Librational control of photochemical reactions in small clusters

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Abstract

A novel approach to the enhancement of photochemical reaction yield in hydrogen containing clusters is outlined and applied to the process of the Cl_2 molecule formation from a UV photolyzed Cl...HCl species. The control mechanism consists in a far-IR preexcitation of the large amplitude hydrogenic bending (librational) mode prior to the HCl photodissociation. Molecular dynamics simulations which properly sample the initial quantum state of the system show that this leads to more than a factor of two enhancement of the Cl_2 yield both in the parent and deuterated clusters.

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I. INTRODUCTION

Hydrogen containing weakly bound clusters possess unusual properties connected with the quantum mechanical motion of the light atom in a shallow intermolecular potential. Namely, the large amplitude hydrogenic bending motions in clusters such as $HCl(Ar)_n$, n=1,2,... strongly influence the electronic ground state properties as well as the (photo)excited state dynamics.[1−15] For the hydrogenic bend in these clusters a significant delocalization from the equilibrium geometry is typical already for the ground v_b=0 state, this effect being even much stronger for v_b=1 and higher states.[2] In the case of a completely solvated HCl molecule in large argon clusters or matrices this bending motion changes into an almost free rotation.[11−12] Therefore, terms like hindered rotation[1] or libration,[16] rather than vibration are often used in this context.

In a recent study, we have proposed to replace in the above clusters one of the argon atoms by a chlorine radical and to exploit the large difference between the v_b=0 and v_b=1 wavefunctions for a photochemical reaction yield control.[17] The idea of vibrational control has been pursued by several groups for more than a decade. It has been demonstrated that e.g., for a partially deuterated water molecule different photofragmentation channels can be opened by a UV photolysis depending on a particular IR vibrational preexcitation of the OH or OD bond.[18−22] The scheme outlined in this paper differs in two major points. First, a weak intermolecular mode in a cluster is preexcited instead of a strongly bound intramolecular vibrational degree of freedom. More importantly, we propose to control by IR-preexcitation the yield of an association chemical reaction initiated by a UV-photolysis instead of controlling the relative yields of photofragments.

Namely, using molecular dynamics simulations we have demonstrated that in a cluster consisting of a HCl molecule trapped on a $Cl(Ar)_{12}$ cluster the Cl_2 yield is enhanced from 2 to 70% by the hydrogenic librational $1 \leftarrow 0$ far-IR preexcitation prior to the HCl molecule UV photolysis. From the experimental point of view this should be a strong, directly observable effect. However, technical difficulties connected with the isolation of the $Cl(Ar)_{12}HCl$ species are non-trivial. In this paper, we focus on a much smaller and simpler Cl...HCl cluster and show that the idea of librational control works here, too.

The ClHCl species has been intensively studied both theoretically and experimentally in connection with the symmetric hydrogen exchange reaction Cl + HCl $\rightarrow$ HCl + Cl and the strongly exothermic Cl_2 + H $\rightarrow$ HCl + Cl exchange reaction.[23–30] The van der Waals region of the system, corresponding to the Cl...HCl cluster has been mapped in terms of potentials and vibrational/librational eigenstates.[31] It follows from this analysis that the Cl...HCl cluster should be more stable than its thoroughly investigated closed shell Ar...HCl analogue, and the possibility of the isolation of the Cl...HCl species under supersonic jet conditions has been considered.[32]

The paper is organized as follows. In Section II we briefly describe the system and computational methods. In Section III we present and discuss the results, and a brief summary is given in Section IV.

