

RESEARCH ARTICLE

Electronic Coherences Built by Ultrashort Pulse Drive the Vibronic Forces at Nonadiabatic Seams

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We show that the quantum force that the electrons in a molecule exert on the nuclei remains local even in the presence of strong nonadiabatic interactions. At every geometry, the total force is the sum of a potential gradient term driven by the local population and a nonclassical, nonadiabatic force driven by the local electronic coherence. On the nonadiabatic seams, the nonadiabatic force competes effectively with the potential terms. Following a sudden photoionization, we show how the nonadiabatic component of the local force drives the dynamics of the structural Jahn–Teller rearrangement of the methane cation toward the C_{2v} geometry using 2 effective nuclear coordinates and 3 coupled electronic states for either CH_4^+ or CD_4^+ . Toward the progress in reaching shorter femtosecond resolution in time-resolved x-ray and electron diffraction experiments, our work provides a quantitative understanding and pictorial visualization of the local forces that drive ultrafast molecular rearrangement and chemical reactivity with a special reference to the role of electronic coherences and nonadiabatic couplings.

Introduction

The availability of short attosecond and few femtosecond extreme ultraviolet (XUV), ultraviolet (UV) and near-infrared (NIR) pulses [1–3] has shed new insights on the dynamics of ultrafast structural molecular rearrangements. Because of their inherent width in energy, ultrashort laser pulses access a coherent set of excited electronic states of molecules. Therefore, nonadiabatic couplings (NACs) between the accessed excited states are central in the redistribution of valence electrons that drives structural rearrangements of the nuclei. The recent developments in time-resolved X-ray and electron diffraction provide femtosecond time resolutions [4–10] and have been demonstrated to be sensitive to excited electronic states dynamics [11–13]. In this paper, we demonstrate theoretically that one can discuss an exact expression for the total quantum force exerted on the nuclei by a vibronic wave packet in the presence of nonadiabatic interactions. The quantum dynamics is run for an ensemble of initially randomly oriented molecules with respect to the polarization direction of the pulse. Our formalism leads to a straightforward expression of the vibronic force for every molecular geometry of a multidimensional grid in reduced nuclear coordinates and coupled electronic states. We show that the total force is local at every molecular geometry represented by a point

in the multidimensional grid of reduced nuclear coordinates and made of 2 terms: a potential gradient term driven by the local population in each electronic state and a nonclassical, nonadiabatic term driven by the local electronic coherences. The direction and magnitude of the potential gradient and nonadiabatic terms of the force are a property of the molecule. They are defined for the molecular geometry that corresponds to each grid point and result from the topology of the potential energy surfaces and derivative NACs. We show that the magnitudes of the 2 terms of the force are modulated by the local populations and by the electronic coherences at each grid point, which can be controlled by shaping the multielectronic state vibronic wave packet by the parameters of the exciting ultrashort pulse.

We illustrate our approach by simulating quantum dynamically the ultrafast Jahn–Teller (JT) rearrangement of the methane cation [14] upon sudden photoionization of the neutral to the 3 lowest states of the cation by an attosecond XUV pulse. Early high harmonic spectroscopy experiments demonstrated a strong isotope effect [15] on the JT rearrangement taking place in the first 1.5 fs after a sudden ionization. This early work triggered several dynamical theoretical studies [16–21], which investigated the ultrafast structural dynamics in the 3 lowest states of the cation, from the unstable T_d to D_{2d} to the C_{2v}

Citation: Pandey G, Cardosa-Gutierrez M, Levine RD, Remacle F. Electronic Coherences Built by Ultrashort Pulse Drive the Vibronic Forces at Nonadiabatic Seams. *Ultrafast Sci.* 2026;6:Article 0167. <https://doi.org/10.34133/ultrafastscience.0167>

Submitted 27 December 2025

Revised 6 April 2026

Accepted 28 April 2026

Published 19 May 2026

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equilibrium geometry on D_0 and the strong isotope effect. More recently, attosecond transient absorption at the carbon K edge combined with theoretical modeling shed light on the steps of the rearrangement [22,23]. A time-resolved Coulomb explosion imaging experiment demonstrated the role of a C_{3v} geometry in the relaxation path leading to H loss, while the C_{2v} distortion leads to H_2 loss [24]. We focus here on the role of the nonadiabatic terms of the force that drive the structural rearrangement and on the strong isotope effect on the nonadiabatic dynamics. We compare the role of the forces on the nuclei due to the NAC in CH_4^+ and CD_4^+ and show that they steer different dynamics of the structural rearrangement to the D_{2d} and C_{2v} geometries. This example demonstrates the important role that the forces on the nuclei due to the NAC can play in steering the nuclear dynamics and the key role of the electronic coherences that are driving them. The difference in the quantum force dynamics that lead to the structural rearrangement in CH_4^+ and CD_4^+ provides the foundation for designing control schemes based on selectively exciting electronic coherences with a short femtosecond pulse.

Theory and Modeling

Ensemble quantum dynamics

The quantum dynamics is run for the 3 lowest, nonadiabatically coupled electronic states of the cation, D_0 , D_1 , and D_2 , which are degenerate at the T_d geometry. We use 2 reduced nuclear coordinates, Q_1 and Q_2 , as in our previous work [20]. These coordinates are defined to describe the structural changes from the T_d through approximate D_{2d} geometries toward the C_{2v} minimum on D_0 (see Fig. 1). They are constructed as linear combination of Cartesian displacements along the JT active vibrational modes of the methane cation. Specifically, Q_1 primarily drives the distortion toward the C_{2v} minimum on the D_0 potential energy surface of the cation, involving both bond-angle and bond-length rearrangements. On the other hand, Q_2 describes motion toward the D_{2d} minimum, which mainly involves angular distortions. These coordinates therefore provide a reduced yet physically transparent representation of the early-time nuclear dynamics, capturing the dominant e and t_2 normal mode distortion responsible for the ultrafast JT rearrangement. A detailed definition of these coordinates in terms of Cartesian displacements and their decomposition into normal modes is provided in [20] and in the Supplementary Materials.

