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ARTICLES

Electron Correlation as the Driving Force for Charge Transfer: Charge Migration Following Ionization in *N*-Methyl Acetamide

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A hole charge created in a molecule, for instance, by ionization, can migrate through the system solely driven by electron correlation. The migration of a hole charge following ionization in *N*-methyl acetamide (a molecular system containing a peptide bond) is investigated. The initial hole charge is localized at one specific site of the molecule. Ab initio calculations show that nearly 90% of the hole migrates to a remote site of the molecule in 4.2 fs. This migration of charge is highly efficient and ultrafast. The underlying mechanism for this migration of a hole charge is identified and compared with a simple model.

I. Introduction

Charge transfer is a fundamental process in nature. As such, it is the topic of various scientific efforts. The term "charge transfer" describes various phenomena, in general, the flow of electronic charge along a single extended chain molecule or between two or more molecules. In most charge transfer processes, an electron (or a hole charge) is transported from a donor to an acceptor. Biophysics provides classic examples for charge transfer, such as photosynthesis[1−3] or reactions involving proteins. Within the scope of molecular electronics, the storage of energy in large molecules is of high interest.[4−6] Usually, it is assumed that in molecular systems nuclear dynamics plays an essential role in the course of the charge transfer process.

Contrary to this assumption, a particular method of analyzing charge transfer[7,8] demonstrates that efficient mediation of charge transfer solely driven by electron correlation is, in fact, possible. To distinguish this mechanism from the conventional ones, it is referred to as *charge migration*. The method is based on ab initio calculations. The analysis of charge migration is carried out at fixed coordinates of the nuclei. Of course, at sufficiently long times, the motion of the nuclei comes into play, but in general, charge migration due to electron correlation is much faster.

In the present work, an application of charge migration following ionization on the molecule *N*-methyl acetamide will be discussed. This molecule consists of a peptide bond and two methyl groups on each end of the molecule; see Figure 1. The initial hole charge due to ionization of the 13a′ orbital is localized on one specific site of the molecule. The results shown in section III predict an effective, ultrafast migration of the hole charge from one "end" of the molecule to the other. The time scale of the charge migration process is a few femtoseconds.

To investigate charge migration following ionization in the molecular system *N*-methyl acetamide, any method that takes electron correlation correctly into account can be used. We applied an ab initio method called charge migration analysis (CMA),[8−10] which is particularly suitable for this kind of problem. The CMA method was developed recently and is based on a general ab initio approximation scheme (abbreviated ADC)[11,12] to evaluate Green's functions and propagators.[13,14]

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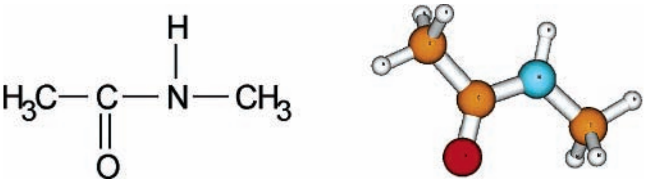

Figure 1. Molecular geometry of *N*-methyl acetamide. Structural formula (left panel) and 3D structure after Hartree–Fock geometry optimization (right panel).

This scheme treats electron reorganization and electron correlation well.

The investigation of the charge migration in *N*-methyl acetamide is motivated by the careful measurements of Weinkauf et al.,[15,16] where a peptide chain was ionized. In that experiment, the initial hole charge was localized on one specific site, say A, of the molecule which defragmented rapidly at a remote site, say B, of the chain. Due to some mechanism, the energy necessary to break the bond at B must have been transported from A to B. Weinkauf et al. suggested that the hole charge migrated to the latter site of the molecule due to a fast electronic transfer mechanism. The time scale of the process could not be determined experimentally.

In the course of analyzing and explaining our numerical results of an effective ultrafast charge migration in *N*-methyl acetamide, two questions arise: (i) Can we determine the time scale of the process, and (ii) what is the underlying mechanism of charge migration? Both questions will be answered in section III.B by analyzing the ionization spectrum of the molecule. In general, an intimate relationship exists between the ionization spectrum and the mechanisms of charge migration. It should be pointed out that the general case of charge migration driven by electron correlation is difficult to understand because many effects contribute. Therefore, it is useful to concentrate on certain cases where the charge migration process is dominated by a single mechanism.