II. SYSTEM AND COMPUTATIONAL METHODS

The equilibrium ground state geometry of the Cl...HCl cluster is collinear with the hydrogen atom lying asymetrically between the two chlorines.[31] The collinear arrangement is primarily due to the quadrupole-quadrupole and dipole-quadrupole interactions between the HCl molecule and the Cl radical which significantly contribute to the attractive intermolecular potential resulting in a 383 cm^{-1} deep minimum at the Cl-Cl separation of 3.9 Å.[31] These interactions align in the collinear geometry the singly occupied p-orbital of the Cl radical perpendicular to the HCl molecular axis. Although the optimal geometry is collinear, the bending potential is very shallow and the hydrogenic librational wavefunctions sample extensively also bent structures. A general non-linear geometry with a bending H-Cl(of the HCl molecule)-Cl(radical) angle θ is schematically depicted in Fig. 1. It follows from a simple analysis of the intermolecular forces[31] as well as from test *ab initio* HF/6-31G* calculations performed by the authors that in order to optimize the electrostatic interaction, the p-orbital of the Cl radical rotates upon bending approximately by the same angle θ from its equilibrium orientation (perpendicular to the Cl-Cl axis), however, in the opposite direction than the HCl axis. This leads to the fact that for θ=90^o this p-orbital lies along the Cl-Cl axis[31] which is, as is also shown below, the most favorable orientation for the Cl_2 molecule formation by HCl photolysis. The ground electronic potential energy surface is further shaped by the spin-orbit coupling, especially for large bending angles.[31] Here, we take the spin-orbit interaction into account only implicitly (by employing the lowest adiabatic surface from Ref. 31 for the construction of librational states), neglecting its influence on the p-orbital dynamics in the ground and (photo)excited electronic states. This makes a simple orbital analysis possible, however, quantitative errors may be introduced for higher librational states which extensively sample regions with large values of the bending angle θ where strong spin-orbit mixing occurs.

The initial librational wavefunctions are generated using the ground adiabatic θ-dependent potential at the fixed optimal Cl-Cl distance of 3.9 Å, using a spherical harmonics basis (up to J=10) similarly as in Ref. 31. This gives for the Cl...HCl system the ground and first excited librational state energies of -304 and -236 cm^{-1}, in good agreement with the published values of -299 and -237 cm^{-1} following from the fully coupled calculation.[31] This agreement indicates that the simple calculations presented here should provide reliable librational wavefunctions for the low-lying states. The calculations in Ref. 31 also show that the $0 \leftarrow 1$ librational transition has a sufficient oscillator strenght to be realized experimentally.

An empirical rule stating that a satisfactory description of photochemical processes is usually achieved using classical trajectories, provided the initial quantum state of the system is properly sampled[32] is applied to the dynamical process under study. Namely, during photodissociation the hydrogen atom acquires a large portion of kinetic energy which brings it close to the classical limit. The chlorine atoms are much colder but they are also significantly heavier which makes again classical approach plausible. However, we have to account for the fact that prior to photolysis the cold and light hydrogen atom which moves with a large amplitude in a very shallow potential well is a strongly quantal object. In this work, we adopt a semiclassical approach in which a swarm of classical trajectories the initial coordinates of which sample properly the initial quantum delocalized hydrogenic librational wavefunction is propagated and analyzed. At typical experimental temperatures of only few Kelvins the initial classical momenta of all particles can be approximately set to zero and the trajectories of the heavy atoms are initiated from their equilibrium positions.

Classical trajectories, started at the moment of HCl photoexcitation and sampling different values of the bending angle θ are propagated for 1 ps with a 0.25 fs timestep using a standard Gear algorithm.[33] The attractive ground state Cl-Cl potential is taken from Ref. 34 while the ground $^1\Sigma$ and first excited $^1\Pi$ HCl potentials are the same as in Ref. 35.

In the end of this section we stress the fact that the computational approach adopted here is a compromise between accuracy and feasibility. Ideally, one would like to have a fully *ab initio* description of the ground and excited electronic states involved together with a numerically exact quantum treatment of the nuclear motions. This would require elaborate post-Hartree-Fock methods including spin-orbit treatment for massive numerical evaluation of potential energy surfaces and possibly also non-adiabatic couplings between them on one side, and at least a three-dimensional wavepacket propagation on an extended space grid on the other side. While this is probably beyond the present computational means, the simple semiclassical dynamical method using empirical potentials employed in this study is very economic. At the same time, the observed effect of librational control is qualitative and strong enough to be revealed by the present approximate approach.

III. RESULTS AND DISCUSSION

The shapes of the ground and first excited librational wavefunctions in the Cl...HCl cluster and its deuterated analog are depicted in Fig. 2. The ground wavefunctions are located around the equilibrium collinear geometry, however, with a significant spread of about 26^o for Cl...HCl and 22^o for Cl...DCl. The first excited wavefunctions peak at strongly bent geometries (θ=35^o for the hydrogenated and θ=29^o for the deuterated cluster) and are significantly broader than the ground state functions. As will be seen later, this difference has a crucial effect on the Cl_2 photochemical yield.