The electronic structure on the grid is computed at the level [SA3-CASSCF (7e,8MO) 6-311G (d,p)]. The calculated vertical ionization energy to the T_d geometry is 13.59 eV, in good agreement with experimental values. This energy is 1.45 eV above the $C_{2v,b}$ global minimum marked in dark blue, located in the $(-Q_1, +Q_2)$ quadrant (see Fig. 1A). The second, $C_{2v,a}$ minimum sampled on the grid is located in the $(+Q_1, +Q_2)$ quadrant and 0.158 eV above the $C_{2v,b}$ global minimum. It is marked in green in Fig. 1A. The metastable D_{2d} minimum, marked in red, is located in the $(+Q_1, -Q_2)$ quadrant at 0.165 eV above $C_{2v,b}$. Isocontours of the potential energy surfaces of D_0 , D_1 , and D_2 are plotted in Fig. 1A to C and the D_0/D_1 , D_0/D_2 , and D_1/D_2 NAC seams in Fig. S1.

We consider an ensemble of 8,000 molecules for CH_4 and CD_4 each, initially randomly oriented with respect to the polarization direction of the pulse, an XUV pulse (13th harmonic of 800 nm, $h\nu 13$) with a photon energy of 20.3 eV. The photoionization is described in the sudden approximation limit for each

polarization direction of the photoionization XUV attopulse. In the quantum dynamics on the grid, the photoionization process is represented as a superposition of the 3 lowest states of the cation. The initial vibronic wave packet has complex amplitudes on each electronic state of the cation defined as the photoionization matrix elements from the ground vibrational state of the neutral in Franck Condon region, which includes distorted geometries at which the T_d degeneracy of the 3 lowest electronic states is lifted. To compute the dynamics of the ensemble of randomly oriented molecules, we implement a singular value decomposition analysis on the ensemble of the 8,000 initial states of the cation randomly oriented with respect to the pulse polarization to determine the exactly 3 (for a sudden process) principal orientations of the density matrix of the ensemble at $t = 0$ [20,25]. The corresponding 3 principal molecular vectors are then propagated using the time-dependent Schrödinger equation (see [20] and the Supplementary Materials for a summary of the methodology). The localization of the initial state of the ensemble on each electronic state of the cation, D_0 , D_1 , and D_2 , is shown in Fig. 1D to F for CH_4^+ and in Fig. 1G to I for CD_4^+ .

Expression of the local quantum force

The exact time dependence of the quantum force in the 2 nuclear coordinates is derived using the Ehrenfest theorem [26] (see also [27]).

$$F_{tot}(Q_i) = d\langle P_i \rangle / dt = -\left\langle \left(\nabla_{Q_i} V(Q_1, Q_2) \right) \right\rangle + \left\langle \left[\tau_{Q_i}(Q_1, Q_2), V(Q_1, Q_2) \right] \right\rangle \\ = \langle F_V(Q_i) \rangle + \langle F_{[r,V]}(Q_i) \rangle, i = 1, 2 \quad (1)$$

In Eq. (1), the averaging is over the density matrix of the ensemble of randomly oriented molecules (see the Supplementary Materials). $P_i = (\hbar/i)\partial/\partial Q_i$, $i = 1, 2$ is the momentum operator, $V(Q_1, Q_2)$ is the 2-dimensional potential, and $\tau_{Q_i}(Q_1, Q_2)$ is the 2 dimensional derivative coupling, $\tau_{Q_i}^{kl}(Q_1, Q_2) = \langle \psi_k(Q_1, Q_2) | \partial/\partial Q_i | \psi_l(Q_1, Q_2) \rangle$, between electronic states k and l , $i = 1, 2$ at the geometry defined by (Q_1, Q_2) . Each component of the total quantum force, $\langle F_{tot}(Q_i) \rangle$, comprises 2 terms. The first term, $\langle F_V(Q_i) \rangle$, is diagonal in the electronic states. It corresponds to the average of the potential gradients of the 3 electronic states and has a classical analog. The second one, $\langle [\tau_{Q_i}, V] \rangle$, is off-diagonal in the electronic states and is purely quantal. It is the contribution of the NAC to the force. $\langle F_{[r,V]}(Q_i) \rangle$ is modulated by the electronic coherences, which we showed previously are robust with respect to averaging over random initial orientations [20,21,25,28].

As derived in the Supplementary Materials, the components of the F_V and the $F_{[r,V]}$ terms along Q_1 and Q_2 are diagonal in the grid point index, which enables the definition of a local force at each molecular geometry, g , sampled on the grid. The potential terms, which are also diagonal in the electronic state index, k , are given by:

$$F_{V,Q_i}^k(g) = \left(\nabla_{Q_i} V_k(Q_1, Q_2) \right)_g P_{gk}(t), i = Q_1, Q_2 \text{ and } k = D_0, D_1, D_2 \quad (2)$$

The direction of $F_{V,Q_i}^k(g)$ is determined by the components of the potential energy surface gradient and does not vary in time.

