

Coherences of charge migration increasing with molecular size: A case study for chloro-alkyne ions $\text{H}(\text{CC})_n\text{Cl}^+$

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A key goal of ultrafast science is to pursue long-lived electronic coherences during molecular processes. The electronic coherence during charge migration can be characterized by the strength of the electronic flux. We report the size dependence of the de- and recoherences of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ by systematic quantum dynamics simulations for $n = 1-4$. The result is counterintuitive, namely the overall extent of electronic coherence increases with molecular size. Charge migration in the longest ions lasts for more than 100 fs, while it stops at about 10 fs in many previously investigated molecules.

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Decoherence is a common quantum effect. In most cases it is undesirable. A sufficiently long coherence time is a prerequisite for various applications such as quantum computation, quantum information, and quantum engineering. For molecular systems, the primary source leading to decoherence of electron dynamics is nuclear motions [1–12]. Recoherences of electron dynamics are generally expected for small molecules [13–18]. De- and recoherences of electron dynamics may be monitored by the dis- and reappearance of charge migration in molecules [15,18–20]. Attempts to manipulate the de- and recoherences of charge migration with ultrashort laser pulses have been reported [16,19].

Charge migration [21] can be launched by laser pulses that prepare the target molecule in a coherent superposition of two or more electronic eigenstates [22–29]. For the ideal case of fixed nuclei, the charge migrates periodically (or quasiperiodically) without any decoherences [30–39]. More realistic representations should account for the effects of nuclear motions on charge migration. A first step towards this demanding goal is provided by the Born-Oppenheimer approximation (BOA) that introduces the parametric dependence of the electronic wave functions on the nuclear configuration, and multiplies them by electronic state selective nuclear wave functions [20]. Note, however, that the BOA neglects nonadiabatic transitions between the electronic states; in particular, it does not account for effects of conical intersections.

Nuclear motions may affect charge migrations in different ways. In the frame of the BOA for the electronic ground state and one excited state, an extreme limiting case is permanent perfect overlap of the nuclear wave functions for the two involved electronic states. In this scenario, charge migration proceeds periodically, forever, similar to the ideal case of fixed nuclei. In general, however, different vibrations in the ground and excited states diminish the overlap of the nuclear wave functions, and this in turn causes decoherence of charge migrations [1–7,12]. In diatomic molecules, the vibrations may even induce (partial) recurrences of the overlap; this implies (partial) recoherences of charge migration [13,14].

Recoherences in polyatomic molecules are rarely reported. Recently, the de- and recoherences of charge migration in the linear iodo-acetylenic cation (HCCl^+) was predicted theoretically [15,16]. Later on a combined experimental and theoretical investigation of the de- and recoherences of charge migration in silane (SiH_4) was reported [18]. Very recently the recoherences of charge migration were found in a fairly large molecule, pyrene ($\text{C}_{16}\text{H}_{10}$) [20]. A general method to study the de- and recoherences of charge migration has also been developed in Ref. [20].

Polyatomic molecules allow different intramolecular vibrational redistributions (IVRs) in the ground and excited states. As a working hypothesis, this should suppress or even prohibit recurrences of the overlap of the nuclear wave functions. Series of molecules with increasing numbers of atoms should, therefore, systematically support rapid decoherence while suppressing recoherences of charge migration. Accordingly, it is challenging to find molecules with sufficiently long-lasting electronic coherences for potential applications as molecular devices and machines [40,41]. In 2022, about 250 molecules were studied to search for long-lasting electronic coherence. Among them only a few molecules have

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electronic coherences lasting up to 10 fs [9]. Here we show that two molecules, $\text{H}(\text{CC})_3\text{Cl}^+$ and $\text{H}(\text{CC})_4\text{Cl}^+$, have long-lasting electronic coherences up to 100 fs. In addition, we investigate the size dependence of the electronic coherences by systematic evaluations of the durations of charge migrations in the chloro-alkynes $\text{H}(\text{CC})_n\text{Cl}^+$, $n = 1-4$. The results are obtained by means of the method developed in Ref. [20]; cf. Eqs. (S1)–(S8) in the Supplemental Material [42], and confirmed by additional calculations at higher level of theory.