II. General Aspects of Charge Migration

The starting point of our investigations is a neutral molecule in its ground state, $|\Psi_0\rangle$. After ionization of the molecule, we trace the hole charge in space and time; that is, we are interested in the time-dependent hole density of the cation. To be independent from experimental conditions, the initial cationic state is created by the sudden removal[17] of an electron. The terms "cationic" and "neutral" are used for simplicity of speech; the following formalism remains valid if the system is not neutral, for example, if the target molecule is an anion. Then, the charge migration would be analyzed in the neutral molecule.

If the migration of the hole charge is *ultrafast*, as found in previous calculations,[7,8] the motion of the nuclei can be neglected. Consequently, the following analysis will be carried out at fixed coordinates of the nuclei. The idea of neglecting the coupling of electronic and nuclear motions in order to describe intramolecular charge transfer can be found in earlier approaches.[18,19] We investigate here the dynamics of intramolecular charge transfer on the basis of ab initio calculations.

The hole density of the ionized molecule reads

$$Q(\vec{r}, t) := \langle \Psi_0 | \hat{\rho}(\vec{r}, t) | \Psi_0 \rangle - \langle \Phi_i | \hat{\rho}(\vec{r}, t) | \Phi_i \rangle$$

where $\hat{\rho}$ is the charge density operator and $|\Phi_i\rangle$ describes the cationic initial state. The first term on the right-hand side, $\langle \Psi_0 | \hat{\rho}(\vec{r}, t) | \Psi_0 \rangle$, is time-independent, whereas the second term is explicitly time-dependent as $|\Phi_i\rangle$ is not an eigenstate of the system. Introducing a one-particle orbital basis, $\{\varphi_p\}$, of, for instance, Hartree–Fock orbitals, the hole density reads

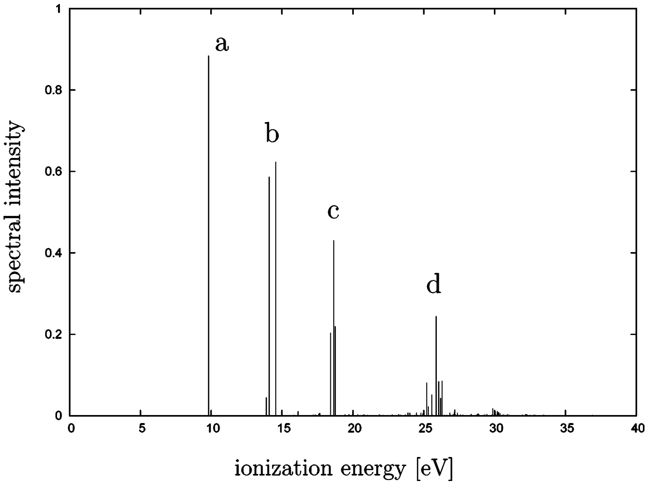

Figure 2. Typical ionization spectrum of a molecule (schematic). Each vertical line shown is related to a cationic state and is located at the corresponding ionization energy. The outer valence lines appearing at low energies in the spectrum are dominated by 1h configurations (cases a and b). At somewhat higher energies, *satellite lines* appear (case c) because the 1h configuration is spread over several lines, due to interaction with 2h1p configurations. At even higher energies (case d), the situation becomes more intricate, as the main lines cease to exist.

$$Q(\vec{r}, t) = \sum_{p,q} \varphi_p^*(\vec{r}) \varphi_q(\vec{r}) N_{pq}(t)$$

where the hermitian hole density matrix, $\mathcal{N}(t)$, with elements $N_{pq}(t)$ was introduced. Diagonalization of $\mathcal{N}(t)$ leads to the hole density

$$Q(\vec{r}, t) = \sum_{p} |\tilde{\varphi}_p(\vec{r}, t)|^2 \tilde{n}_p(t) \tag{1}$$

introducing the so-called *natural charge orbitals*, $\tilde{\varphi}_p(\vec{r}, t)$, and *hole occupation numbers*, $\tilde{n}_p(t)$. It should be noted that the hole occupation numbers, $\tilde{n}_p(t)$, and natural charge orbitals, $\tilde{\varphi}_p(\vec{r}, t)$, depend explicitly on time. This is due to the explicit time dependence of the hole density matrix, $\mathcal{N}(t)$. The hole occupation number, $\tilde{n}_p(t)$, tells us which part of the created hole charge is in the natural charge orbital, $\tilde{\varphi}_p(\vec{r}, t)$, at time t.