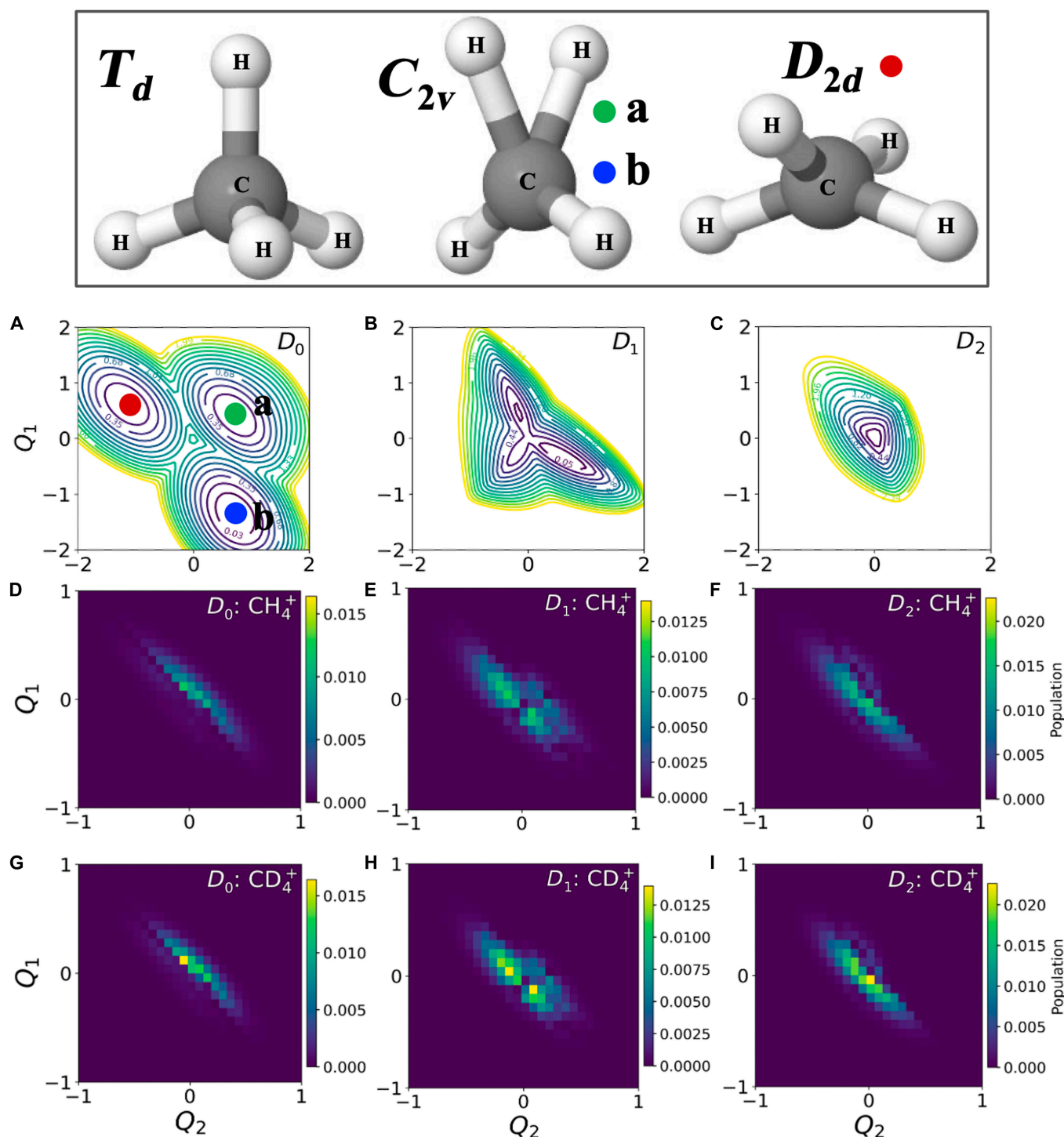


Fig. 1. Top row: Geometries of the T_d , C_{2v} , and D_{2d} geometries. Second row: Potential energy surfaces of the 3 electronic states in the reduced coordinates (Q_1 , Q_2). (A) D_0 , (B) D_1 , and (C) D_2 . The 2 C_{2v} minima on the grid are marked a (green dot) and b (dark-blue) respectively. C_{2v} is the global minimum, T_d is at (0, 0), D_{2d} , marked in red, is at (0.6, -1.15). Third and fourth rows: Localization of the initial states for CH_4^+ : (D) D_0 , (E) D_1 , and (F) D_2 and for CD_4^+ : (G) D_0 , (H) D_1 , and (I) D_2 .

The magnitude of the force is modulated by $P_{gk}(t)$, the total population at grid point g for electronic state k [Eq. (S5)]. On the other hand, for a given pair of electronic states, k l , the direction of $F_{[\tau, V]}$ at each grid point, g , is determined by the 2 components of the derivative coupling, $\tau_{Q_i}^{kl}$, multiplied by the energy difference between the 2 coupled states. The $F_{[\tau, V]}$ force is modulated by the magnitude of the local electronic

coherence, $C_{gkl}(t)$, between the electronic states k and l at grid point g [Eq. (S6)] and its sign:

$$F_{[\tau, V]}^{gkl}(Q_i) = \tau_{Q_i}^{kl} (V_{l,g} - V_{k,g}) 2\text{Re}[C_{gkl}(t)], \quad (3)$$

$$i = 1, 2 \text{ and } k = 0, 1, 2 \quad l > k$$

The electronic coherences oscillate with the energy differences between the electronic states, which, on the NAC seams,

are typically of the order of vibrational frequencies. This makes $F_{[\tau,V]}$ term efficient for steering the direction of motion of the wave packet and the dynamics of the structural rearrangement.

