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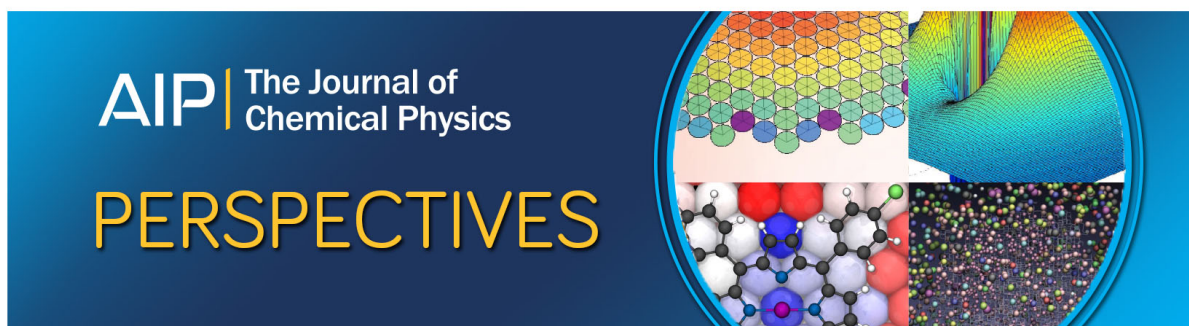
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Communication: Electronic flux induced by crossing the transition state

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We present a new effect of chemical reactions, e.g., isomerizations, that occurs when the reactants pass along the transition state, on the way to products. It is based on the well-known fact that at the transition state, the electronic structure of one isomer changes to the other. We discover that this switch of electronic structure causes a strong electronic flux that is well distinguishable from the usual flux of electrons that travel with the nuclei. As a simple but clear example, the effect is demonstrated here for bond length isomerization of Na₂ ($2^1\Sigma_u^+$), with adiabatic crossing the barrier between the inner and outer wells of the double minimum potential that support different “Rydberg” and “ionic” type electronic structures, respectively. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5018236>

Intramolecular fluxes, in particular, electronic fluxes play a key role in unraveling the details of molecular reaction dynamics.^{1,2} Here we discover a new mechanism of intramolecular electronic flux during chemical reactions, e.g., isomerizations. It occurs when reactants cross the transition state on the way to products. The different isomers are supported by wells of the potential energy surface that are separated from each other by transition states. The electronic structures at the potential wells may differ from each other, e.g., covalent or ionic. Crossing the transition state adiabatically from one potential well to the other thus induces a change of electronic structure. This causes a special intramolecular electronic flux that is well distinguishable from the flux of electrons that travel with the nuclei. Alternative mechanisms that have been described in the literature include electronic fluxes induced by non-adiabatic transitions,^{3,4} the flux of valence electrons that travel with the nuclei^{5,6} or in oblique directions,² or electronic flux during charge migration;^{7,8} see also Refs. 9–12.

As an example, we consider bond length isomerization of Na₂ ($2^1\Sigma_u^+$) by adiabatic barrier crossing in its double minimum potential. Here the inner and outer potential wells at short and long internuclear distances support different “Rydberg” and “ionic” electronic structures. For convenience, we use the same assignments as suggested in Ref. 13 and adapted in Refs. 14–19, but with quotation marks in recognition of the discussion in Ref. 20. Adiabatic barrier crossing in Na₂ ($2^1\Sigma_u^+$) has been observed by means of femtosecond pump-probe spectroscopy, with impressive complementary quantum dynamics simulations.^{14,17–19} “Adiabaticity” here means that there are no transitions to neighbouring electronic states, on the femtosecond (fs) to picosecond (ps) time scale

of the experiment. Important consequences of the switch from “Rydberg” to “ionic” structures have already been predicted by Arasaki *et al.*,^{15,16} i.e., the switch causes significant changes of the transition dipole matrix elements so that photoionizations from the inner or outer potential wells yield different energy and angle resolved photoelectron spectra with femtosecond resolution. These predictions stimulated joint experimental and theoretical investigations that confirmed the rather strong variations of the transition dipole matrix elements.¹⁷ Here we discover the consequences for the electronic fluxes.