To illustrate several mechanisms of charge migration, we briefly describe the appearance of a typical ionization spectrum; see Figure 2.

The spectrum shown consists of vertical lines, where each line represents an eigenstate, $|I\rangle$, of the cation. The energetic position of each line is given by the ionization energy.

For the following discussion, we expand the exact cationic state, $|I\rangle$, in a series of electronic configurations, as traditionally done in configuration interaction (CI) calculations:[13,14]

$$|I\rangle = \sum_j c_j^{(I)} a_j |\Phi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} a_a^\dagger a_k a_l |\Phi_0\rangle + ... \tag{2}$$

where $|\Phi_0\rangle$ is a reasonable approximation to the exact ground state of the neutral molecule, c_j are coefficients, and a and $a^\dagger$ represent the annihilation and creation operators, respectively; thus, a_j annihilates one electron in the occupied orbital, φ_j. Throughout this work, the following usual convention is used: Indices $i, j, k, ...$ indicate occupied orbitals, whereas indices $a, b, c, ...$ indicate virtual (unoccupied) orbitals. Thus, the exact cationic state consists of this picture of one-hole (1h) excitations, $a_j|\Phi_0\rangle$, two-hole-one-particle (2h1p) excitations, $a_a^\dagger a_k a_l|\Phi_0\rangle$, and so on. A 2h1p excitation means that one electron has been removed accompanied by an excitation of another electron into an unoccupied orbital of $|\Phi_0\rangle$. Without correlation effects, there would be a line in the spectrum for each occupied orbital, φ_i, with the spectral intensity equal to 1. If Koopmans' theorem[14] is valid, the energy of each line then is given by its orbital energy, ϵ_i. If correlation effects are weak, the ionization spectrum is dominated by *main lines* typically when ionizing the outer valence part of the spectrum. *Main lines* are dominated by 1h configurations; see the lines marked with "a" and "b" in Figure 2. In this case, the molecular orbital picture remains valid. At somewhat higher energies in the ionization spectrum, *satellite lines* appear; see "c" in Figure 2. Satellites are weaker than the main lines, are dominated by 2h1p excitations, and have only small or moderate overlap with 1h configurations. At even higher energies, see "d" in Figure 2, the situation becomes more intricate as the main lines cease to exist.[8,17] However, this region is not of concern in this work.

We now discuss a special case, charge migration due to *hole mixing*; others can be found in the literature.[8] Consider the two lines marked with "b" in Figure 2, which belong to the ionization out of the outer valence and assume that the corresponding two states of the cation are combinations of two 1h configurations. In other words, each of these two cationic configurations is "spread" over two lines in the spectrum. These two lines in the spectrum are superpositions of two 1h configurations, $a_j|\Phi_0\rangle \equiv |\Phi_j\rangle$ and $a_k|\Phi_0\rangle \equiv |\Phi_k\rangle$. In a CI expansion, these states read

$$|I_{jk}\rangle \approx a|\phi_j\rangle + b|\phi_k\rangle$$

$$|I_{kj}\rangle \approx b|\phi_j\rangle - a|\phi_k\rangle$$

where a and b are real coefficients and $a^2 + b^2 = 1$. The calculation of the hole density matrix and subsequent diagonalization leads to the hole occupation numbers[8]

$$\tilde{n}_{j,k}(t) = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - 4(ab)^2 \sin^2(\omega t)} \tag{3}$$

where $\omega = E_{I_{jk}} - E_{I_{kj}}$ is given by the energetic distance of the two lines considered in the spectrum. The upper equation shows that the initial hole charge at time $t = 0$ oscillates with the frequency, ω, between the two natural charge orbitals $\tilde{\varphi}_j(\vec{r}, t)$ and $\tilde{\varphi}_k(\vec{r}, t)$. This behavior is due to electron correlation and cannot be explained in a Hartree–Fock picture.

III. Ultrafast Charge Migration in *N*-Methyl Acetamide from One End to the Other

A. Tracing the Charge in Time and Space. Consider a neutral molecule in its ground state. Assume there is a valence orbital localized at a specific site of the molecular system, say, at one end of the molecule. Is it possible that after ionization out of this orbital the initial hole charge migrates through the system, say, to the other end of the molecule? We now consider the migration of a hole charge in the molecule *N*-methyl acetamide.