Upon UV photoexcitation, the unpaired p-orbital of the Cl species in the HCl molecule is twisted into the π-plane, perpendicular to the HCl molecular axis (see dotted p-orbital contours in Fig. 1). Due to the strongly repulsive character of the excited potential and the light mass the hydrogen atom flies within few femtoseconds out of the scene (except for practically collinear configurations the weight of which is, however, negligible). In the simple orbital treatment presented here, we assume that after the rapid exit of the hydrogen atom the two unpaired chlorine p-orbitals are aligned in the same way as directly after the photoexcitation, i.e. one is in the π-plane while the other lies in the H-Cl-Cl plane with the angle to the Cl-Cl axis being 90^o-θ. Here, θ represents the initial bending angle, as sampled by the classical trajectory. At this point we project the two p-orbitals on the Cl-Cl axis which gives the contribution to the attractive ground electronic Cl-Cl interaction, the rest having a non-bonding character. It follows from Fig. 1 that the weight of the bonding part $\omega_B(\theta)$ equals to $2sin^2\theta/\pi$. Namely, the factor $2/\pi$ comes from the projection of the p-orbital of the photolyzed chlorine into the H-Cl-Cl plane, integrated over all possible orbital orientations in the π-plane (see Fig. 1). In the H-Cl-Cl plane, the bonding contribution (projection to the Cl-Cl axis) is $sin\theta$ for each of the two chlorine atoms. Since the non-bonding part of the interaction with weight 1-$\omega_B(\theta)$ is repulsive with only a very shallow van der Waals minimum it cannot stabilize the Cl_2 species. As a result, in the non-bonding situation the recoil from the photolyzed H atom leads to direct separation of the two chlorine atoms for all angles θ sampled by the studied librational wavefunctions. Therefore, from the point of view of the formation of the Cl_2 molecule we only have to consider, with the proper weight $\omega_B(\theta)$, the bonding Cl-Cl interaction in the molecular dynamics simulations.

The following picture is obtained from a set of classical trajectories described in the previous section. Except for very small angles $\theta < \lambda$ which result in a strong H-Cl collision and a consequent complete disintegration of the cluster, a highly vibrationally excited but stable Cl_2 molecule is always formed in simulations employing the ground state Cl-Cl potential. The limiting angle λ equals to 4^o for the Cl...HCl cluster and grows to 11^o for Cl...DCl due to a larger recoil and a more efficient light particle-heavy particle collision in the deuterated complex. Fig. 3 shows the time evolution of the Cl-Cl distance for a typical reactive trajectory started with $\theta = 40^o$ for which the librational first excited state population is already significantly larger than that of the ground librational state for both hydrogenated and deuterated clusters. After an initial period of less than 20 fs which is influenced by the presence of the hydrogen atom a regular Cl_2 vibrational pattern is observed. The ground state Cl-Cl Morse potential[34] supports 104 bound vibrational states. For the Cl...HCl case, the Cl_2 molecule is stabilized at v=76 (0.264 eV below the dissociation limit), while for the deuterated species at v=81 (0.174 eV below the dissociation limit). The higher final Cl_2 vibrational state in the deuterated complex is due to the doubled recoil energy.

Within our model, the Cl_2 photochemical quantum yield Y can be expresses as

$$Y = \int_{\lambda}^{\pi} \mid \Phi(\theta) \mid^2 \omega_B(\theta) sin\theta d\theta, \tag{1}$$

where $\Phi(\theta)$ is the (ground or first excited) librational wavefunction, λ is the limiting bending angle for reactive trajectories, and $\omega_B(\theta)$ is the relative weight of the two p-orbital projections on the Cl-Cl axis corresponding to the ground Cl_2 potential, as defined above. For the Cl...HCl cluster initially in the ground librational state a quantum yield of 16% is observed, this number rising to 35% upon the $1 \leftarrow 0$ librational preexcitation. In the deuterated species these numbers are only 11 and 25% respectively, due to the less delocalized character of the librational wavefunctions and the fact, that geometries with small initial bending angles θ are unfavorable for the photochemical formation of the Cl_2 molecule due to kinematic and even more importantly p-orbital orientation factors. We see that switching on the librational control mechanism results in the hydrogenated (deuterated) cluster in a factor of 2.2 (2.3) increase of the Cl_2 photochemical quantum yield, which is a strong enough effect to be observable in an experiment.

IV. CONCLUSIONS

In summary, we present in this paper a new scheme for the photochemical reaction yield control in small hydrogen containing clusters and demonstrate its efficiency for the Cl_2 molecule formation from UV photolyzed Cl...HCl and Cl...DCl clusters. The control mechanism consists in the far-IR preexcitation of the large amplitude librational (bending) motion prior to the photodissociation of the HCl or DCl molecule. Molecular dynamics simulations which account for the quantum nature of the initial librational state show that the librational control mechanism enhances the quantum yield of the formation of the Cl_2 molecule by more than a factor of two, from 16 to 35% in the Cl..HCl and from 11 to 25% in the Cl...DCl complex.