For reference, we first focus on charge migration in HCCCl^+ . The system is initially prepared in the superposition of the electronic ground state $|g\rangle$ and the first excited state $|e\rangle$ as

$$|\Psi(t=0)\rangle = [c_g |g\rangle + c_e |e\rangle] \otimes |0_g\rangle, \quad (1)$$

where $|0_g\rangle$ is the vibrational ground state in the electronic ground state $|g\rangle$. The experimental preparation of this type of initial state for HCCl^+ has been reported in Ref. [27]. Subsequently the molecular system propagates freely. The time-dependent part $\Delta\rho_{\text{el}}(z, t)$ of the one-dimensional electron density along the z axis (the molecular axis), cf. Eq. (S6) in the Supplemental Material [42], is shown in Fig. 1(a) for $t < 100$ fs in a colored contour plot; throughout this paper we use red and blue colors to represent positive and negative contour values, respectively. First, we recognize the rather slow electron dynamics with a period of about 60 fs. This is due to the electrons which follow the motions of the nuclei. Accordingly, the period of ca. 60 fs is just the vibrational period of the CCl bond stretch in the electronic excited state. Second, we discover the much faster electron dynamics with period ≈ 1 fs, for $0 < t < 5$ fs and for another time window of a few fs close to $t = 60$ fs. Apparently the charge migrates back and forth along the molecular axis between the CC triple bond region and the vicinity of the chlorine atom. Specifically, the (negative) charge migrates from the CC triple bond to the chlorine atom during the first half period and back in the next half period.

The fast component of the electron dynamics is also documented in Fig. 1(b) for the electronic flux along the z axis. In fact, charge migration is even more prominent in the electronic flux $F_z(z, t)$ than in the electron density $\Delta\rho_{\text{el}}(z, t)$. The reason is that flux is proportional to velocity. The contribution of the slow component of the dynamics shown in Fig. 1(a) to the flux $F_z(z, t)$ is so small that it is invisible in Fig. 1(b). Consequently, the flux reveals the attosecond component of the electron dynamics, exclusively. In other words, the electronic flux reveals attosecond charge migration. We shall investigate, therefore, charge migration in HCCCl^+ and likewise in $\text{H}(\text{CC})_n\text{Cl}^+$ in terms of the electronic flux $F_z(z, t)$ along the molecular axis. This reveals the following phenomena.

The overall amplitude of charge migration in HCCCl^+ quickly decreases in a few fs. This phenomenon is known as the decoherence of charge migration. After a relatively long time, there is a partial recoherence of charge migration with amplitude reaching a local maximum at about $t = 60$ fs, followed by decoherence again. Further details of the electronic charge migration can be unraveled by focusing on the time dependence of the electronic flux at a fixed spatial coordinate $z = z_0$. The essential properties of the de- and recoherences of charge migration do not depend on different choices

of z_0 [15,20]. The time dependence of the electronic flux $F_z(z = z_0, t)$ calculated at $z_0 = 0$ (the center of mass of the molecule) is shown in Fig. 1(c) (red curve). The de- and recoherence displayed in Fig. 1(c) are even more pronounced than in Fig. 1(b). They depend on the overlap $S_{ge}(t)$ between the nuclear wave packets of the electronic ground state $|g\rangle$ and the first excited state $|e\rangle$, cf. Eqs. (S4)–(S5) in the Supplemental Material. The absolute value $|S_{ge}(t)|$ is also shown in Fig. 1(c). The envelop of the electronic flux $F_z(z = 0, t)$ agrees well with the absolute value $|S_{ge}(t)|$ of the nuclear overlap. Consequently the timescales of the de- and recoherences of charge migration can be analyzed quantitatively in terms of $|S_{ge}(t)|$.

Similarly to Fig. 1(b), the electronic fluxes $F_z(z, t)$ of the cations $\text{H}(\text{CC})_n\text{Cl}^+$ ($2 \leq n \leq 4$) are shown in Fig. 2 to illustrate the corresponding charge migrations for $t < 100$ fs. We readily recognize some common features. First, the processes are ultrafast with periods smaller than 2 fs. Specifically, the periods are 1.04, 1.43, 1.53, and 1.93 fs for $n = 1, 2, 3$, and 4, respectively, i.e., the periods increase with molecular size. Second, the direction of charge migration is always unidirectional. It flips from one half period to the next half period. Note that the short-time behaviors of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ ($1 \leq n \leq 4$) are consistent with previously reported results with the frozen nuclei approximation [37].