Results

Population dynamics in the cation states

The computed highest ionization yield for a sudden photoionization of the neutral ground state by an ultrashort XUV pulse at a mean energy of 20 eV is to the D_2 state (42.6% for CH_4^+ and 43.3% for CD_4^+), followed by the D_1 state (34% for CH_4^+ and 33.8% for CD_4^+) and 23.4% for CH_4^+ and 22.9% for CD_4^+ for the D_0 state. The initial states are localized around T_d along the antidiagonal $[(+Q_1, -Q_2)(-Q_1, +Q_2)]$, roughly along the line joining the D_{2d} and C_{2v} minima, on each 3 lowest electronic states (see Fig. 1D to F for CH_4^+ and Fig. 1G to I for CD_4^+). The relaxation from D_2 to D_1 occurs around the T_d geometry because the potential of D_2 is an almost 2-dimensional parabola with a minimum at T_d (see Fig. 1C). At short times, the population from D_2 relaxes to D_0 , transiently passing through D_1 , the amount of direct relaxation from D_2 to D_0 being smaller (see Fig. 2A). D_1 has 3 minima located roughly along the D_1/D_0 seams in the vicinity of the T_d point and in between the 2 C_{2v} and the D_{2d} minima on D_0 (Fig. S1). The population initially photoionized to D_1 travels outside of the region of strong NAC

around T_d toward the D_{2d} minimum, where the coupling to D_0 is weaker and remains trapped on D_1 . On the other hand, the population on D_1 that relaxed from D_2 reaches the C_{2v} minimum very quickly, with a first maximum at 1 fs (Fig. 2B). The relaxed fraction of wave packet on D_0 then reaches D_{2d} geometries in 5 to 10 fs, with a first maximum in the D_{2d} region at 8 fs (Fig. 2C and see population dynamics movies of the Supplementary Materials).

The isotope effect in the initial populations on D_0 , D_1 , and D_2 results in slightly narrower distributions of the initial state around the T_d initial configuration in CD_4^+ [see Fig. 1G to I]. However, as shown in Fig. 2, a strong isotope effect in the population dynamics develops in the first 15 fs. Because of the mass effect, the CD_4^+ wave packets on D_1 and D_2 reach the regions of strong NAC about a factor 1.4 slower than the CH_4^+ ones, which slows down the initial population transfer from D_2 . In addition, the electronic coherences built at the photoionization step reach the NAC regions with different relative phases, leading to different efficiencies of the amplitude transfer [21]. This effect is particularly clear when monitoring the population transfer locally, in the C_{2v} region (Fig. 2B) and in the D_{2d} (Fig. 2C). For both geometries, the dynamics of the populations in CD_4^+ are substantially different from those of CH_4^+ beyond being slowed down because of the H/D mass ratio.

Dynamics of the local gradient and nonadiabatic force components

In Figs. 3 and 4, we show the local terms of the force, F_V on D_0 and $F_{[\tau,V]}$ for the D_0/D_1 seam, computed for CH_4^+ and CD_4^+ , respectively, at the 3 selected points on the D_0/D_1 seams shown in the inset of Fig. 3B. The gradient of the potential energy as well as the derivative couplings and potential energy differences are identical for the 2 isotopomers. On the other hand, one can see by comparing the 2 figures that the weighting of these by the local population on D_0 for the F_V term and by the local D_0/D_1 electronic coherence for the $F_{[\tau,V]}$ one [see Eqs. (2) and (3)] is markedly different from a $\sqrt{\mu_D/\mu_H} \approx 1.4$ scaling of the time profiles. The slow down for CD_4^+ induces different phase relations between the coherences and the phase of the derivative coupling, which modifies population transfer and coherences.

At point 1 (Figs. 3A and 4A), the $D_0 F_V$ and $D_0/D_1 F_{[\tau,V]}$ terms oriented along Q_2 (orange) are negligible. The total force is oriented along Q_1 (blue), which corresponds to a C_{2v} distortion. Up to 2 fs, the F_V and $F_{[\tau,V]}$ terms are oriented along $-Q_1$ and of similar magnitude for both isotopomers. Then, F_V decreases and remains negative, while $F_{[\tau,V]}$ remains large and oscillates along Q_1 with the period of the D_0/D_1 electronic coherence. While the nonadiabatic $F_{[\tau,V]}$ dominates for the 2 isotopomers, the time profile of force is substantially different, reflecting the different dynamics of the electronic coherences. As a result, the total force at this grid point oscillates up and down along Q_1 , as shown by the snapshots on the right of Figs. 3A and 4A, but with a different phase. At point 2 (Figs. 3B and 4B), on the other hand, the $D_0 F_V$ term along Q_2 dominates and induces a D_{2d} distortion. It is negative, and its magnitude is modulated by the population on D_0 (see 3 snapshots on the right). Since the potential term dominates, the dynamics of the force is driven by the population on the seams. Here too, the dynamics of the force is different for the 2 isotopomers. At point 3 (Figs. 3C and 4C), all 4 components are important, and

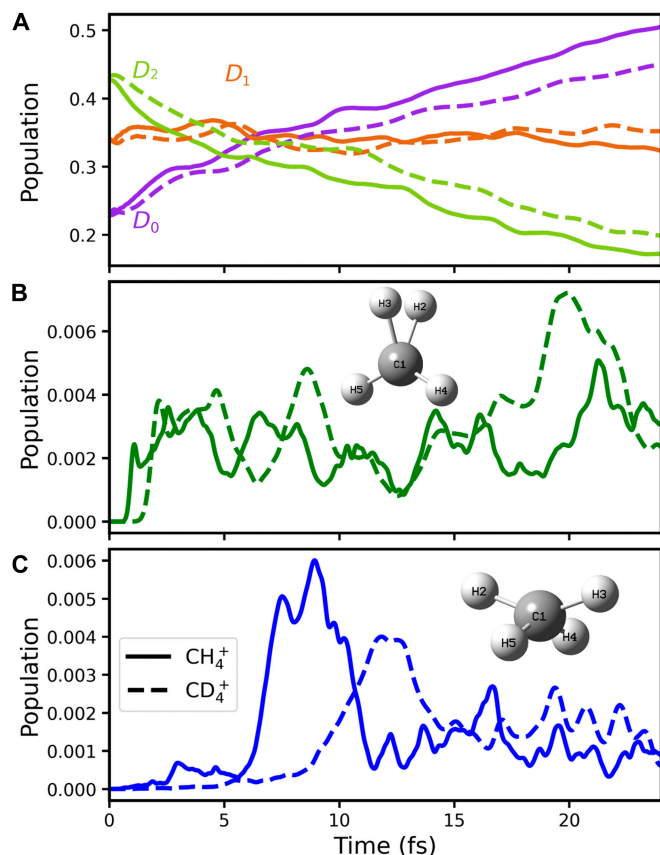


Fig. 2. (A) Population dynamics in the 3 lowest states of the cation following sudden photoionization by a $h\nu_{13}$ ultrashort XUV pulse. D_0 (violet), D_1 (brown), and D_2 (light green). (B) Population in the 2 C_{2v} minima marked a and b in Fig. 1A. CH_4^+ (C) Population in D_{2d} . CH_4^+ Full lines, CD_4^+ dashed lines.