Our calculations consist of several steps. The first step is a geometry optimization[14] of the neutral molecule (e.g., via the Hartree–Fock method); see Figure 1. The molecule is of plane geometry, except for the protons of the two methyl groups which reach out of the plane. These protons are ordered such that the whole molecule has a mirror plane; accordingly, it belongs to the C_s symmetry group with the irreducible representations a′ and a″. To describe the orbitals, the basis DZP (a double-ζ basis with additional polarization functions) was used. The configuration of the Hartree–Fock ground state of *N*-methyl acetamide is

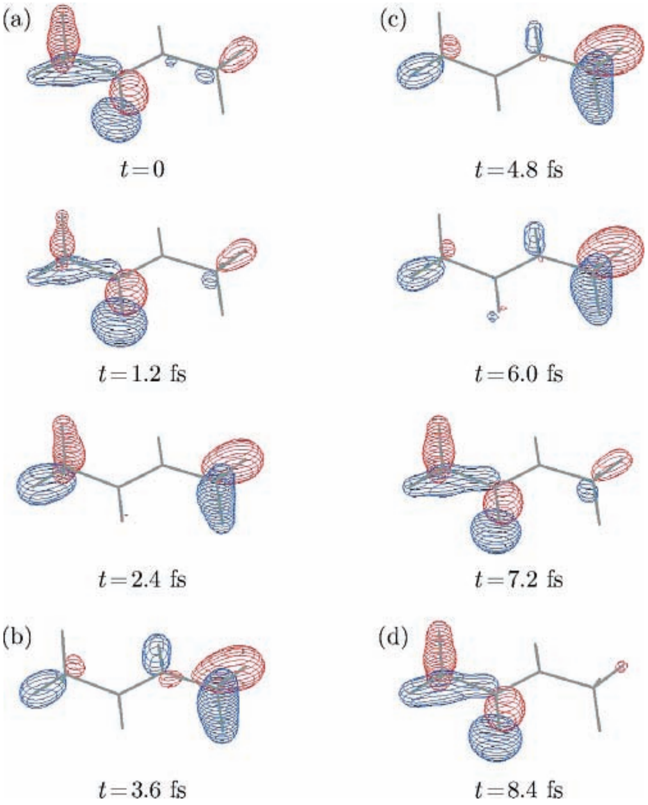

Figure 3. Migration of charge in *N*-methyl acetamide. Shown is the relevant natural charge orbital at different times. The spatial orientation of the molecule is as depicted in Figure 1. (a) At $t = 0$, the natural charge orbital is identical to the 13a′ orbital. The hole charge is mainly localized at the oxygen atom and around the acetyl-C atoms. (b and c) At $t = 3.6$ fs and $t = 4.8$ fs, respectively, the natural charge orbital is essentially the 14a′ orbital. Now, the hole charge is mainly localized on the other side (the "right"-hand side) of the molecule, near the *N*-methyl atoms. (d) At $t = 8.4$ fs, the hole charge has migrated back into the 13a′ orbital—to the "left"-hand side of the molecule.

$$\begin{aligned}&(\text{core})(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(11a')^2(12a')^2(1a'')^2\\&\qquad(2a'')^2(13a')^2(14a')^2(15a')^2(3a'')^2(16a')^2(4a'')^2\end{aligned}$$

Then, the molecule gets ionized by the sudden removal of an electron. At fixed geometry of the ionized molecule, the ab initio charge migration analysis (CMA) method was applied[8−10] in order to calculate the hole occupation numbers and the natural charge orbitals. The CMA method was developed recently by the authors, yielding to the analysis of charge migration in larger molecular systems.

In fact, we found that the molecular orbital 13a′ is mainly concentrated at a specific site of the molecule. After ionization out of the 13a′ orbital, the relevant time-dependent natural charge orbital is depicted in Figure 3. Shown is that natural charge orbital, $\tilde{\varphi}_j(\vec{r}, t)$, with a hole occupation number, $\tilde{n}_j(t)$, close to 1 at all times t. The hole charge will be with high probability in this natural charge orbital at all times t. As can be seen from Figure 3a, at time $t = 0$, the hole in the 13a′ orbital is located mostly near the oxygen atom and around the acetyl-C atoms, which is in Figure 1 the left-hand side of the molecule. Parts b and c of Figure 3 show that, at 3.6 and 4.8 fs, respectively, the initial hole charge is localized mainly around