Apart from the common features, there are also differences. The amplitudes of the electronic fluxes during charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ for $n > 1$ never decrease to zero in the entire time window of Fig. 2. In contrast, for HCCCl^+ , the amplitude decreases quickly to zero before the next partial recoherence. The spatial region in which the charge migrates increases systematically when n increases. Specifically, we recognize n subregions for charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ for $1 \leq n \leq 4$. These subregions roughly correspond to the domains of the CCl bonds and the CC single bonds. The electronic flux $F_z(z, t)$ in these domains represent charge migrations between the Cl atom and the neighboring CC triple bond, or between the two neighboring triple bonds, respectively. The total numbers of migrating electrons are more or less the same for all $\text{H}(\text{CC})_n\text{Cl}^+$ cations. Due to the increasing spatial range of charge migration with molecular size, the amplitude of charge migration in the domain of the CCl bond decreases accordingly.

Further systematic differences of charge migration in the four cations concern the timescales of the de- and recoherences. As discussed before, a good quantity for analyzing the timescales of de- and recoherences is the nuclear overlap $|S_{ge}(t)|$. Accordingly, the time dependence of the nuclear overlaps is shown in Fig. 3 for $\text{H}(\text{CC})_n\text{Cl}^+$. The strongest partial recoherences of charge migration for $n = 1-4$ are at $t = 60.74, 60.98, 74.33$, and 91.12 fs, respectively. These correspond to the periods of the CCl bond stretches in the first excited state $|e\rangle$. More precisely, for $n = 1$ and 2, the CCl bond stretch implies the relative motion between the Cl atom and the $\text{H}(\text{CC})_n$ fragment, whereas, for $n = 3$ or 4, it also involves the motion between the CCCI and the $\text{H}(\text{CC})_{n-1}$ fragments. Apparently the reduced mass of the vibrating fragment increases with n , causing the corresponding increase of the periods of the dominant decoherence. In addition, there are many less prominent partial recurrences of the nuclear overlap $|S_{ge}(t)|$ that correspond to partial minor recoherences