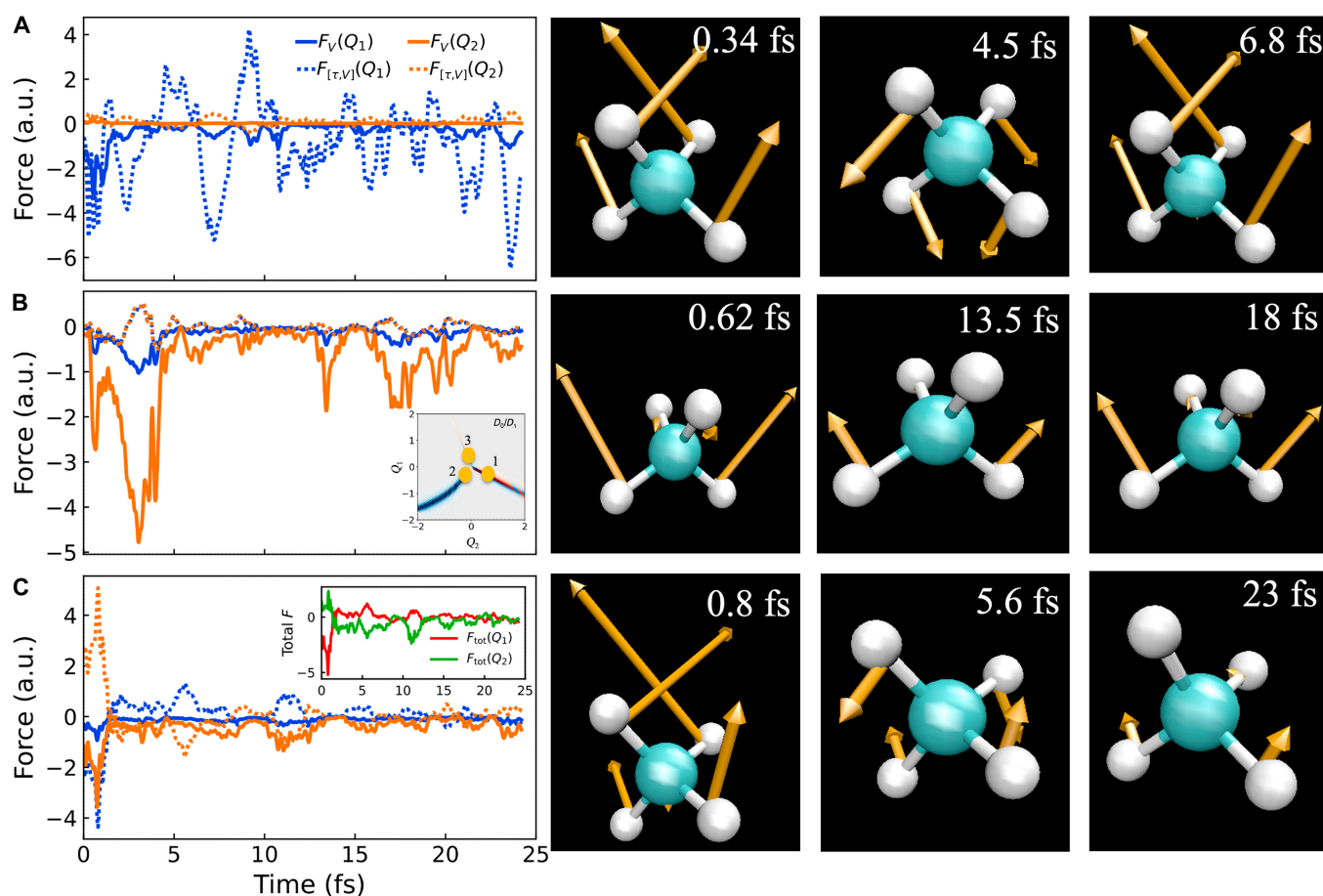


Fig. 3. (A to C) The components along the 2 coordinates Q_1 (blue) and Q_2 (orange) of the local time-dependent forces F_V on D_0 (full line) and $F_{[r,V]}$ for D_0/D_1 (dotted line), computed for CH_4^+ at the 3 points on the D_0/D_1 seams shown in the inset of (B). (a) point 1, (b) point 2, and (c) point 3. The inset in (C) shows the total force along Q_1 (red) and along Q_2 (green). Force values in (A) to (C) are multiplied by 10^5 . Right panels show the total force on each atom at selected times from the left panel.

the total force is shown in the inset. The distortion is complex and varies substantially at the 3 times shown in the snapshots on the right in Figs. 3C and 4C, with a different time evolution for the 2 isotopomers.