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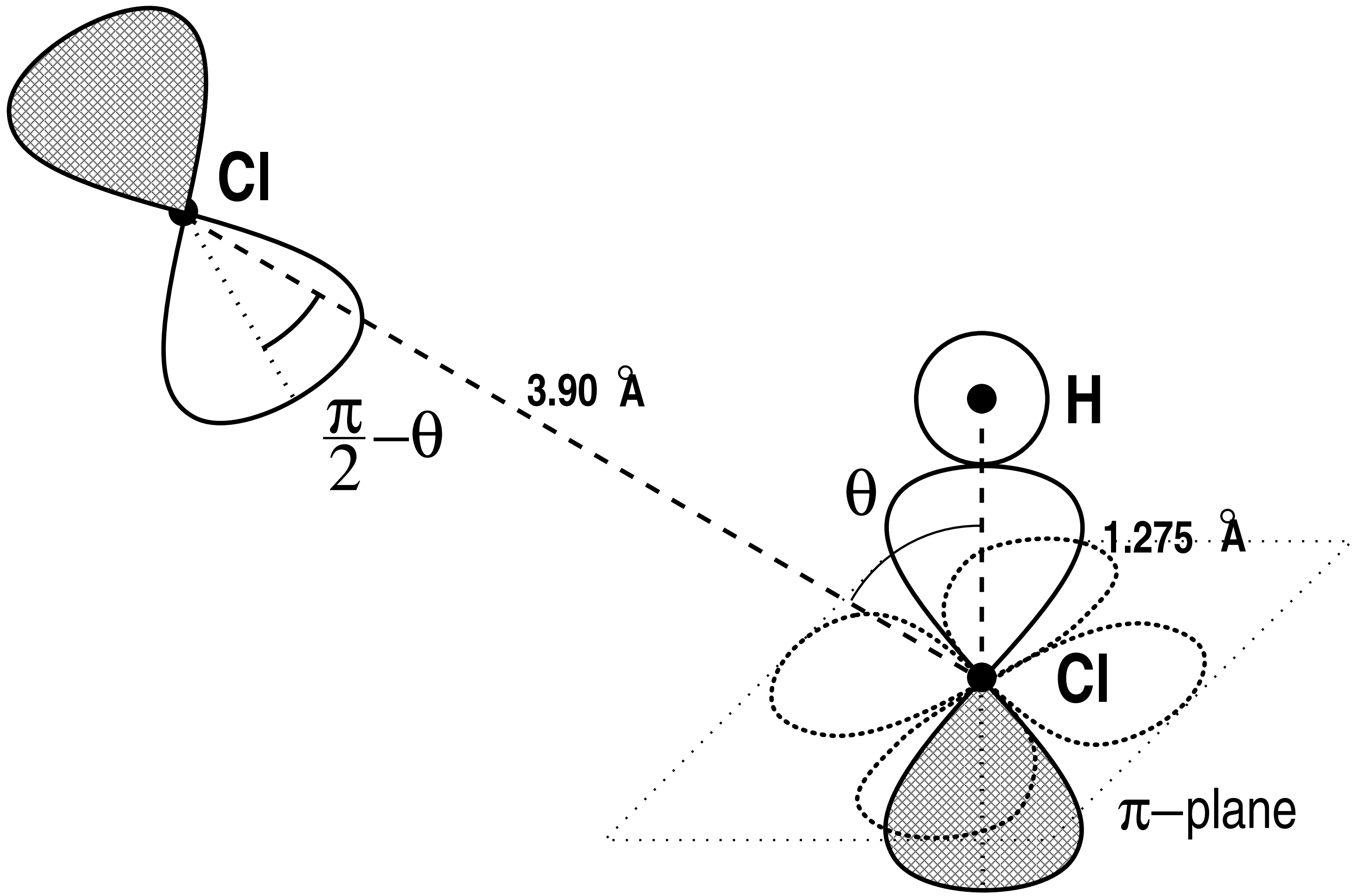
FIGURES

FIG. 1. The structure of the Cl...HCl complex for a general value of the bending angle θ with a schematic plot of the singly occupied p-orbital of the Cl radical and the bonding situation in the HCl molecule. Upon HCl UV photoexcitation the unpaired p-orbital of the HCl chlorine is twisted into the π-plane (dotted orbital contours).