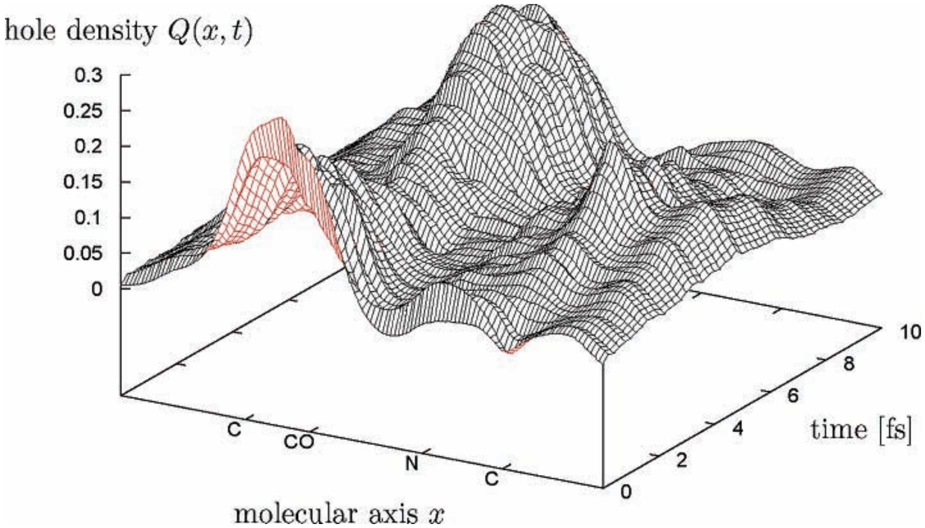

Figure 4. Hole density, $Q(x, t)$, plotted against the molecular axis x as a function of time. The atoms along the molecular axis x are indicated. An ultrafast charge migration over the peptide bond of *N*-methyl acetamide can be seen.

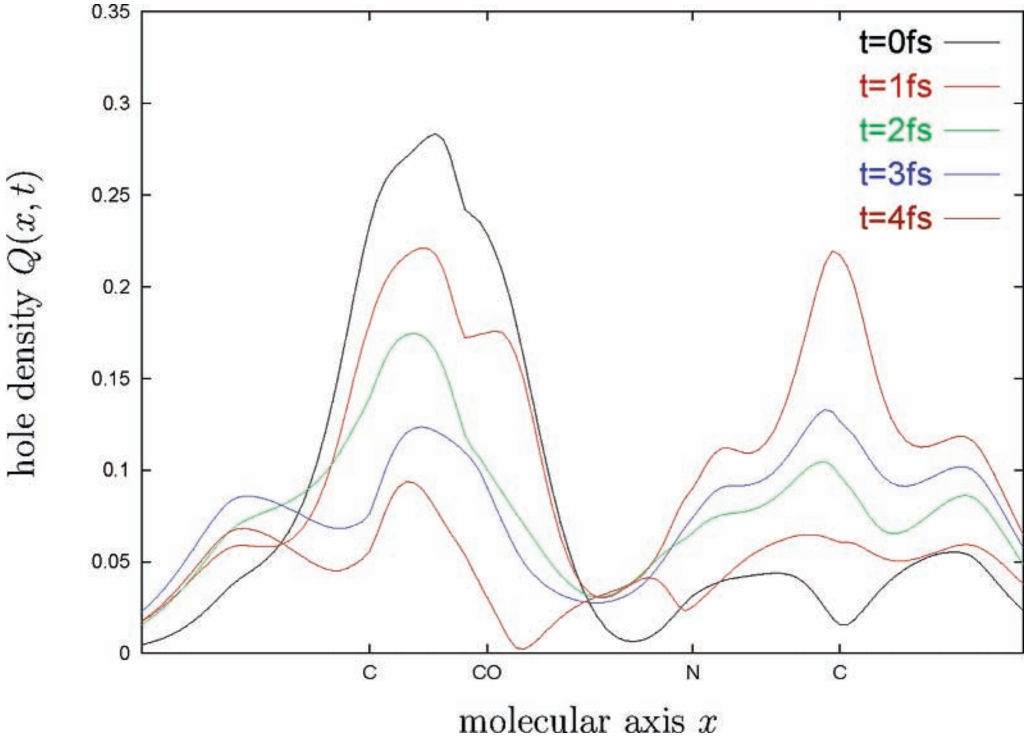

Figure 5. Cuts through Figure 4 at times 0, 1, ... , 4 fs. The hole density is plotted against the molecular axis x at fixed times. The hole charge migrates in ∼4 fs from the left-hand side to the right-hand side of the molecule. Note that the hole density remains very small at all times in the vicinity of the peptide bond.