The $D_0 F_V$ (dark red) and the $D_0/D_1 F_{[r,V]}$ (orange) terms are plotted for CH_4^+ and for CD_4^+ at 6 grid points located on the D_0/D_1 NAC seams (marked in blue) in the (Q_1, Q_2) coordinates in Fig. 5 for selected values of time so as to span the rise in the C_{2v} and D_{2d} geometries plotted in Fig. 2B and C. F_V and $F_{[r,V]}$ differ in their direction and their magnitude changes in time according to the population and electronic coherence, resulting in different steering of structural rearrangement at different times. As can be seen from Fig. 5A to C and the full range of the time evolution of the force terms provided in the Supplementary Materials, in CH_4^+ , at short times, the $F_{[r,V]}$ component of the force is instrumental in sending population toward the D_{2d} and to both C_{2v} regions. In particular, it leads to a pronounced maximum in the D_{2d} geometry in the range of 6 to 10 fs. This is rather different from CD_4^+ , for which the rise is delayed compared to CH_4^+ (see Fig. 2C), in agreement with the magnitude of the components of the force shown in Fig. 5E and F. The maximum in the population of the C_{2v} geometry at longer times, at 20 fs, shown in Fig. 2B, can be understood for the dynamics of the terms of the force shown in Fig. 5D and for the full time range in the Supplementary Materials. In CD_4^+ ,

the force components shown in Fig. 5C explain the rise in the D_{2d} geometry at 10 fs shown in Fig. 2C.

Population transfers occur in localized regions on the NAC seams where the F_V terms and the NAC $F_{[r,V]}$ terms are commensurate but not necessarily codirectional. Figure 6 shows a vector field plot of the total force in the entire (Q_1, Q_2) grid at selected times computed for CH_4^+ . At early times, the total force is dominated by the steep gradient that steers the wave packet away from T_d symmetry point (Fig. 6A). Note that forces larger than 10^{-5} atomic units (a.u.) are not shown for clarity and the forces reported in Fig. 6 only show the moving front of the vibronic wave packet. As the wave packet reaches the nonadiabatic seams (Fig. 6B to D), the coherence-driven $F_{[r,V]}$ term becomes commensurate with the potential gradient term F_V . Consequently, the total force field vectors develop strong spatial structures that reflect the changes in the total force direction due to $F_{[r,V]}$. The resulting fluctuations in the vector directions demonstrate how electronic coherences actively steer the nuclei. The forces in the NAC regions then steer the subsequent dynamics in regions where only the potential terms operate, as can be seen in Fig. 6E and F.

Conclusion

In the very well-known Born–Oppenheimer approximation, the force on the nuclei is local. However, the Born–Oppenheimer

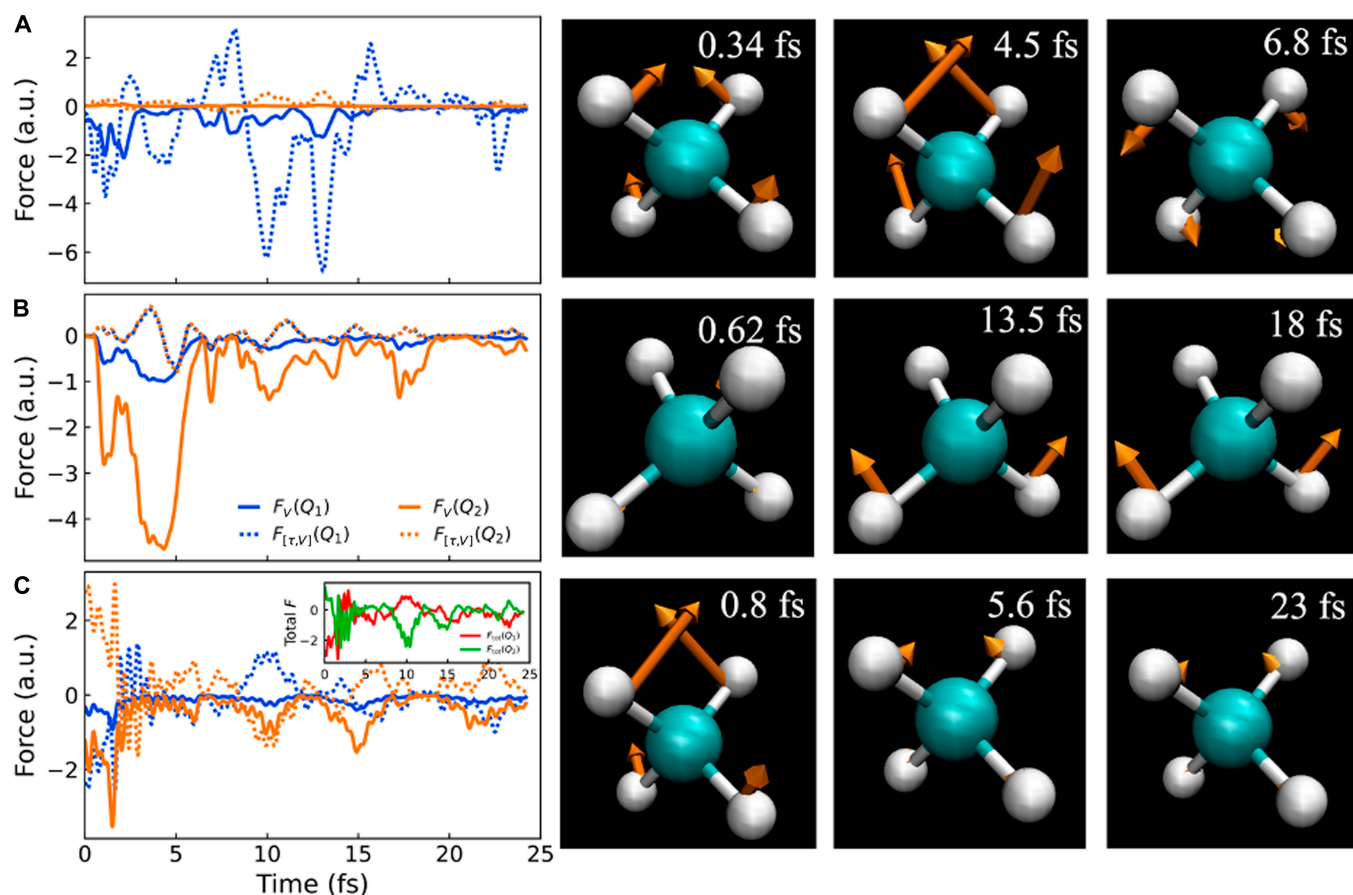


Fig. 4. (A to C) The components along the 2 coordinates Q_1, Q_2 of the local time-dependent forces F_V on D_0 and $F_{[r,v]}$ for D_0/D_1 , computed for CD_4^+ at the 3 points on the D_0/D_1 seams shown in the inset of Fig. 3B, (a) point 1, (b) point 2, and (c) point 3. The inset in (C) shows the total force along Q_1 (red) and along Q_2 (green). Force values in (A) to (C) are multiplied by 10^5 . Right panels show the total force on each atom at selected times from the left panel.