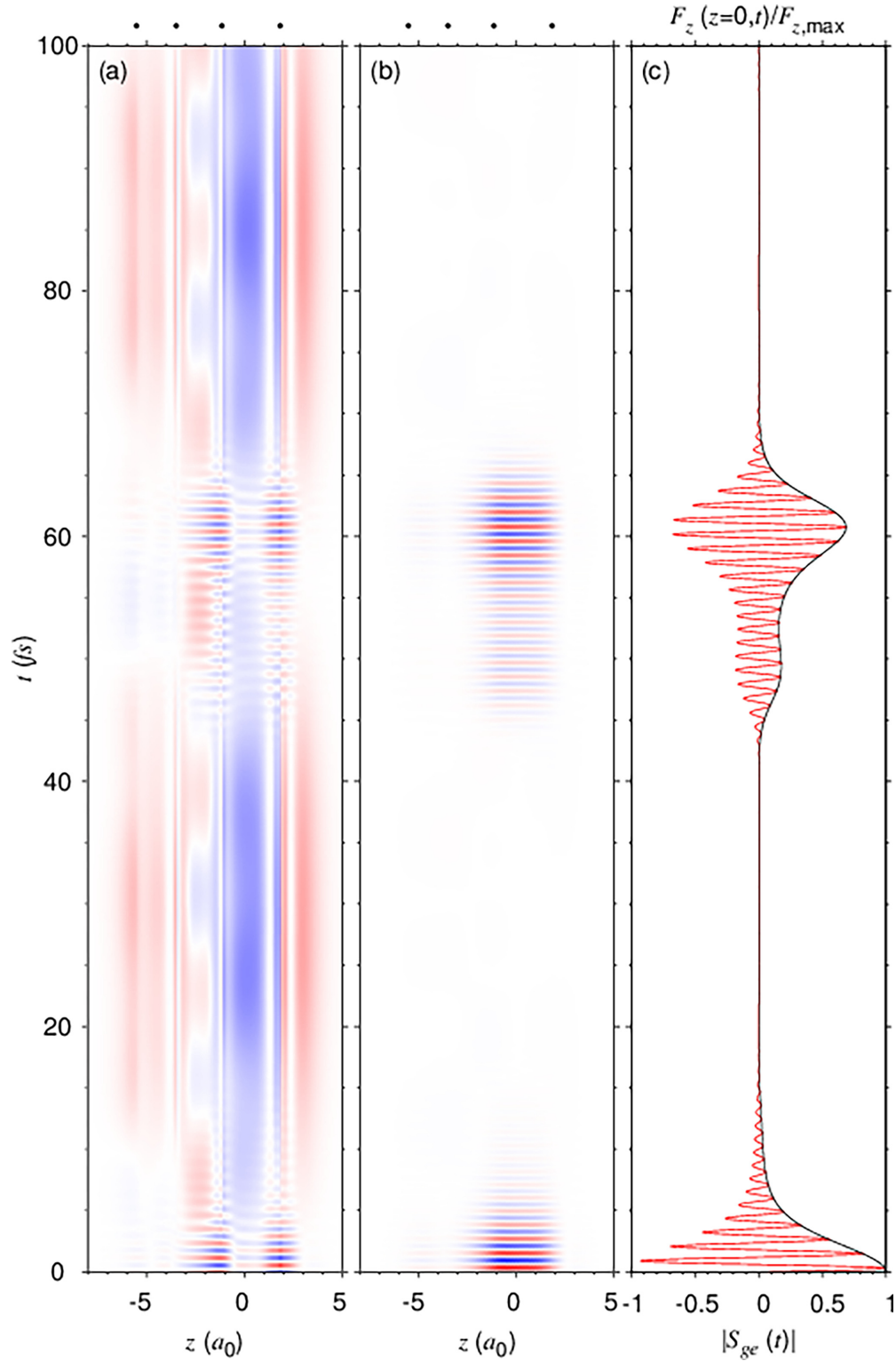


FIG. 1. Electron dynamics and charge migration with de- and recoherences in HCCCl⁺ along the molecular axis (z axis). (a) The time-dependent part $\Delta\rho_{el}(z, t)$ of the one-dimensional reduced electron density for $t < 100$ fs. (b) The electronic flux $F_z(z, t)$ along the z axis for $t < 100$ fs. (c) Cut of (b) for the electronic flux at $z = z_0 = 0$ (red curve) in units of $F_{z, \max} = 0.717 \text{ fs}^{-1}$, and the absolute value $|S_{ge}(t)|$ of the overlap (black curve) of the two nuclear wave packets of the electronic ground and first excited states. The black dots on the top of the panels (a) and (b) mark the corresponding positions of the nuclei of H, C, C, Cl.

