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Attosecond Charge Migration Can Break Electron Symmetry While Conserving Nuclear Symmetry

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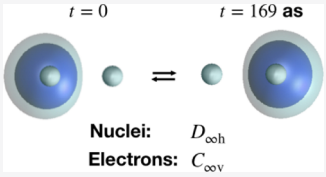
ABSTRACT: Charge migration moves electrons from one molecular site to another, in a typical time domain from few hundred attoseconds to few femtoseconds. On this timescale, the nuclei stand practically still, implying that the nuclear point group symmetry is conserved. Because electrons move ultrafast, this can lead to a surprising effect, namely, breaking the spatial symmetry of the electron density in spite of the conservation of nuclear framework symmetry. We demonstrate theoretically that attosecond charge migration achieves this electron symmetry breaking if the electrons are prepared in a coherent superposition of nondegenerate electronic ground and excited states which transform according to different irreducible representations. Two simple examples provide a proof-of-principle, namely, periodic attosecond charge migration in the $\sigma_g + \sigma_u$ superposition state of the aligned H_2^+ cation (nuclear point group $D_{\infty h}$, but electron symmetry breaking $D_{\infty h} \rightarrow C_{\infty v}$) and in the $A_1 + B_2$ superposition state of the oriented H_2O molecule (C_{2v} vs $C_{2v} \rightarrow C_s$).



■ INTRODUCTION

Progress in ultrafast spectroscopy and quantum reaction dynamics has advanced to the forefront of investigations of the fastest processes in molecules from femtochemistry[1] to attochemistry.[2,3] A fascinating effect at the border between femtochemistry and attochemistry is charge migration—this is a purely quantum mechanical process which moves the electronic charge from one molecular site to another, on typical timescales from a few hundred attoseconds (this is why it may be called "attosecond charge migration") to a few femtoseconds; for pioneering work and recent literature surveys, see refs.[4−12] Note that the "charge migration" is a generic term, which means, in general, the ultrafast shift of part of the electronic density from one molecular site to another, and this comprises many different mechanisms, for example, in linear molecules such as $HCCI^+$[12−14] or the present H_2^+, it may describe the shift of charge from one molecular end to the opposite one. In ring-shaped molecules, it may describe charge circulation[9,10,15] or the breathing of electronic charges in ring-shaped or linear molecules.[16−18] A recent milestone is the first joint experimental and theoretical reconstruction of charge migration in an oriented linear molecular cation.[12−14] Attosecond charge migration is important because it may induce subsequent processes, such as site-selective bond breaking,[5] or affect the cosmologic distribution of isotopes.[19]

Here, we point to an intuitive effect which is inherent in many examples of attosecond charge migration, but has escaped the general attention, see, for example, refs 20−25: breaking the spatial symmetry of the electron density in spite of nuclear framework symmetry conservation. Nuclear framework symmetry is conserved because the nuclei stand practically still during attosecond charge migration. Meanwhile, the symmetry of the ultrafast electronic system can be broken as follows: The symmetry of the electronic system in the nondegenerate molecular ground state Ψ_g is identical to the nuclear framework symmetry $\mathcal{G}$. If the ground state is superposed with an excited state Ψ_e to form a superposition state Ψ that represents charge migration and that does not transform according to a one-dimensional representation of $\mathcal{G}$, then the symmetry of the initial electron density is reduced. The electron symmetry in the state Ψ is determined by the maximal subgroup of $\mathcal{G}$, in which Ψ transforms according to a one-dimensional representation.