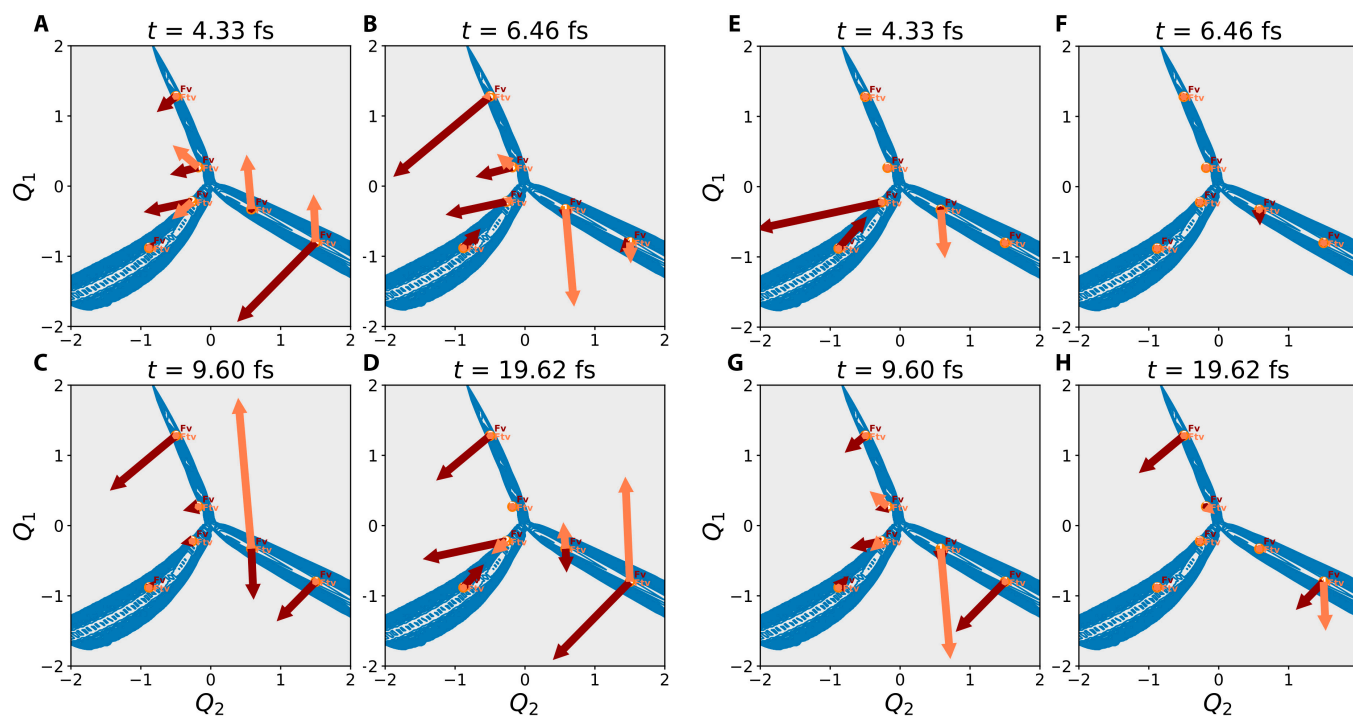


Fig. 5. The 2 terms of forces, F_V (dark-red arrows) and $F_{[r,v]}$ (orange arrows), in the (Q_1, Q_2) plane at 6 points on the D_0/D_1 seams (marked in blue) showing qualitatively different directions of the force, computed at selected times. (A to D) CH_4^+ and (E to H) CD_4^+ . The 3 inner ones are the ones shown in Figs. 3 and 4. The values of the times were selected to relate to the population dynamics of the C_{2v} and D_{2d} geometries plotted in Fig. 2B and C.