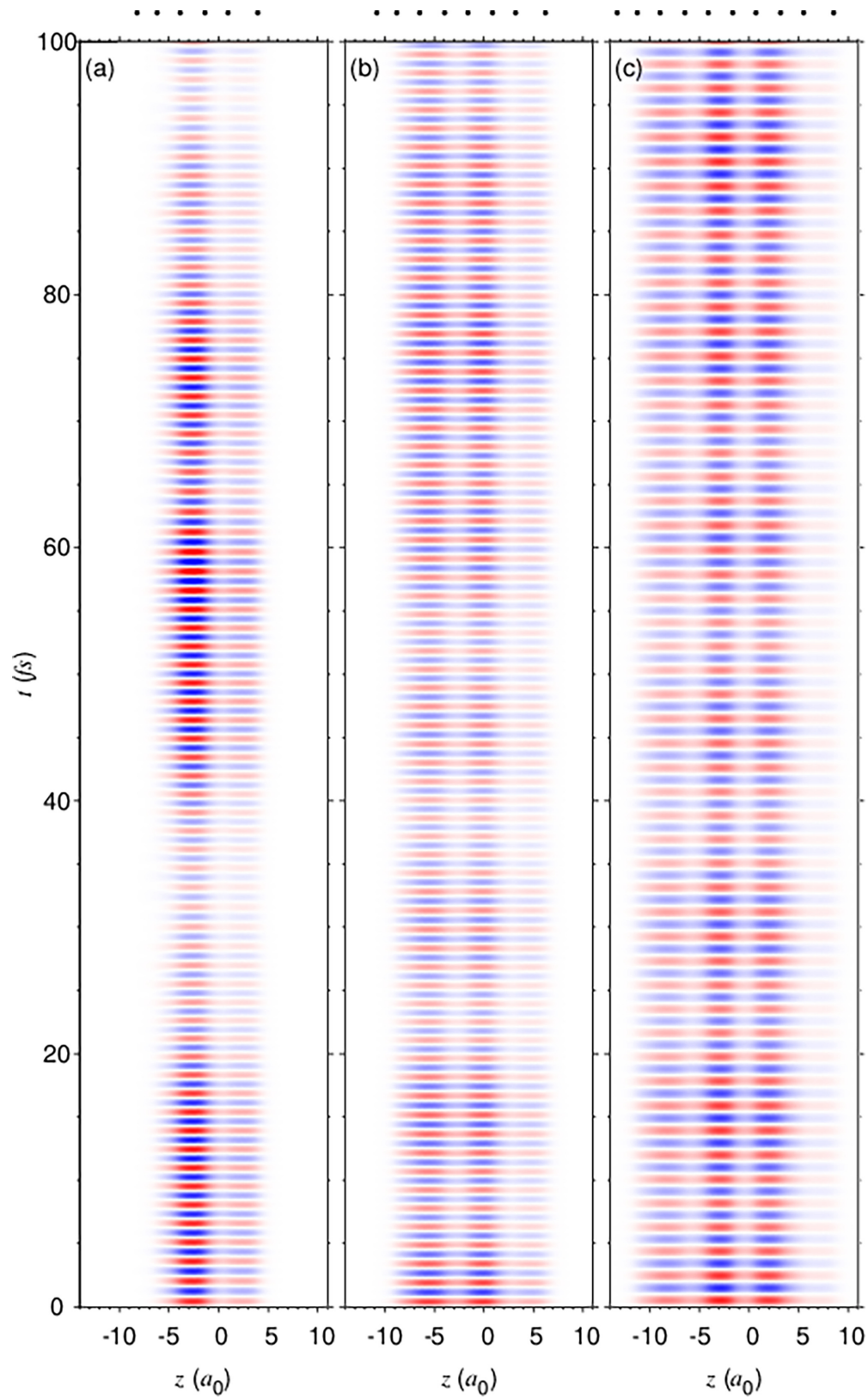


FIG. 2. The electronic flux $F_z(z, t)$ of $\text{H}(\text{CC})_n\text{Cl}^+$ for $t < 100$ fs for (a) $n = 2$, (b) $n = 3$, and (c) $n = 4$. As in Fig. 1, the black dots on the top of each panel indicate the positions of the nuclei. In each panel the leftmost and rightmost dots represent H and Cl, respectively.

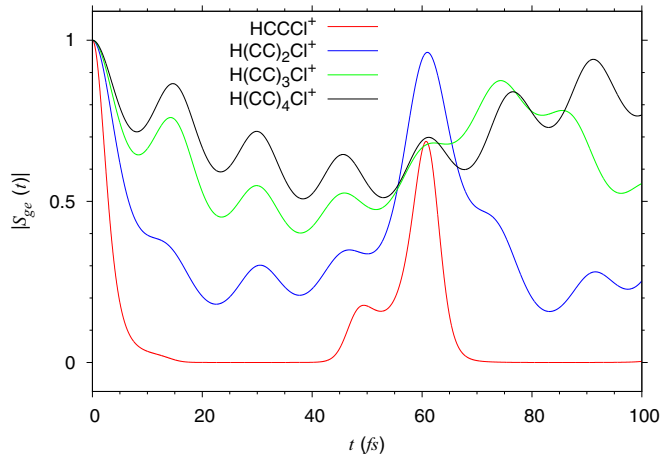


FIG. 3. Absolute value $|S_{ge}(t)|$ of the overlap of the two nuclear wave functions of the ground and first excited states of $\text{H}(\text{CC})_n\text{Cl}^+$ ($n = 1-4$), for $t < 100$ fs. The decay of each curve during the first few fs is fitted to e^{-t^2/τ^2} to estimate the initial decoherence time. Accordingly the first decoherence times of $\text{H}(\text{CC})_n\text{Cl}^+$ for $n = 1-4$ are 3.7, 8.3, 10.2, and 11.2 fs, respectively.