the *N*-methyl group—on the opposite side of the acetyl group of the molecule. At these times, the natural charge orbital matches essentially the 14a′ orbital. This molecular orbital overlaps by nearly 90% with the hole charge at $t = 4.2$ fs. In other words, the hole charge has migrated in 4.2 fs from the “left”-hand side of the peptide bond to the “right”-hand side of the peptide bond. After 8.4 fs, the hole charge has mainly returned to the oxygen atom and the acetyl-C atoms. At that time, the natural charge orbital matches essentially the 13a′ orbital again. This is a very effective and ultrafast mechanism of charge migration over a peptide bond.

To illustrate this ultrafast migration of charge in *N*-methyl acetamide, the hole density, $Q(x, t)$, is shown in Figure 4. The hole density, $Q(x, t)$, at a point along an axis, x, through the molecule is obtained by integrating the hole occupations in the plane perpendicular to the axis x. The axis through the molecule in Figure 4 was chosen along the longest spatial extension of the molecule in its ground state and is called the “molecular axis” in the following. For convenience, the positions of the atoms along the molecular axis are indicated in Figure 4. That figure shows the bold maxima of the hole density at times $t = 0$, $t \approx 4.2$ fs, and $t \approx 8.4$ fs. These maxima are situated on different sides of the molecule. Figure 5 shows cuts through the 3D presentation at different times. These cuts make it more obvious that the hole occupation numbers in the region of the peptide bond remain very small at all times. Thus, the hole charge in a way “jumps” from one side of the molecule to the other.