■ MODELS AND METHODS

As a proof-of-principle, the effect is demonstrated for the aligned H_2^+ cation and the oriented H_2O molecule. The nuclear configurations belong to the molecular point groups $D_{\infty h}$ and C_{2v}, respectively. Textbooks suggest that the electronic states should be labeled according to the irreducible representations of the same groups. In contrast, attosecond charge migration may transiently reduce the electron symmetry group down to $C_{\infty v}$ and C_s, respectively. Electron symmetry breaking is demonstrated by means of quantum dynamic simulations of attosecond charge migration in the model systems, based on quantum chemistry calculations of the

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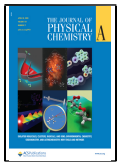

electronic eigenstates Ψ_g and Ψ_e and their energies E_g and E_e. For this purpose, we adapt experimentally and theoretically established methods.[12−14] Accordingly, the model systems H_2^+ and H_2O are aligned or oriented with their principle axes along the laboratory z-axis; the H_2O molecule is in the yz-plane. We assume that the nuclei remain fixed in the $D_{\infty h}$ and C_{2v} geometries of their ground states.

The electrons are prepared in superposition states $\Psi(t)$ of two nondegenerate electronic eigenstates, Ψ_g and Ψ_e, where Ψ_e corresponds to the dominant singlet excitation of Ψ_g. Without loss of generality, we assume equal contributions for both states. The literature on charge migration has many examples of time-dependent two-state superposition states which lend themselves to rather easy derivations of fundamental effects.[8−14,16,20,21,25−28] For example, the first joint experimental and theoretical reconstruction of charge migration was carried out by the experimental preparation of a two-state superposition state of the cation $HCCI^+$, which could then be used to facilitate the theoretical analysis.[12−14] Another example is the derivation of schemes for ultrafast laser control of charge migration, starting from simple two-state superposition scenarios which could then serve as a platform for extensions to the laser control of multistate superposition states.[26−28] Likewise, our derivation of the effect of electron symmetry reduction starts out from the representations by two-state "$\Psi_g + \Psi_e$" superposition states, but in the Conclusions section, we shall point to extensions to multiple state superposition states. The time evolution of these states is given by[12−14] $\Psi(t) = \sqrt{1/2}[\exp(-iE_g t/\hbar)\Psi_g + \exp(-iE_e t/\hbar)\Psi_e]$, with $\hbar$ being the reduced Planck constant. The corresponding densities $\rho(t) = |\Psi(t)|^2$ are periodic with period $T = 2\pi\hbar/(E_e - E_g)$. Below, we shall consider illuminating snapshots of the densities, namely, $\rho(t) = \rho^+ \equiv (1/2)|\Psi_g + \Psi_e|^2$ at $t = 0, T, \ldots$ and $\rho(t) = \rho^- \equiv (1/2)|\Psi_g - \Psi_e|^2$ at $t = T/2, 3T/2, \ldots$. For reference, the densities of the electronic ground and excited states are $\rho_g = |\Psi_g|^2$ and $\rho_e = |\Psi_e|^2$. These all-electron densities yield the corresponding one-electron densities (denoted by subscript "1e") by integration over the coordinates of all electrons but one, and by summing over all electron spins. An important difference with the scenario of refs 12−14, in which the electronic eigenfunctions Ψ_g and Ψ_e have the same irreducible representations $IRREP_g = IRREP_e$, is that $IRREP_g \neq IRREP_e$ in the present applications.

The electronic structure of H_2^+ and H_2O is calculated at the TD-CAM-B3LYP/def2-TZVPP level of theory, as implemented in Gaussian16.[29] The H_2^+ bond length is 1.057 Å. For water, the OH bond lengths are 0.965 Å at a bond angle of 102.8°. For H_2^+, $E_e - E_g = 12.25$ eV. For H_2O, $E_e - E_g = 11.95$ eV. The respective ground states are represented as single reference Slater determinants. The excited states are represented as a linear combination of singlet excited configuration state functions, combined according to the expansion coefficients obtained from linear response time-dependent density functional theory (LR-TDDFT). The choice of the CAM-B3LYP functional is found to give accurate excitation energies.[30] On the other hand, the associated wave functions have a simple structure at the LR-TDDFT level of theory. The coefficients of excited state configurations are directly extracted from the output of the quantum chemistry package using ORBKIT.[31−33] The pseudowave function coefficients obtained are truncated below some threshold, and the many-electron states are then re-normalized prior to postprocessing using ORBKIT. Electronic densities are plotted using VMD.[34] More details on the hybrid time-dependent density functional theory/configuration interaction method can be found in refs 33 and 35.

