Ultrafast charge migration in the laser induced dynamics of LiH validated by a computation-free isotope effect

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ABSTRACT

Charge migration in LiH molecule and its isotopomers LiD and LiT is examined by quantum dynamics including the non-adiabatic effects of nuclear motions. Upon excitation by an ultrafast UV pulse, mass-independent charge migration occurs between the ground and first excited Σ state. The opposite polarity of these states and a relatively small energy gap between them allow the charge to oscillate at early time of the dynamics during 2 fs after the pulse is over. When the nuclei move, a mass-dependent revival of coherence is computed with a period of 80, 107, 123 fs for LiH, LiD, and LiT, respectively.

1. *Introduction*

To understand the stable geometry of the ground electronic state of molecules, the motion of electrons and nuclei was separated due to a large difference between their mass [1]. This idea is at the heart of the adiabatic approximation, and it enables the simplification of the Schrödinger equation so that it can be solved for molecular systems at lower excitation energies. However, non-adiabatic effects due to the motion of the nuclei occur in special regions on the potential energy surfaces where adiabatic potentials almost reach one another and therefore interact strongly [2-5]. At and near such regions the wave function must be described as a double sum of separable terms for the dynamics of the electrons and nuclei, and electronic reorganizations can take place [6-8]. Attosecond pulses have opened the door for investigations of very early time of molecular dynamics [9] and in 2014 charge migration was experimentally seen in phenylalanine [10] and then in other molecules [11-16]. On a computer, two types of approximations – "frozen" and "moving" nuclei – were employed to study the dynamics of charge migration. In general, the effect of nuclear motion is not significant at early time of the propagation [17-19]. Here we discuss a pure electronic reorganization in a molecule even *before* its nuclei start moving as proposed in [7] when in a sudden like excitation we create a coherent superposition of electronic states of different character. The new point is that we here report molecular quantum dynamics simulations where the nuclei are allowed to move while the system evolves in time. We demonstrate the effect in a manner that is essentially computation-free by comparing the separately computed ultrashort time dynamics of three isotopomers. The three transition dipoles essentially overlap one another at early times while they clearly exhibit a mass dependent recurrence at longer times.

LiH is a classical prototype for studying charge migration [20]. In the ground electronic state (GS) the atoms are bound by a fairly ionic chemical bond, $Li^{\delta+}H^{\delta-}$. The lowest excited $^1\Sigma$ state is of opposite character $Li^{\delta-}H^{\delta+}$ [21] and so the charge is reorganized in going from the ground to excited state. The polarization of a one-cycle IR pulse has been shown as the key ingredient in controlling the dynamics of the state population in LiH [22]. Changing the carrier envelope phase (CEP) of the ultrafast laser pulse, one can stimulate charge transfer from H to Li or vice versa and thereby determine the predominate population of the $1^1\Sigma$ ($Li^{\delta-}H^{\delta+}$) or $2^1\Sigma$ and $4^1\Sigma$ ($Li^{\delta+}H^{\delta-}$) excited states[21,22].

The energetic gap between the GS and first excited $1^1\Sigma$ state is atypically small and because of their opposite polarity these states are optically coupled by a relatively strong transition dipole.

In addition, our computations take into account six other electronically excited $^1\Sigma$ states. We use a one cycle UV pulse centered at 3.5 eV to excite the $1^1\Sigma$ state primarily and with limited access to the higher excited states. Once the pulse starts, a coherent superposition of the GS and $1^1\Sigma$ is created and these two states will be most populated during the propagation. Thus, the unique electronic structure of LiH and the correct settings of the laser pulse allow us to follow the charge oscillations between the coherently excited two lowest electronic states. The nuclei are not constrained in their movement and to probe the effect of their motion, the ultrashort time evolution of the expectation value of the transition dipole moment (the transition density) for the three isotopomers, LiH, LiD, and LiT, is compared. In this paper we examine the early time charge oscillations while allowing the unconstrained dynamics of the nuclei.

2. *Results and discussion*

We chose LiH as an example because the first excited $1^1\Sigma$ state is relatively close to the ground state in the Franck-Condon region, Figure 1. The potential energy curve of $1^1\Sigma$ is shallower, and it is less tightly bound than the ground state.