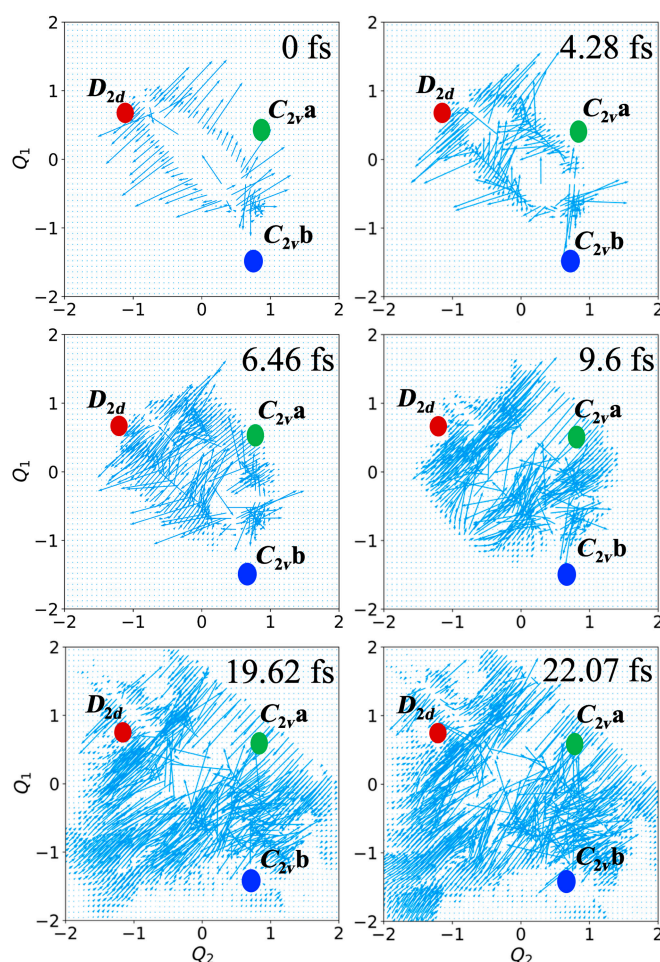


Fig. 6. The total force, $F_V + F_{[r,V]}$, computed at every grid point in the (Q_1, Q_2) plane at selected times for CH_4^+ . The force magnitudes larger than 1×10^{-5} atomic units (a.u.) are not shown for clarity. These high values are localized around the T_d geometry ($Q_1 = 0, Q_2 = 0$). The 2 C_{2v} minima on D_0 sampled on the grid are marked by green dot and dark-blue dot. $C_{2v,b}$ is the global minimum, D_{2d} is marked by a red dot (see also Fig. 1).

approximation fails critically when several electronic states are near in their energies. We demonstrate that even in the presence of strong NAC, the exact force remains local on a grid in the coordinates. Taking the ultrafast JT rearrangement of the methane cation as a prototypical example of nonadiabatic dynamics, we show that the local nonclassical, nonadiabatic $F_{[r,V]}$ terms compete effectively with the local potential F_V terms in the regions of large NAC. The F_V and the $F_{[r,V]}$ terms are no codirectional. Their respective directions are determined by the features of the potential energy surfaces and their coupling, which are the same for CH_4^+ and CD_4^+ . There is, however, a qualitative difference in the dynamics of the 2 terms. The F_V term oscillates with the local population at a given grid point so that its direction does not change sign. On the other hand, the $F_{[r,V]}$ oscillates with the amplitude of the electronic coherence and does change sign. At a given grid point on the NAC seam, the $F_{[r,V]}$ terms can therefore steer the dynamics in a direction different from that of the potential gradient. Overall, we show that the differences in the electronic coherences in the 2 isotopomers lead to a different dynamics driven by the force and results in a strong isotope effect in population transfer and in the dynamics of the structural rearrangement. Tuning these

nonclassical terms of the force by targeting the excitation of specific electronic coherence with broad in energy attosecond or few femtosecond pulses in an ensemble of randomly oriented molecules therefore opens the way to control of structural rearrangements with electronic coherences. When modeled beyond the independent atomic model, time-resolved x-ray diffraction (TR-XRD) [4–6,8,9,11,13,29] and ultrafast electron diffraction [7,10,12,30] provide observables of the multielectronic-state vibronic wave function [5,6,31,32] that could be related to the structural changes driven by the nonadiabatic terms of the force exerted by the vibronic wave packet on the nuclei. In TR-XRD, structural rearrangement around conical intersection seams can be inferred from the inelastic scattering term of the photon scattering cross-section that depends directly on electronic coherences at each geometry of the vibronic wave packet [4–6,8,29]. Another TR-XRD observable is the anisotropy in the optical transition dipole, which, on a femtosecond time scale, reflects both the electronic and nuclear dynamics induced by an ultra-short excitation [33]. Electronic coherences affect both the elastic and the inelastic parts of the scattering cross-section in mega-electron-volt ultrafast electron diffraction, which depends on both electronic and nuclear charge distributions [12,30].

Acknowledgments

Funding: F.R., M.C.-G., and G.P. acknowledge the support of the Fonds National de la Recherche (F.R.S.-FNRS, Belgium), #T.0247.24. Computational resources have been provided by the Consortium des Equipements de Calcul Intensif (CECI), funded by the F.R.S.-FNRS under grant #2.5020.11. M.C.-G. is supported by a fellowship of the Excellence of Science (EOS 40007519) program from the FWO and F.R.S.-FNRS. G.P. is supported by a fellowship of the IPD-STEMA postdoctoral funding of ULiege.

Author contributions: F.R. and R.D.L. conceived the idea and designed the modeling. G.P. and M.C.-G. conducted the modeling. All authors analyzed the results and contributed to the writing of the manuscript.

Competing interests: The authors declare that they have no competing interests.

Data Availability

The data are freely available upon reasonable request.

Supplementary Materials

Section S1 and S2
Tables S1 to S4
Movies S1 to S8
References [34,35]

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Electronic Coherences Built by Ultrashort Pulse Drive the Vibronic Forces at Nonadiabatic Seams

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Citation: Pandey G, Cardosa-Gutierrez M, Levine R, Remacle. Electronic Coherences Built by Ultrashort Pulse Drive the Vibronic Forces at Nonadiabatic Seams. *Ultrafast Sci.* 2026;6:0167. DOI: 10.34133/ultrafastscience.0167

We show that the quantum force that the electrons in a molecule exert on the nuclei remains local even in the presence of strong nonadiabatic interactions. At every geometry, the total force is the sum of a potential gradient term driven by the local population and a nonclassical, nonadiabatic force driven by the local electronic coherence. On the nonadiabatic seams, the nonadiabatic force competes effectively with the potential terms. Following a sudden photoionization, we show how the nonadiabatic component of the local force drives the dynamics of the structural Jahn–Teller rearrangement of the methane cation toward the C_{2v} geometry using 2 effective nuclear coordinates and 3 coupled electronic states for either CH₄⁺ or CD₄⁺. Toward the progress in reaching shorter femtosecond resolution in time-resolved x-ray and electron diffraction experiments, our work provides a quantitative understanding and pictorial visualization of the local forces that drive ultrafast molecular rearrangement and chemical reactivity with a special reference to the role of electronic coherences and nonadiabatic couplings.

Image

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Ultrafast Science (ISSN 2765-8791) is published by the American Association for the Advancement of Science. 1200 New York Avenue NW, Washington, DC 20005.

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