We employ the Symmetry-Adapted-Cluster Configuration Interaction (SAC-CI) method²¹ with aug-cc-pVTZ basis set²² for the *ab initio* calculations of the electronic properties of Na₂ ($2^1\Sigma_u^+$). The resulting double minimum potential agrees well with the experimental result.²⁰ The quantum dynamical methods for evaluations of the time propagations of the radial nuclear density ρ_n and electronic flux j_e are adapted from Ref. 23, assuming that the systems vibrate without any rotation (rotational quantum numbers $JM = 00$). In this case, the three-dimensional (3D) electronic flux has only one component, namely, the radial $j_e(r, t)$, where r is the distance of the electron from the nuclear center of mass (NCM). The angular components vanish. With the standard one-electron density $\rho_e(\mathbf{r}, t) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \int d\mathbf{R} \Psi^*(\mathbf{r}_1 \cdots \mathbf{r}_N, \mathbf{R}, t) \Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, \mathbf{R}, t)|_{\mathbf{r}_1=\mathbf{r}}$ we obtain the radial electron density by integrating over the two angles $\rho_e(r, t) = \int \rho_e(\mathbf{r}, t) d\Omega$. The continuity equation relates $j_e(r, t)$ to the radial electron density^{2,23}

$$j_e(r, t) = -r^{-2} \int_0^r dr' r'^2 \frac{\partial \rho_e(r', t)}{\partial t}. \quad (1)$$

Separate applications of Eq. (1) to the one-electron densities of the core and valence electrons yield the corresponding fluxes of the core and valence electrons.² Below we center attention on the radial component of the electronic flux $j_e(r, t)$ of the two

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valence electrons of Na_2 . Details of the *ab initio* results and analysis as well as the extension of the quantum dynamical methods from the one-electron²³ to the present multi-electron systems will be published elsewhere.

The double minimum potential of Na_2 ($2^1\Sigma_u^+$) is illustrated in Fig. 1(a). Also shown are snapshots of the radial nuclear density ρ_n travelling from the inner wall (0 fs) via the minimum of the inner potential well (64 fs) to the barrier (160 fs) and then to the minimum (316 fs) and the outer wall of the outer well (540 fs); the initial state ($t = 0$ fs) is generated from the ground state by means of a pump laser pulse (wavelength: $\lambda = 340$ nm, duration: 35 fs) adapted from Ref. 18. The complete adiabatic time evolution of ρ_n during one vibrational period is documented in Fig. 2(a). Figure 2(b) shows the resulting radial electronic flux j_e . Apparently, it consists of two contributions: (i) the flux of the electrons that travel with the nuclei, essentially parallel to the time evolution of ρ_n ; (ii) the novel transient electronic flux that rises and decays during the short time windows when the molecule crosses the barrier. The fluxes (i) and (ii) are clearly distinct from each other—in fact they are oppositely directed.

In order to understand the origin of the traditional (i) and the novel (ii) electronic fluxes, it is helpful to consider the underlying switch of the electronic structure of Na_2 ($2^1\Sigma_u^+$) from the domain of the inner potential well via the barrier to the outer potential well. This is illustrated by the one-electron densities at the corresponding inter-nuclear distance in

Figs. 1(b)–1(d), respectively. All densities have $D_{\infty h}$ symmetry, with two equivalent peaks at the nuclei. For short bond lengths, the double-peaked density is embraced by contours that illustrate molecular compactness. For long distances, the electron density consists of two individual peaks centered at the nuclei, indicating the separation of the Na atoms. When the internuclear distance increases from small to large distances, the two centers of the electron density move with the two nuclei, causing electron flux (i) that flows with the nuclei, as illustrated in the lower part of Fig. 2(b). Very importantly, the electron density at the inner well has two additional outer lobes at rather large distances from the nuclei, cf. Fig. 1(b): They may be considered as signatures of the Rydberg electronic structure; the ionic structure at the outer potential well [Fig. 1(d)] does not possess these “Rydberg lobes.” The electron density at the transition state [Fig. 1(c)] illustrates the disappearance of the outer lobes as the molecule stretches from the inner to the outer potential wells: Apparently, the “Rydberg lobes” move inward, from far to short distances, whereas the nuclei move outward, from the inner to the outer potential wells, until the lobes are “eaten up” by the peaks of the electron density at the nuclei at the transition state. This motion and disappearance of the “Rydberg lobes” causes the novel electronic flux (ii), in opposite direction to flux (i) of the electrons that travel with the nuclei, cf. Fig. 2(b).

We emphasize that the new phenomenon of the electronic flux (ii) due to reconstruction of the electronic structure at the