B. Analysis of Results. We described an ultrafast charge migration following ionization in *N*-methyl acetamide in the

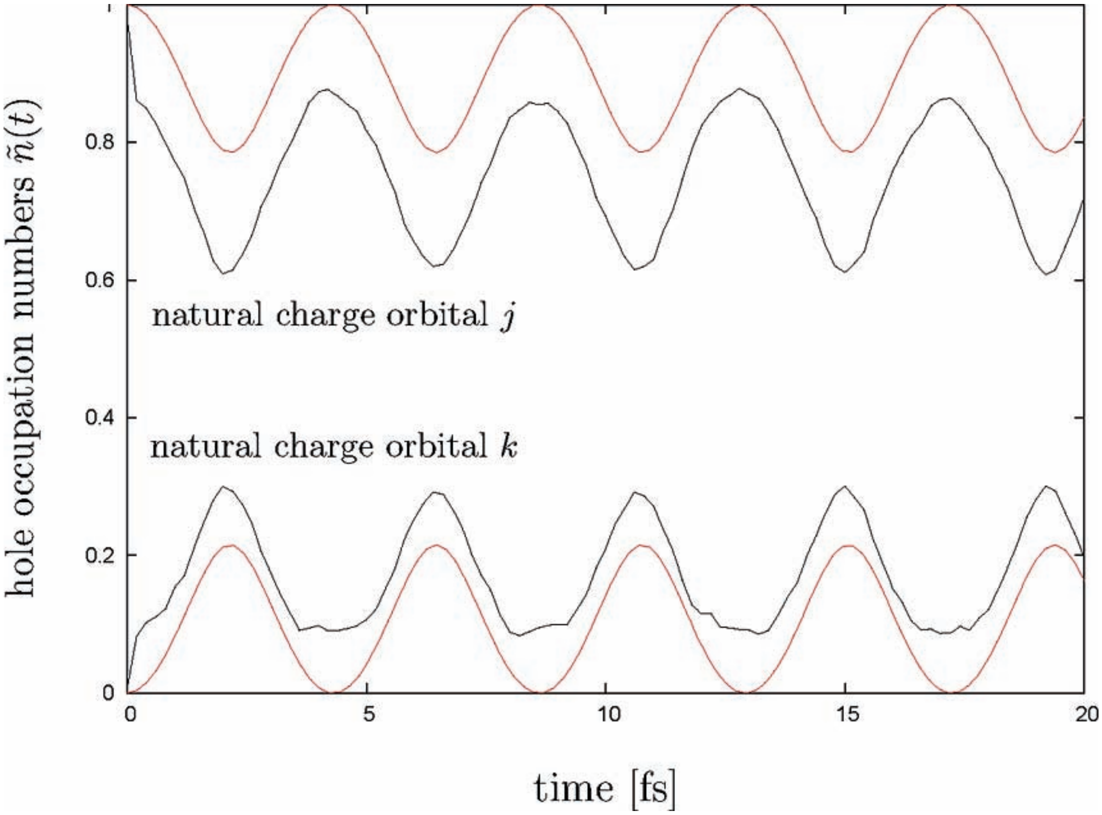

Figure 6. Hole occupation numbers (black curves), $\tilde{n}(t)$, of the two involved natural charge orbitals. At time $t = 0$, the 13a′ orbital of the molecule *N*-methyl acetamide was ionized. The red curves result from the analytical expressions in eq 3, where only two 1h states are considered.

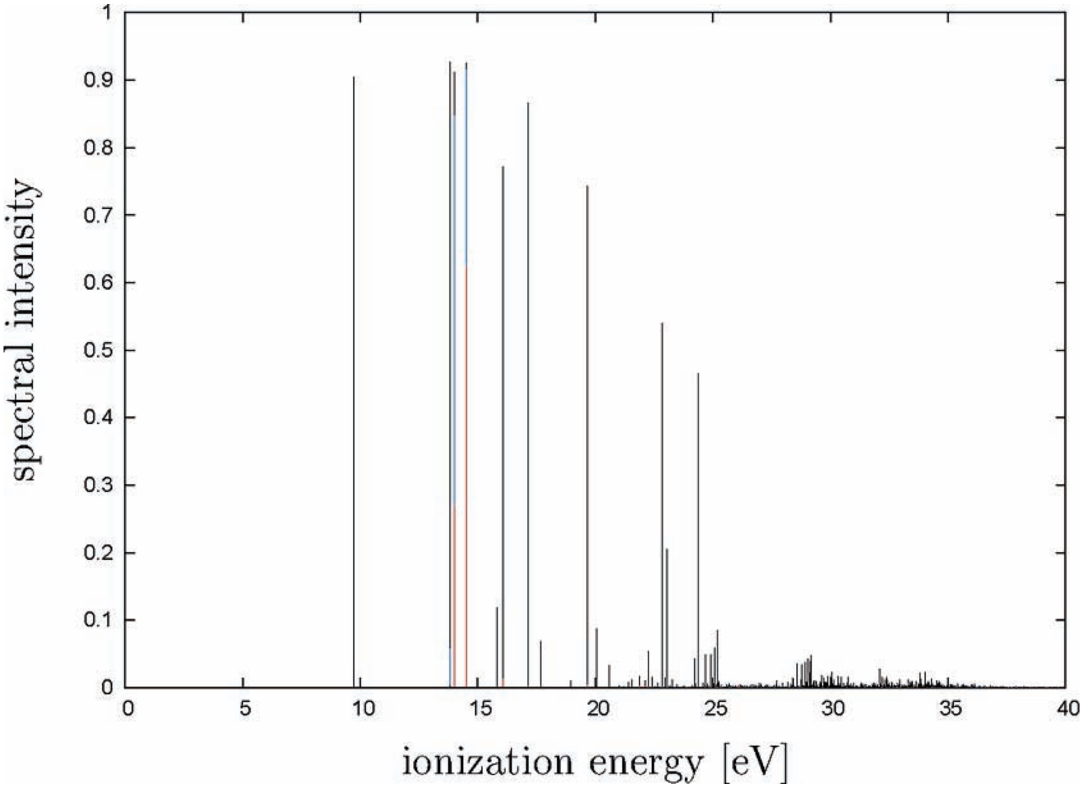

Figure 7. Ionization spectrum belonging to the irreducible representation a′ of *N*-methyl acetamide. The red colored lines correspond to the ionization out of the 13a′ orbital. The blue lines correspond to the ionization out of the 14a′ orbital. Note that the intensities of the two lines just below 15 eV are essentially a sum of two contributions, which are the intensities belonging to the ionization out of the 13a′ and 14a′ molecular orbitals.