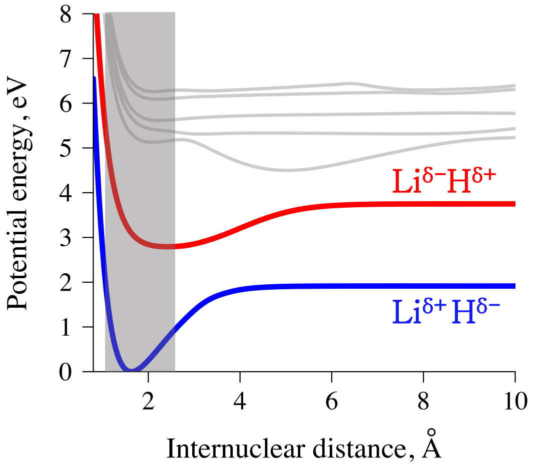

Figure1. Potential energy curves of LiH of Σ symmetry: the GS is shown in blue, the first excited $1^1\Sigma$ is in red, other excited $^1\Sigma$ are plotted in grey, the Frank-Condon region is identified as a shaded grey area. The curves computed at the state averaged CAS-SCF (4, 20) level of theory are taken from [23].

The ultrashort laser pulse creates a non-stationary coherent superposition of the GS and $1^1\Sigma$ states with a much smaller component of higher electronic states. For the very short initial period after excitation, we can imagine the nuclear motion to be frozen. Then, as in [7] and explicitly for LiH in[24], the wave function is written as a coherent sum of the two electronic states that we designate as A and B with complex amplitudes $X=|X|\exp(i\phi_X),\, X=A,B$ and $\hbar=1$

$$\begin{aligned}&\left\||A|\Psi_A\exp(-iE_At+i\phi_A)+|B|\Psi_B\exp(-iE_Bt+i\phi_B)\right|^2\\&=|A|^2\Psi_A^2+|B|^2\Psi_B^2+2|A||B|\Psi_A\Psi_B\cos\left(\left(E_B-E_A\right)t-(\phi_B-\phi_A)\right)\end{aligned} \tag{1}$$

It shows the charge overlap $\Psi_A\Psi_B$ oscillating with the frequency $\left(E_B-E_A\right)$. For most molecules this is a high frequency but for LiH it is in the femtosecond range. The coherent charge migration is therefore expected to survive for a measurable while. It is up to the exact dynamical simulation to validate this.

For the exact numerical dynamics, we use a UV laser pulse with a central frequency of 3.5 eV and a one cycle width (σ = 0.40 fs) as shown in Figure 2 and in Figure S1 and equation (3) of the Supplementary Materials (SM). We use a pulse along the molecular axis and compute for two opposite directions that take the charge away from Li or vice versa. Changing the direction of the pulse field corresponds to changing the CEP from 0 to π. The wave packet is propagated on a grid of internuclear coordinate by solving the time-dependent Schrödinger equation numerically essentially following [25]. The computational details are given in the SM.