of charge migration. The interval between two neighboring minor recoherences is roughly 15 fs for all cases. This corresponds to the vibrational period of one or more CC triple-bond stretches in the first excited state $|e\rangle$.

Figure 3 reveals a very important phenomenon, namely the overall coherence increases with n , i.e., with the length of the cations. As is known, each vibrational degree of freedom is a source of decoherence. Consequently the number of sources of decoherence increases when the molecular size increases. Each source makes a positive contribution to the total decoherence. It is expected that the larger the molecule is, the faster the decoherence. The overall counterintuitive trend of the decoherence of $\text{H}(\text{CC})_n\text{Cl}^+$ suggests that there must be significant differences between the contributions of specific vibrational modes to the total decoherence. Accordingly, we investigate the contributions of individual normal modes to the decoherences. The results are documented in Table I for

the four $\text{H}(\text{CC})_n\text{Cl}^+$ cations. For easy comparison, a number between 0 and 1 is used to quantify the contribution of each mode. According to Ref. [20], a good choice for this number is the value of $1 - |S_{ge,j}(t)|_{\min}$. Here $|S_{ge,j}(t)|_{\min}$ is the minimum overlap of the corresponding one-dimensional nuclear wave packets along the j th normal mode; cf. Eq. (S5) in the Supplemental Material [42]. Larger numbers mean larger contributions to the decoherences. According to Table I there are only two or three normal modes that make significant contributions to the decoherences of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$. These two or three normal modes are shown in Fig. 4 by arrow plots. All these modes are symmetric, which is consistent with the findings in Ref. [12].

The results shown in Table I allow us to explain the counterintuitive increase of the overall coherence with the molecular size of $\text{H}(\text{CC})_n\text{Cl}^+$. For $n = 2, 3$, or 4, the first three normal modes in Table I make dominant contributions to the decoherence of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$. Apparently, these contributions decrease systematically with molecular size. Consequently, the decoherence of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ decreases when n increases from 2 to 4. From HCCCl^+ to $\text{H}(\text{CC})_2\text{Cl}^+$ the number of dominant sources of decoherence increases due to a moderate contribution from mode 12. However, this does not compensate the large decrease of the contributions of the first two dominant modes. Therefore the decoherence of charge migration in $\text{H}(\text{CC})_2\text{Cl}^+$ is smaller than in HCCCl^+ . Table I also shows that the number of the modes that make non-negligible contributions to decoherence increases with molecular size. This is as expected. But again, those additional contributions are rather small, and they cannot compensate the large decrease of the dominant contributions.

We have investigated systematically the de- and recoherences of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ for $n = 1-4$ with quantum dynamics in terms of normal mode coordinates. Detailed analysis of the contributions from individual normal modes shows that the de- and recoherences of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ are dominated by two (for $n = 1$) or three (for $n = 2-4$) normal modes; cf. Fig. 4. The fast decrease of the contributions of the dominant two or three modes when

TABLE I. Dominant normal mode (j) contributions to the decoherence of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ ($n = 1, 2, 3, 4$). The contributions are quantified as $1 - |S_{ge,j}(t)|_{\min}$ as in Ref. [20]. Modes with contributions smaller than 0.003 are not listed.

