a lifetime at the middle of the resonance of 1.36×10^{-16} s.

Table I gives several data about the geometries of the five points on the ion stability curve at the different \angle OHs. These are R_{OH} , the distorted O—H distance; energy, the energy of the BOS (which is real at this point); ΔR_{OH} , the distance between the distorted H and equilibrium H positions; and Fall, the ratio of real energy decrease to the distance H traveled during the distortion. This last column gives a qualitative picture of the actual force of dissociation of the O—H bond.

Figure 3 shows a diagram of the molecule with arrows attached to the atom centers, the length and direction of which show the forces on the atoms from the delayed charge density, as discussed in Sec. III.

This resonance is short lived, but in the 30° direction the fall is quite large. If we assume the energy of the orbital behaves with bond length like a particle in a box model, we expect the energy to vary $\propto (\text{length})^{-2}$ and the Fall $\propto -(\text{length})^{-3}$. Thus, in classical language, very short antibonding orbitals may have short lifetimes, but nevertheless live long enough for the nuclei to move quickly to the nearby ion stability point. In actuality, a proper treatment of the nonlocal complex BOS would average over many motions and could certainly produce quantitative changes in this picture.

TABLE I. Distances and real energies at various points in Fig. 1.

| Angle | R_{OH} (Å) | Energy (eV) | ΔR_{OH} (Å) | Fall (eV/Å) |
|------------|--------------|-------------|---------------------|-------------|
| 40° | 1.266 | 2.101 | 0.511 | −1.796 |
| 30° | 1.276 | 2.172 | 0.389 | −3.121 |
| 20° | 1.333 | 2.363 | 0.383 | −2.671 |
| 10° | 1.391 | 2.754 | 0.368 | −1.717 |
| 0° | 1.506 | 3.277 | 0.681 | −0.160 |

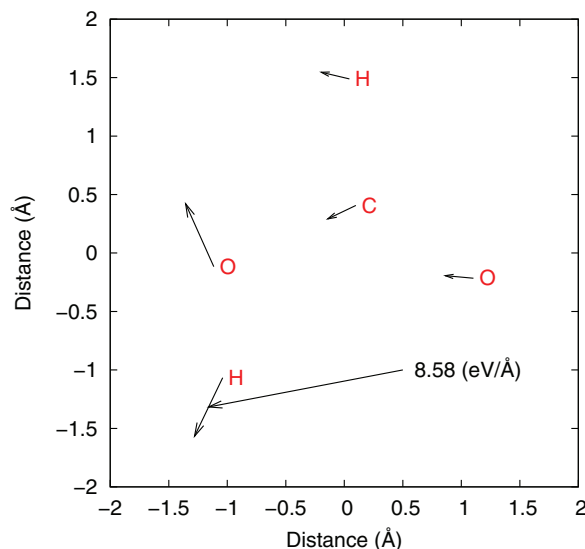


FIG. 3. (Color online) The directions and the relative sizes of the forces on the atoms during the temporary negative ion arising from the O—H resonance. The scales on the figure are in angstrom so the lengths of the force vectors are relative, but the absolute value of one is shown on the graph for calibration. It is seen that there are strong relative forces tending to lengthen the O—H bond. In the actual molecule these will be modified by the value of $|a(E)|^2$ from Eq. (6).

V. C=O RESONANCE

In their analysis of the effects of the C=O resonance, Rescigno *et al.* [6] devise a number of geometry points along what they call the “reaction coordinate,” which is the abscissa in the lower panel of their Fig. 4. In this panel they mark eight different points along the path for special attention. Table II shows the bond lengths at these points. For completeness we note that point 8 along the reaction coordinate is of a character different from the others. The O—H bond is extended until

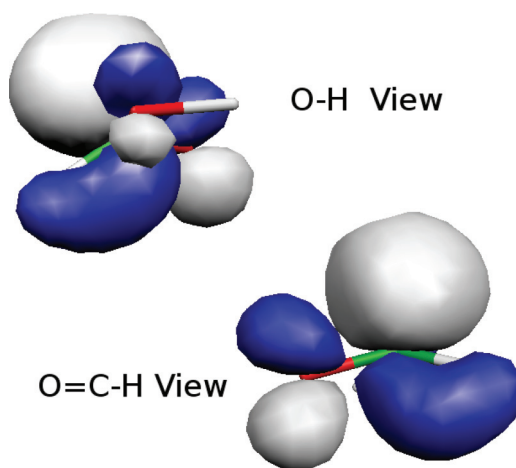


FIG. 4. (Color online) Two views of the QBS function at point 7. It is seen from the O—H view that there is no significant probability amplitude at the O—H H atom, and from the other side that most of it is around the C—H H atom.

TABLE II. Eight special geometry points along a reaction coordinate. Point 1 is the neutral molecule geometry shown in Fig. 1 [6]. Points 2–7 are given as increments added to point 1 values. Distances are in angstrom and angles in degrees. The last column refers to the dihedral angle between the C—H bond and the O—C—O plane. Further comments concerning point 8 are in the text.

| | $R_{C=O}$ | R_{C-O} | $D\angle H$ |
|---|--|-----------|-------------|
| 1 | Neutral formic acid geometry | | |
| 2 | 0.02 | 0.04 | 0 |
| 3 | 0.04 | 0.08 | 0 |
| 4 | 0.08 | 0.16 | 0 |
| 5 | 0.08 | 0.16 | 20 |
| 6 | 0.08 | 0.16 | 30 |
| 7 | 0.08 | 0.16 | 40 |
| 8 | Point 7 plus unspecified further extensions of the O—H bond length | | |

the distance is outside the conical intersection point of the planar system. To the right of point 7 their Fig. 4 converts from plotting adiabatic energies to plotting computed diabatic energies, and point 8 is set at the crossing. No details are given.