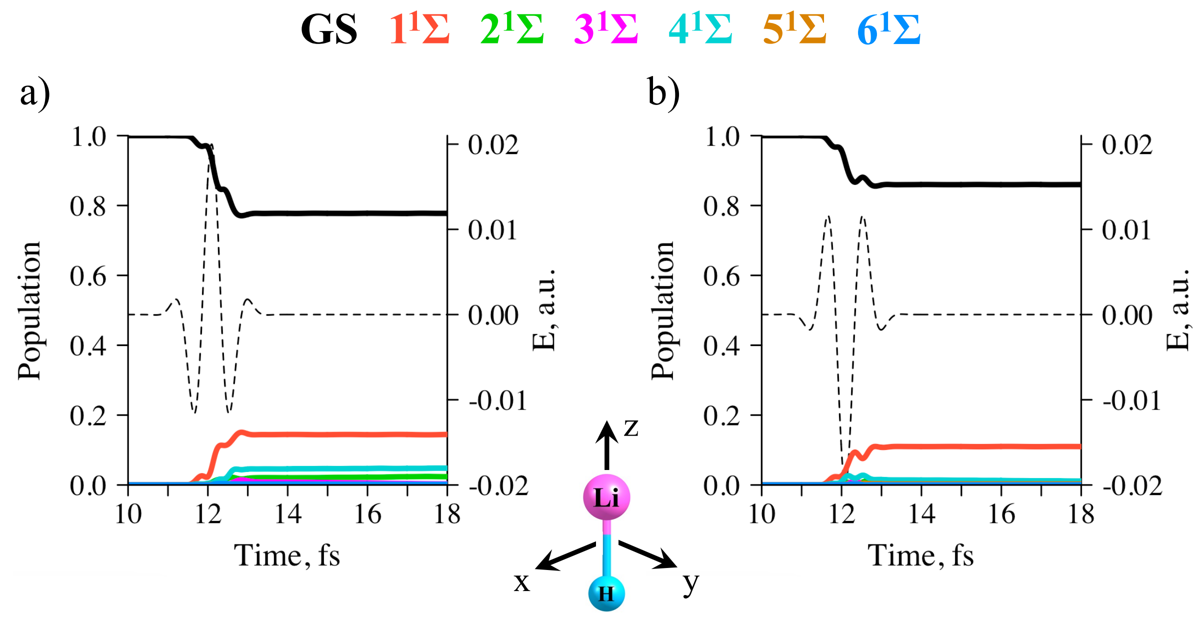

Figure 2. Population of the GS and 6 excited states of Σ symmetry of LiH for a) +z direction of the field; b) -z direction of the field with the coordinate system shown in the insert. The pulse profile, E, is shown with a dashed line as a function of time.

As shown in Figure 2, the laser barely populates the excited states beyond the first one and therefore the laser polarization essentially affects only the first excited state. As a check of the limited role of the higher states we included only the GS and $1^1\Sigma$ state in the propagation scheme with both +z and -z pulses (Figures S3a and S3d of SM) and the dynamics of the coherent charge exchange between the two states remained the same. We furthermore broadened the width in time making the pulse a multi-cycle one and also for this pulse, the GS and $1^1\Sigma$ state were mostly populated during the propagation (Figures S3c and S3f of SM).

In the computations, the pulse is centered at 12 fs. From 11.5 to 13 fs, the population is oscillating according to the direction of the pulse and then it becomes constant (Figure 2). After 30 fs the non-adiabatic couplings can be seen in the mixing of higher electronically excited states with some delay for the heavier isotopomers (Figure S4 of SM).

We now focus on the very early times of the numerically exact quantum dynamics including the nuclear motion, that we describe along a dense grid of points R_g, g =1,2,.. . The charge migration between the two electronic states is exhibited by computing the electronic transition dipole $\mu^{el}(t)$ between the two states A and B integrated over all grid points R_g at each time t:

$$\mu^{el}(t)=\sum_g c^*_{Ag}(t)c_{Bg}(t)\mu^{el}_{AB}(R_g) \tag{2}$$

We first show the integrand of equation (2), the transition density (electronic coherence weighted by the transition dipole), as a two-dimensional heatmap, Figure 3, for the pulse polarized in +z (Figures 3a) and -z (Figures 3b) directions.

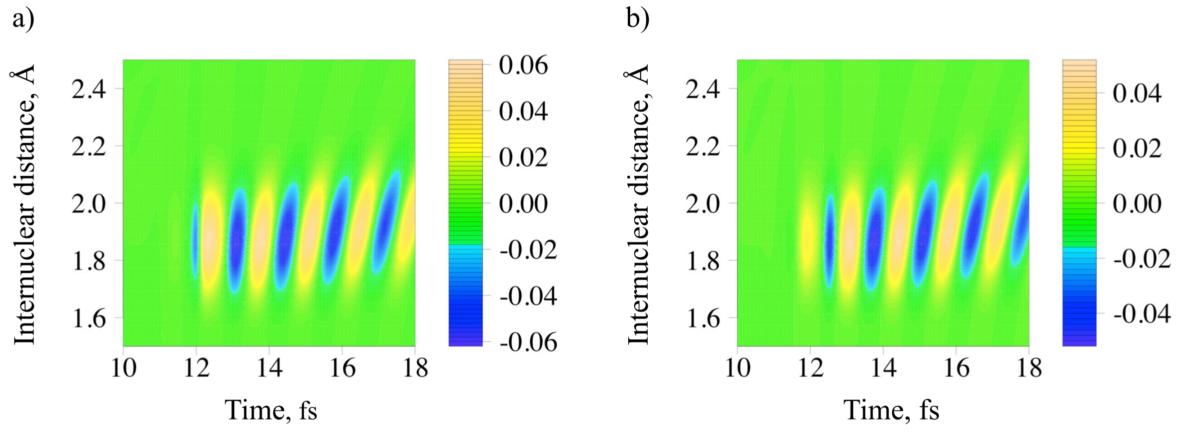

Figure 3. Heatmaps of the transition density between the GS and $1^1\Sigma$ states of LiH as a function of internuclear distance and time for a) +z direction of the pulse: b) -z direction of the pulse.