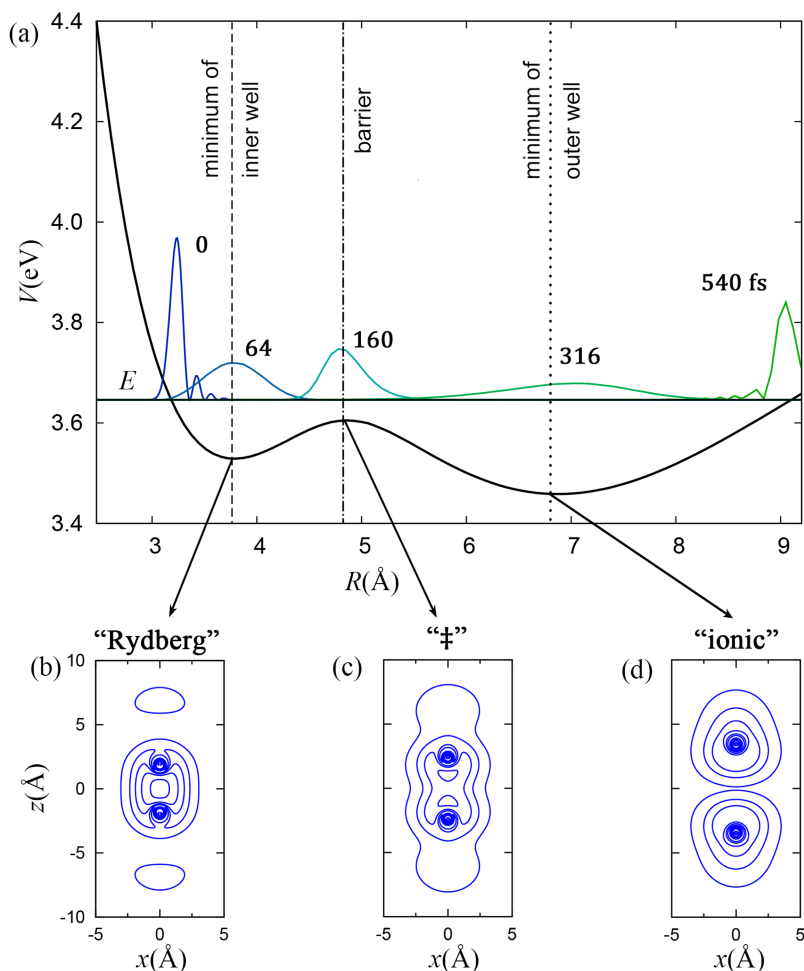


FIG. 1. (a) Double minimum potential of Na_2 ($2^1\Sigma_u^+$) versus internuclear distance R , with five snapshots of the nuclear density $\rho_n(R, t)$ illustrating its time evolution from the inner well via the transition state to the outer well. The initial state ($t = 0$ fs) with mean energy E (indicated by the horizontal line) is adapted from Ref. 18. [(b)–(d)] One-electron density for the valence electrons at the minimum of the inner potential well (“Rydberg,” $R = 3.8$ Å), at the transition state (“‡,” $R = 4.9$ Å), and at the minimum of the outer potential well (“ionic,” $R = 6.9$ Å), illustrated by equidistant contours in the x - z plane. Zero density contours are at infinity, i.e., the one-electron density of the valence electrons is positive everywhere, without any nodes.

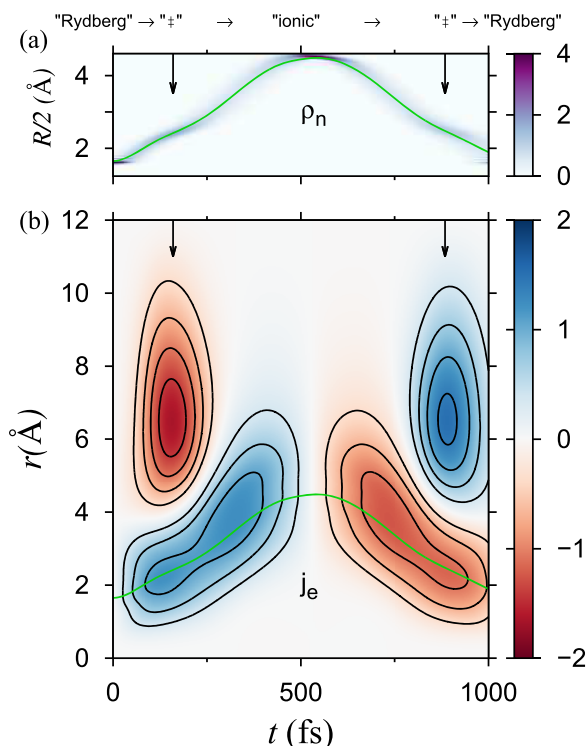


FIG. 2. (a) Time evolution of the nuclear density $\rho_n(R/2, t)$ of Na_2 ($2^1\Sigma_u^+$) versus the distance $R/2$ of the nuclei from the nuclear center of mass (NCM) compared with the snapshots shown in Fig. 1(a) (color code in unit of $1/\text{\AA}$). The initial state ($t = 0$ fs) is generated from the ground state by means of a pump laser pulse with wavelength $\lambda = 340$ nm and 35 fs duration. The time evolution of the mean distance $\langle R/2 \rangle$ is indicated by the continuous green line. (b) Time evolution of the valence electronic flux $j_e(r, t)$ depending on the distance r of the electron from the NCM, illustrated by equidistant equiflux contours and color codes (in units of $1/\text{ps}$). The branch of $j_e(r, t)$ at short distances r represents (i) the electrons that travel with the nuclei along their mean positions $\langle R/2 \rangle$ which is indicated by the continuous green line, adapted from panel (a). The other two, even stronger transient parts (ii) of $j_e(r, t)$ at larger values of r are induced by the changes of the electronic structure (“Rydberg” \rightarrow “ionic” and back, “ionic” \rightarrow “Rydberg”) at the transition state “ \ddagger .” Note that the two distinct parts (i) and (ii) of $j_e(r, t)$ flow in opposite directions.