■ RESULTS AND DISCUSSION

Let us consider first the attosecond charge migration in aligned H_2^+ prepared in the superposition of its ground ($\Psi_g = \sigma_g$) and first excited ($\Psi_e = \sigma_u$) electronic states, with irreducible representations Σ_g^+ and Σ_u^+, respectively. Figure 1 shows the

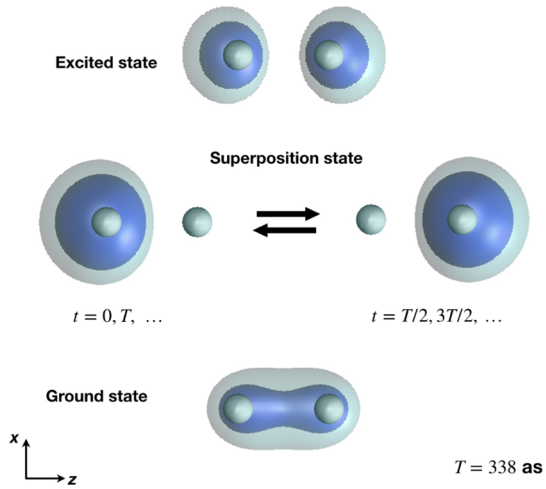

Figure 1. Electron density symmetry breaking $D_{\infty h} \rightarrow C_{\infty v}$ during attosecond charge migration in the $\sigma_g + \sigma_u$ superposition state of aligned H_2^+ with the nuclei fixed in $D_{\infty h}$ symmetry. Middle panels: Contour plots of alternating electron densities ρ^+ and ρ^- ($C_{\infty v}$) at $t = 0, T/2, T, 3T/2, \ldots$ ($T = 338$ as). Lower and upper panels: Electron densities ρ_g and ρ_e of the electronic ground (σ_g) and excited (σ_u) states ($D_{\infty h}$). The contours are at $\rho = 0.06$ and $0.03\ a_0^{-3}$. The nuclei conserve the $D_{\infty h}$ symmetry, illustrated as balls.

corresponding electron densities ρ_g and ρ_e, together with the alternating snapshots ρ^+ and ρ^- of the time-dependent density $\rho(t)$ at times $t = 0, T, \ldots$ and $t = T/2, 3T/2, \ldots$, respectively. Apparently, the electron moves periodically from one proton to the other, and back, with period $T = 338$ as. This phenomenon was predicted in 1944 in Eyring, Walter and Kimball's textbook on Quantum Chemistry;[4] since then, attosecond charge migration in H_2^+ has been investigated in depth,[8,16,36−41] but without noting explicitly the reduction of the electron symmetry from the nuclear point group to a subgroup. The snapshots ρ^+ and ρ^-, however, clearly show that the $D_{\infty h}$ symmetry of the electronic densities of eigenstates σ_g, σ_u is broken to $C_{\infty v}$ during attosecond charge migration in the $\sigma_g + \sigma_u$ superposition state.

The result shown in Figure 1 is confirmed in the frame of molecular point group theory: Consider the $D_{\infty h}$ character table for H_2^+, cf. Table 1. All characters of the electronic ground state $\Psi_g = \sigma_g$ with $IRREP_g = \Sigma_g^+$ are equal to 1, whereas the excited state $\Psi_e = \sigma_u$ with $IRREP_e = \Sigma_u^+$ has characters 1 and −1. In order to determine the transformation

Table 1. Selected Part of the Character Table for $D_{\infty h}$

$D_{\infty h}$	E	$2C_\infty$	$\infty\sigma_v$	i	$2S_\infty$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_u^+	1	1	1	−1	−1	−1