The heatmaps show charge oscillations between two states of opposite polarity centered about the equilibrium position of the GS. The initial direction of the charge migration is seen to be controlled by the direction of the electrical field. Several oscillations of the charge are resolved before the wave packets are moving away from the Franck-Condon region and this occurs at about 15 fs or roughly 2 fs after the pulse is over.

Once the nuclear wave packets are moving out of the FC region, one expects the impact of nuclear motion on the charge coherence. To probe the role of the mass, we repeated the computation for the heavier isotopomers LiD and LiT and show the time-dependent transition dipole between the GS and $1^1\Sigma$ state – the sum from Equation 2 (Figure 4 and Figure S5 and S6 of SM).

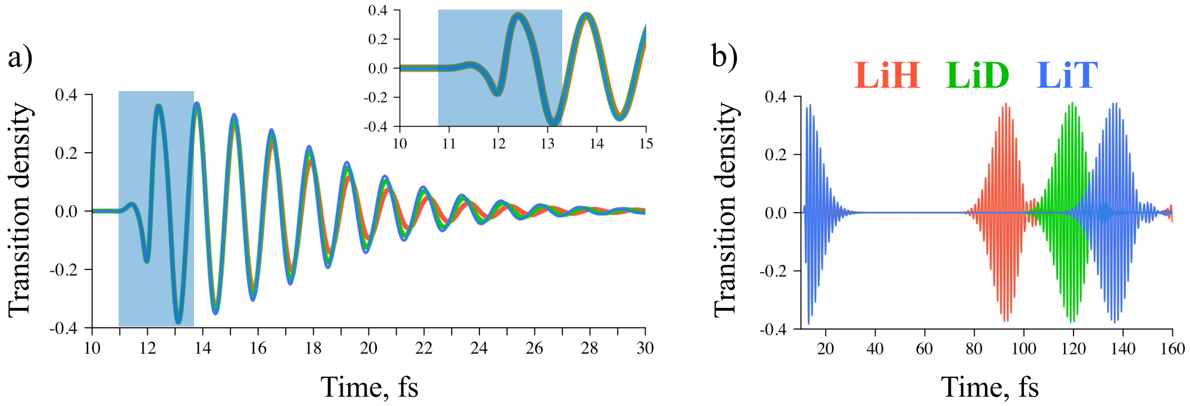

Figure 4. Time evolution of the transition density between the GS and $1^1\Sigma$ states of LiH, LiD, LiT +z direction of the pulse. The results for the -z direction of the pulse are shown in the SM. The two time profiles are for a) duration of 30 fs with a zoomed in picture of a shorter time up to 15 fs, the span of the pulse is indicated by the shaded blue area; b) duration of 160 fs. Note the overlap of the transition densities of the three isotopomers at the short times.

During first 2 fs's after the pulse ended, the identical charge oscillation is seen for all the isotopomers independently of their mass. The sign of the oscillations depends on the direction of charge migration, which is determined by the polarization of the pulse (Figure S5a and S6a). The shallow shape of the potential energy curve of $1^1\Sigma$ allows the isotopomers' wave packets to move relatively slowly and be localized in the FC region during first fs of the dynamics but after 16 fs, the transition density becomes more delocalized as shown in Figure 3. At longer times, Figure 4b, dephasing sets in, and finally a significant mass-dependent recurrence occurs because the momentum and so the velocity of the isotopomers' wave packets depends on the mass.

3. Conclusions

We have probed the very early time coupled electron-nuclear dynamics of laser pumped LiH and its isotopomers. As expected, once the nuclei move, the three isotopomers behave quite differently. The longer time effect of the mass is primarily due to the speed of vibration along the bond distance as can be seen from the relative times when the coherence recurs, Figure 4b. However, during a few fs's after the pulse is over, the transition density of the three isotopomers overlaps as clearly shown in Figure 4a. That the ultrashort time evolutions of the transition density are superposable for the free isotopomers provides a computation–free demonstration of an electronic reorganization that is mass-independent.

Author contributions

All authors have contributed to the analysis of the results and the writing of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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