transition state is clearly distinct from the electronic flux (i) that travels with the nuclei that are reflected from the barrier. This is documented in Fig. 3 which shows results analogous to Fig. 2, except that the initial state is prepared by a laser pulse with a longer wavelength ($\lambda = 346$ nm) such that the mean energy is just below the potential barrier. As a consequence, the nuclear density bifurcates at the potential barrier into partial waves that are reflected and transmitted. The corresponding part of the electronic flux (i) that travels with the reflected nuclei evolves in the domain $r < 4$ Å, whereas the electronic flux (ii) due to reconstruction of the electronic structure at the transition state evolves in the domain $r > 4$ Å. Figure 3 shows that flux (ii) appears whenever the system approaches or leaves the transition state.

Figure 2(b) shows that the maximum of the flux due to change of electronic structure (ii) is even stronger than the electronic flux (i) that travels with the nuclei. On a first glance, this is surprising because the maximum electron density of the “Rydberg lobes” that causes flux (ii) is much smaller than the peaks that dominate flux (i). The apparent paradox is resolved with the help of a classical analog, i.e., the

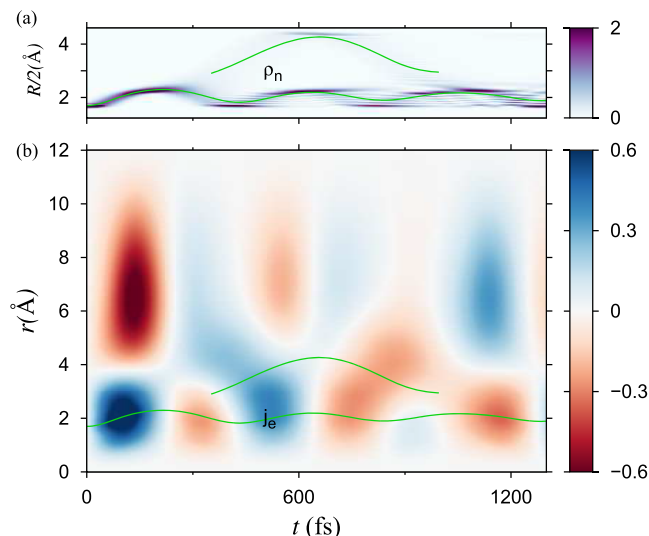


FIG. 3. Nuclear density $\rho_n(R/2, t)$ (a) and valence electronic flux $j_e(r, t)$ (b), analogous to Fig. 2 but for a pump laser pulse with longer wavelength $\lambda = 346$ nm and 35 fs duration. The long and short continuous green lines illustrate the mean distances $\langle R(t)/2 \rangle_i$ and $\langle R(t)/2 \rangle_o$ of the reflected and transmitted nuclear partial waves in the domains, $R/2 < 2.5$ Å and $R/2 > 2.5$ Å, respectively.

underlying flux density may be interpreted as a product of the electron density times the velocity. Obviously, the low density “Rydberg lobes” disappear rather abruptly at the transition state and, therefore, much faster than the high density peaks that move with the nuclei, hence the product of density times velocity is larger for flux (ii) than for (i), albeit in opposite directions.

In conclusion, the present discovery suggests that electronic fluxes due to changes of electronic structure by crossing transition states should be a rather general phenomenon. It is easy to predict that different chemical reactions that react along the reaction path, or along neighboring paths,²⁴ offer a wealth of rich details. The fluxes are always transient, but they may be weak or strong, short- or long-lived depending on the system and on the energy (or speed) for crossing the barrier. The present case of electronic fluxes (i) and (ii) running in opposite directions also reminds of the previous discovery of antagonistic nuclear fluxes.²⁵ This analogy also points to a way of measuring the electronic fluxes experimentally. As in Ref. 25, one should monitor the time evolution of the density; in the next step, one invokes the continuity equation, together with the proper boundary conditions (zero electron flux at infinity), in order to deduce the flux. Note that the boundary conditions are essential, i.e., the electron density *per se* does not allow us to deduce the flux.²⁶

The effect discovered in this communication is quite intuitive and easy to understand: “Somehow” the switch of electronic structure from reactants to products “must be” accompanied by an electronic flux at the transition state. But its transient time evolution and its clear distinction from the flux of electrons that travel with the nuclei have never been documented and quantified before, for any other adiabatic chemical reaction. The present results should stimulate systematic investigations of the new effect in many chemical reactions.

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