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behavior of the $\sigma_g + \sigma_u$ superposition state, we note that it must be assigned to one and only one IRREP. The corresponding symmetry operations on both σ_g and σ_u must, therefore, yield the same characters. That means, these characters must be equal to 1. This condition does not hold for all the symmetry operations of the molecular point group $D_{\infty h}$. It is satisfied, however, for the subset $\{E, 2C_\infty, \infty\sigma_v\}$. This defines the molecular point subgroup $C_{\infty v}$ of $D_{\infty h}$, cf. Table 2. In summary, attosecond charge migration in the $\sigma_g + \sigma_u$ superposition state of H_2^+ reduces the symmetry group $D_{\infty h}$ of the electronic eigenstates σ_g and σ_u to $C_{\infty v}$. Its IRREP in $C_{\infty v}$ is Σ^+.

Table 2. Selected Part of the Character Table for $C_{\infty v}$

$C_{\infty v}$	E	$2C_\infty$	$\infty\sigma_v$
Σ^+	1	1	1

Our second example is for attosecond charge migration in the oriented H_2O molecule, prepared in the superposition of the ground state Ψ_g with $IRREP_g = A_1$ and the lowest-lying excited bound state Ψ_e with $IRREP_e = B_2$, corresponding predominantly (98%) to the $3a_1 \rightarrow 2b_2$ excitation. The derivation of electron symmetry breaking in the $A_1 + B_2$ superposition state is analogous to the first example: Figure 2 shows the corresponding one-electron densities $\rho_{1e,g}$ and $\rho_{1e,e}$, together with the alternating snapshots ρ_{1e}^+ and ρ_{1e}^- of the time-dependent density $\rho_{1e}(t)$ of the $\Psi_g + \Psi_e$ superposition state at times $t = 0, T, \ldots$ and $t = T/2, 3T/2, \ldots$, respectively, with $T = 346$ as. As in the case of H_2^+, the one-electron density moves periodically between two molecular sites neighboring the opposite protons. In the case of H_2O, the charge migration is, however, less obvious than for H_2^+ because the number of electrons which participates in charge migration in H_2O is small ($\approx$1) compared to the total number of electrons (=10). As a consequence, the time-dependent one-electron density $\rho_{1e}(t)$ appears to be rather robust. Nonetheless, the snapshots ρ_{1e}^+ and ρ_{1e}^- clearly show that attosecond charge migration in the $A_1 + B_2$ superposition state of H_2O breaks the electron symmetry C_{2v} down to C_s.

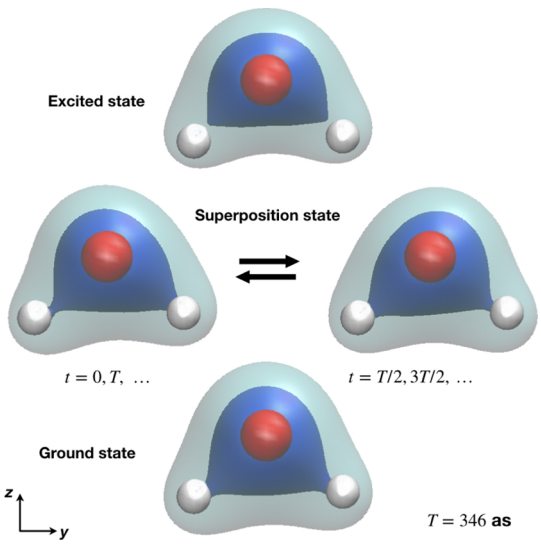

Figure 2. Electron density symmetry breaking $C_{2v} \rightarrow C_s$ during attosecond charge migration in the $A_1 + B_2$ superposition state of oriented H_2O (T = 346 as). Middle panel: Contour plots of alternating electron densities ρ_{1e}^+ and ρ_{1e}^- (C_s) at $t = 0, T/2, T, 3T/2, \ldots$ (T = 346 as). Lower and upper panels: Electron densities ρ_g and ρ_e of the electronic ground (A_1) and excited (B_2) states (C_{2v}). The contours of the corresponding one-electron densities are at ρ_{1e} = 0.325 and 0.06 a_0^{-3}. The nuclei conserve the C_{2v} symmetry and are illustrated as balls.