previous section. To explain the time scale of the process and determine the underlying mechanism of the charge migration, we now consider the hole occupation numbers, $\tilde{n}(t)$. Figure 6 shows the hole occupation numbers, $\tilde{n}(t)$, of the two involved natural charge orbitals as a function of time (black curves). The natural charge orbital j where the initial hole charge has been created is at time $t = 0$ identical to the 13a′ molecular orbital, and the natural charge orbital k at time $t = 0$ is identical to the 14a′ molecular orbital. As can be seen, the hole occupation numbers oscillate in time and $\tilde{n}_j(t)$ is always substantially larger than $\tilde{n}_k(t)$. The natural charge orbitals themselves also vary strongly in time. At time $t = 4.2$ fs when the hole occupation, $\tilde{n}_j(t)$, reaches a maximum of nearly 0.9, the role of the original orbitals in the natural charge orbitals is swapped: Now, j is mainly the 14a′ orbital and the natural charge orbital k looks very much similar to the 13a′ molecular orbital. That means, nearly 90% of the hole charge has migrated out of the 13a′ orbital and into the 14a′ orbital in just 4.2 fs. The 13a′ molecular orbital is situated at one end of the molecule. Since the spatial distribution of the other involved molecular orbital, 14a′, is such that it is situated on the other side of the molecule, a migration of the charge in 4.2 fs from one end of the molecule to the other has taken place.

The black curves in Figure 6 resemble strongly the analytical plot (red curves) derived for a hole mixing situation, according to eq 3. The main difference between the ab initio numerical result and the analytical plot is that the former shows an extremely fast response on an attosecond (10^{-18} s) time scale; see Breidbach et al.[20] for details. To see whether a mixing of two 1h states indeed occurs in the full ab initio calculations, we look at the ionization spectrum, Figure 7, which belongs to the irreducible representation a′. Lines resulting from the ionization out of the 13a′ orbital are marked red in the spectrum. More precisely, the weights of the $(13a')^{-1}$ 1h configuration in each cationic state are marked red in Figure 7. The blue lines correspond to the ionization out of the 14a′ orbital. There are two lines with strong spectral intensity around 14 eV in Figure 7. The spectral intensities of these two lines belong to the 1h configurations $(13a')^{-1}$ and $(14a')^{-1}$. Both 1h configurations are spread over the same two lines in the spectrum. This is a typical case of hole mixing. The energetic gap between these two lines is 0.48 eV. An oscillation with the period $T = 2\pi/\omega = 8.6$ fs is expected in agreement with the results described further above. Taking only these two lines into account, we analytically obtain the red curves in Figure 6. Thus, the ultrafast migration of charge in *N*-methyl acetamide following ionization investigated in this work is due to the mixing of two 1h states.

IV. Summary

Charge transfer is of enormous importance for various effects, for example, in biophysics and in molecular electronics. Typical examples are photosynthesis,[1−3] the reactions involving proteins, or within the scope of molecular electronics the conductivity of large molecules.[4−6]

We searched for a valence orbital localized at a specific site of the molecule *N*-methyl acetamide. The molecule *N*-methyl acetamide consists of a peptide bond and two methyl groups (see Figure 1). In fact, we found that the 13a′ orbital is mainly concentrated at a specific site, namely, at one end of the molecule. Is it possible that after ionization of this orbital the initial hole charge migrates through the system, say, to the other end of the molecule? To investigate charge migration following ionization in the molecular system *N*-methyl acetamide, a newly developed ab initio method called charge migration analysis (CMA) was applied.[8−10] The CMA method aims in the long run at the investigation of charge migration in larger molecular systems such as oligopeptides. This represents a first step toward the analysis of charge migration in biophysically relevant systems.

After ionization out of the molecular orbital 13a′, the results of the CMA presented here predict an effective, ultrafast charge migration from one end, say A, of the molecule to the other, say B. Within ∼4.2 fs, nearly 90% of the hole charge has migrated from one end of the molecule to the other. Within this process, the hole density in the vicinity of the peptide bond remains very small at all times.

We found that an efficient ultrafast charge migration due to electron correlation is involved. The mechanism of charge migration is due to the mixing of two 1h states. These results could inspire future charge transfer analyses to figure out conditions under which efficient charge migration occurs. Considering the dynamics of the nuclei could in this case additionally lead to the hole charge not oscillating back to A but possibly remaining at site B. Furthermore, the efficient ultrafast migration of charge over one or more peptide bonds might also occur in larger molecules such as oligopeptides.

It would be of high interest to compare our results of charge migration following ionization with experiments. On one hand, efforts could be made to augment experiments in relatively large molecules such as those of Weinkauf et al.[15,16] by aiming at a time resolution on a femtosecond scale. On the other hand, the experimental investigation of the explicit charge migration in smaller molecules, such as *N*-methyl acetamide, for instance, would also be very attractive.

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