HCCCl ⁺										
normal mode j	5	6	2	1	7					
contribution to decoherence	1.000	0.795	0.017	0.017	0.004					
H(CC) ₂ Cl ⁺										
normal mode j	7	10	12	11						
contribution to decoherence	0.695	0.408	0.341	0.005						
H(CC) ₃ Cl ⁺										
normal mode j	7	18	16	14	15					
contribution to decoherence	0.453	0.203	0.111	0.075	0.008					
H(CC) ₄ Cl ⁺										
normal mode j	9	23	22	24	16	19	17	18	14	15
contribution to decoherence	0.334	0.122	0.104	0.041	0.029	0.006	0.005	0.005	0.003	0.003

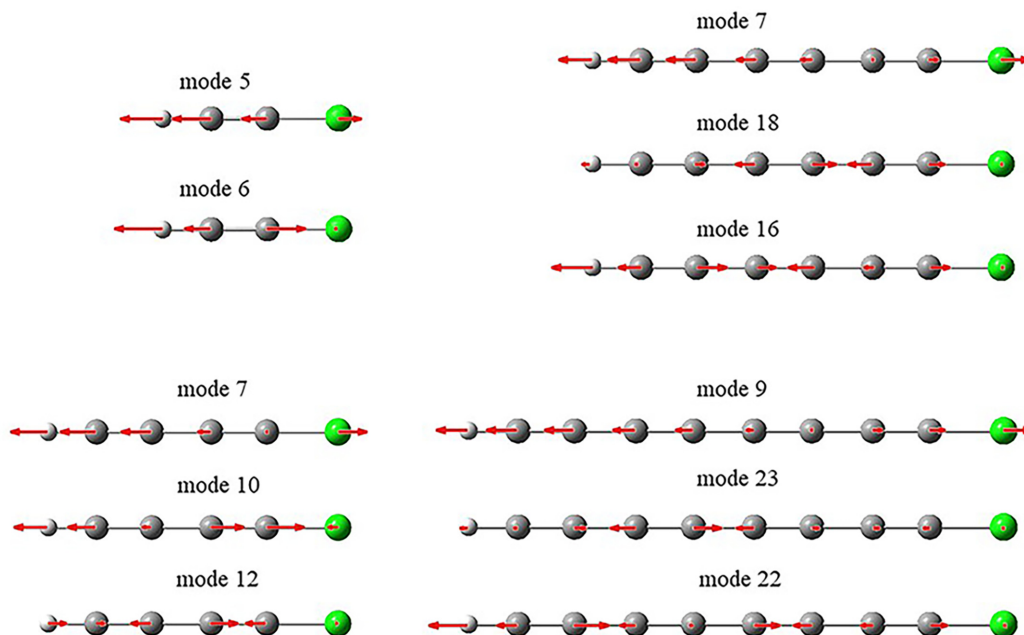


FIG. 4. The most important normal modes that dominate the de- and recoherences of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$. There are two modes for $n = 1$ and three modes for $n > 1$; cf. Table I.

n increases leads to the counterintuitive fact that the overall coherence of charge migration in $\text{H}(\text{CC})_n\text{Cl}^+$ increases with molecular size.

The present increase of electronic coherences during charge migration with molecular size in $\text{H}(\text{CC})_n\text{Cl}^+$, $n = 1$ –4 cannot be extrapolated to other systems. The decoherence of charge migration depends on the difference between the two potential energy surfaces of the ground and excited states. There are no general rules for these differences for specific molecules. It may even happen that the difference along one vibrational mode is larger than the sum of the differences along many other modes; cf. the data in Table I. Accordingly, it is easy to predict that one may find a relatively large molecule which has a longer coherence time than certain smaller molecules. But it is nontrivial to really find a specific example, in particular an example with sufficiently long coherence time.

It should be noted that for $\text{H}(\text{CC})_n\text{Cl}^+$ ($n = 2$ –4) the amplitudes of charge migration never decrease to zero during the first 100 fs; in particular the amplitude of charge migration in $\text{H}(\text{CC})_4\text{Cl}^+$ is always larger than 50% of its maximum. This 100 fs time window of continuous charge migration is one order of magnitude longer than the cases that

have been reported previously. The long-lived coherence will be maintained even for $t > 100$ fs until the effects such as mode-mode coupling, anharmonicity, or nonadiabatic transitions become non-negligible. The longest molecular ion of the present series, $\text{H}(\text{CC})_4\text{Cl}^+$, should be a promising candidate for applications that need long-time coherence of electron dynamics. Our discovery should be stimulating for searches for analogous effects in other large systems.

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The data supporting this study's findings are available within the article or the Supplemental Material.

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