The result shown in Figure 2 is explained in the frame of molecular point group theory, analogous to the previous derivation: Consider the character table for C_{2v}, cf. Table 3. All the characters of the electronic ground state Ψ_g with $IRREP_g = A_1$ are equal to 1, whereas the excited state Ψ_e with $IRREP_e = B_2$ has characters 1 and −1. During attosecond charge migration, the transformation behavior of the $A_1 + B_2$ superposition state must lead to the same characters for all symmetry operations, that is, the characters must be equal to 1. This condition is satisfied for just the subset $\{E, \sigma_{yz}\}$, which establishes the molecular point subgroup C_s, cf. Table 4. As a result, attosecond charge migration in the $A_1 + B_2$ superposition state of H_2O conserves nuclear C_{2v} symmetry, but breaks the electron symmetry group down to C_s.

Table 3. Selected Part of the Character Table for C_{2v}

C_{2v}	E	C_2	$\sigma = \sigma_{xz}$	$\sigma' = \sigma_{yz}$
A_1	1	1	1	1
B_2	1	−1	−1	1

Table 4. Selected Part of the Character Table for C_s

C_s	E	$\sigma = \sigma_{yz}$
A'	1	1

■ CONCLUSIONS

In conclusion, we have presented two examples serving as a proof-of-principle for the effect of electron symmetry breaking during attosecond charge migration with conserved nuclear symmetry. By extrapolation, they establish a simple, general, and novel rule and method: Attosecond charge migration in superposition states of two or more electronic eigenstates of aligned or oriented molecules or molecular ions with two or more different IRREPs reduces the electron symmetry down to a molecular point subgroup. We emphasize that the occurrence of different IRREPs is essential here; in contrast, charge migration may also be represented by a superposition state of two or more electronic eigenstates with the same IRREP, see, for example, refs 12, 14, and 16. These superposition states may well describe the ultrafast changes in the electronic density, with corresponding very rapid shifts of part of the density from one molecular site to another, typically in the attosecond time domain, but those changes do not break the electron symmetry. For the given set of different IRREPs, the subgroup of the reduced electron symmetry consists only of the subset of symmetry operations, which yield the same characters. For the usual case where the superposition state includes the totally symmetric electronic ground state, these characters are equal to 1. This extrapolation is obvious for attosecond charge migration in the superposition of electronic states with one-dimensional (1D) IRREPs, cf. Tables 1−4. It should also hold for applications involving 2D or 3D IRREPs, for example, benzene[11,15,18,42,43] or Mg-porphyrin;[9] explicit derivations will be published elsewhere. The novel rule is

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significant because it is well known that the electron symmetry may have an enormous effect on the reaction dynamics, see, for example, the Woodward−Hoffmann rules.[44] It is therefore easy to predict that the present rule for electron symmetry reduction should have significant effects on sequel reactions which are triggered by charge migration, for example, site-selective bond breaking, as discovered in ref 5.

As an outlook to longer time domains, charge migration is just a transient ultrashort phenomenon which may trigger subsequent processes but disappears because of decoherence by nuclear motions.[15,18,38,45−51] The consequences depend on the molecular system. For example, in the case of H_2^+, nuclear motions cause dissociation of the σ_u contribution to the $\sigma_g + \sigma_u$ superposition state, whereas the σ_g partial wave remains bound.[38] In this case, the nuclei conserve the $D_{\infty h}$ symmetry, and the electronic $D_{\infty h} \rightarrow C_{\infty v}$ symmetry breaking is a transient phenomenon during attosecond charge migration.[38] The effect could be monitored by attosecond photoionization of the coherently coupled states,[52] by time-resolved measurements of the asymmetries in photoelectron angular distributions,[16] by high harmonic spectroscopy which allows attosecond time resolution and is sensitive to symmetry,[53−56] or by exploring electron migration dynamics by electron diffraction with ultrashort X-ray pulses.[57−61]

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Notes

The authors declare no competing financial interest.

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