In the next few paragraphs we compare our Feshbach theory results with some of those in Rescigno *et al.* [9]. In looking at their Fig. 4 energies we emphasize that they plot total energy, while we report energies relative to the energy of the neutral molecule at each geometry.

The PC orbitals we use for the C=O resonance are p_z AOs centered at the two nuclei at either end of the C=O antibonding orbital. There are 20 at either end, and their kinetic energies range from 0.05 to ≈ 20 eV. We examine here the results of applying the Feshbach method to their designated geometries, points 1 and 7.

The point 1 geometry is the equilibrium point of neutral formic acid. Thus the resonance position should be that measured in the laboratory. The current FEDM procedure gives 1.73 eV as the resonance center and 0.118 eV as the width at the center. Aflatooni *et al.* [18] give the center as 1.73 ± 0.05 eV in remarkable agreement. Rescigno *et al.* obtain ≈ 1.90 eV for the center, which they consider reasonable agreement, and ≈ 0.14 eV for the width (estimated from their Fig. 4) (see also Trevisan *et al.* [19]).

At the geometry of point 7 the present FEDM procedure gives 0.125 eV as the center of a near-zero energy resonance, while Rescigno *et al.* report a slightly negative result (in this case relative to the neutral molecule energy) without giving its value. Previous experience with the Feshbach-FEDM has found agreement with experiment within $\approx \pm 0.15$ eV. Thus, our result and that obtained by Rescigno *et al.* previously should be considered equivalent [20].

In light of the arguments in Sec. III, the QBS of the Feshbach theory is expected to give a qualitative picture of the relative charge distribution over the molecule at an energy close to the resonance or the stable negative ion geometrically nearby. Figure 4 shows two views of the probability amplitude for the SOMO in the Feshbach QBS function. This shows the charge distribution is mainly centered around the O=C—H end of the molecule rather than near the O—H bond. From this one concludes that the π - σ

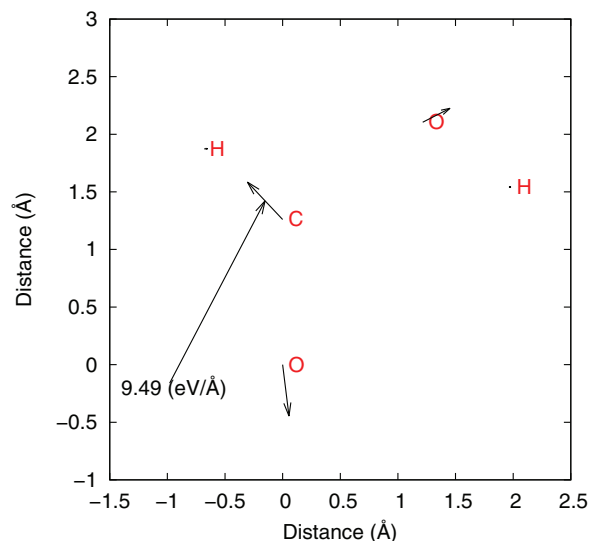


FIG. 5. (Color online) See the caption of Fig. 3 for an explanation. Clearly the forces tending to lengthen the C=O are much larger here at point 7—hardly a surprise, of course, since the resonance is based upon a C=O antibonding orbital. The calibration number for the force is for the full length, but close to one-third is out of the plane.

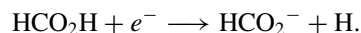
interaction could enhance DEA to formic acid having the H split from C rather than O, were not the asymptotic energy too high for that process at ≈ 1.73 eV. The resulting carbanion would be 1.95 eV less stable than the common formate ion, HCO_2^- .

Figure 5 shows a diagram of the forces on the atoms along the same line as with Fig. 3. The main difference between the two presentations is that, unlike the earlier figure, the forces here are not all *in* the plane of the drawing. The perpendicular components are not large in most cases.

It is seen from the diagram that the force on the O—H H atom is too small to show direction at this scale. The value for the total is 0.44 eV/\AA and the vector is approximately 45° out of the plane. We conclude that there should be very little enhancement of the expected DEA process in formic acid due to the C=O resonance.

VI. CONCLUSION

The application of the Feshbach resonance theory to formic acid shows that the π - σ interaction caused by out-of-plane motions of the C—H H atom should have little involvement in the DEA process:



This should also be true for glycine, $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$, as shown in Gallup *et al.* We expect similar behavior in other simple organic acids.

As discussed in Sec. I, there are certainly cases where π - σ interactions operate, but relatively few examples are known where an H atom leaves C in a C-containing ion. One such, however, is the theoretical study of DEA to acetylene, by Chourou and Orel [21] on H leaving $\text{H}-\text{C}\equiv\text{C}^-$. This was carried out as a wave-packet study with a local complex BOS. Here the H atom moves out of linearity with the remainder of the ion. The obvious geometric difference between formic

acid and acetylene is the location of the leaving H atom. In acetylene it is leaving the actual C atom whose hybridization is modified by the bending. In formic acid it is leaving an O atom at least one step away from the rehybridization activity.

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