FIG. 2. Squares of the delocalized ground and first excited librational (bending) wavefunctions for the Cl...HCl and Cl...DCl cluster.

FIG. 3. Time evolution of the Cl-Cl distance for a reactive trajectory with the initial bending angle $\theta = 40^o$ in the Cl...HCl and Cl...DCl clusters. The final Cl_2 vibrational state is v=76 in the former and v=81 in the latter complex.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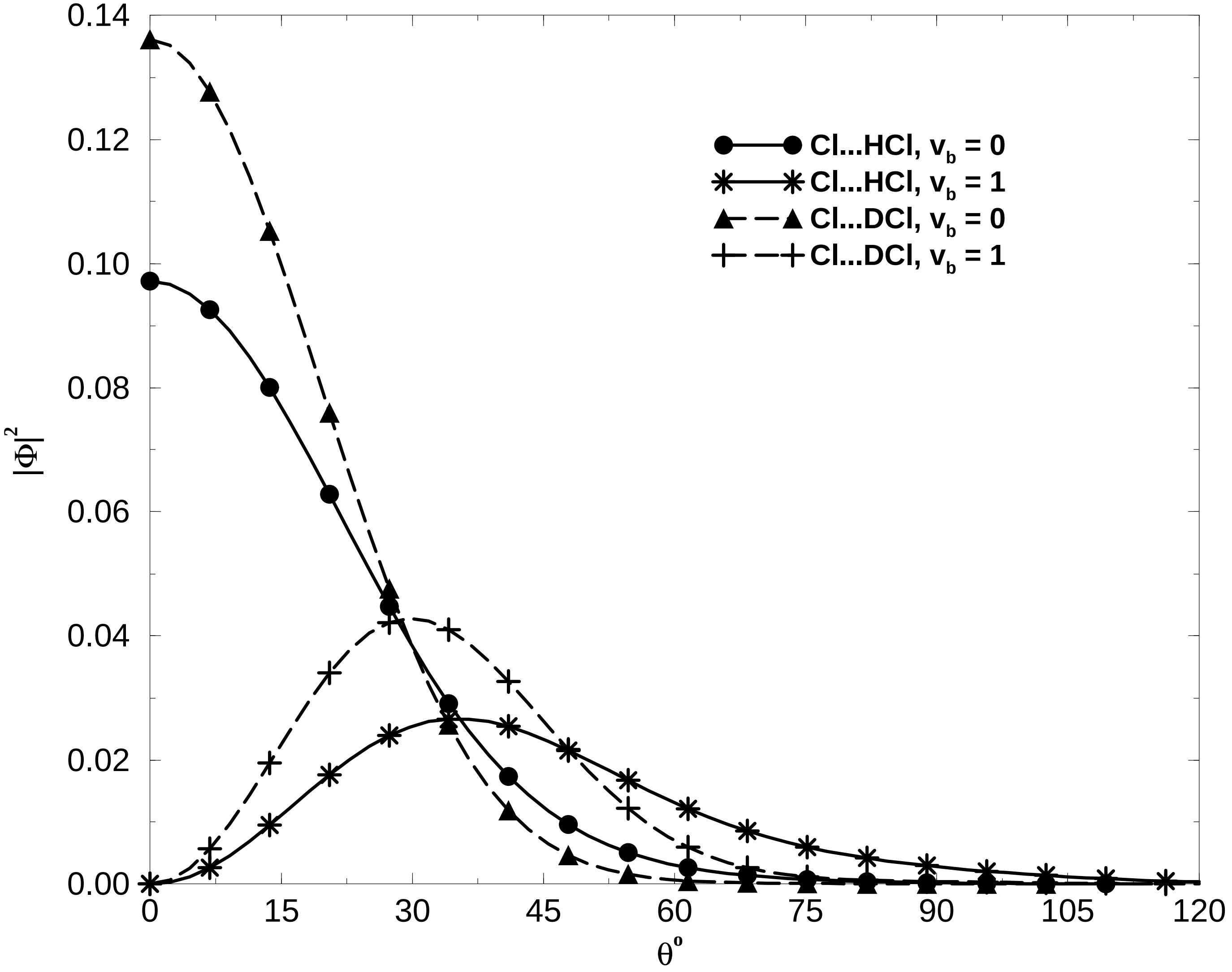
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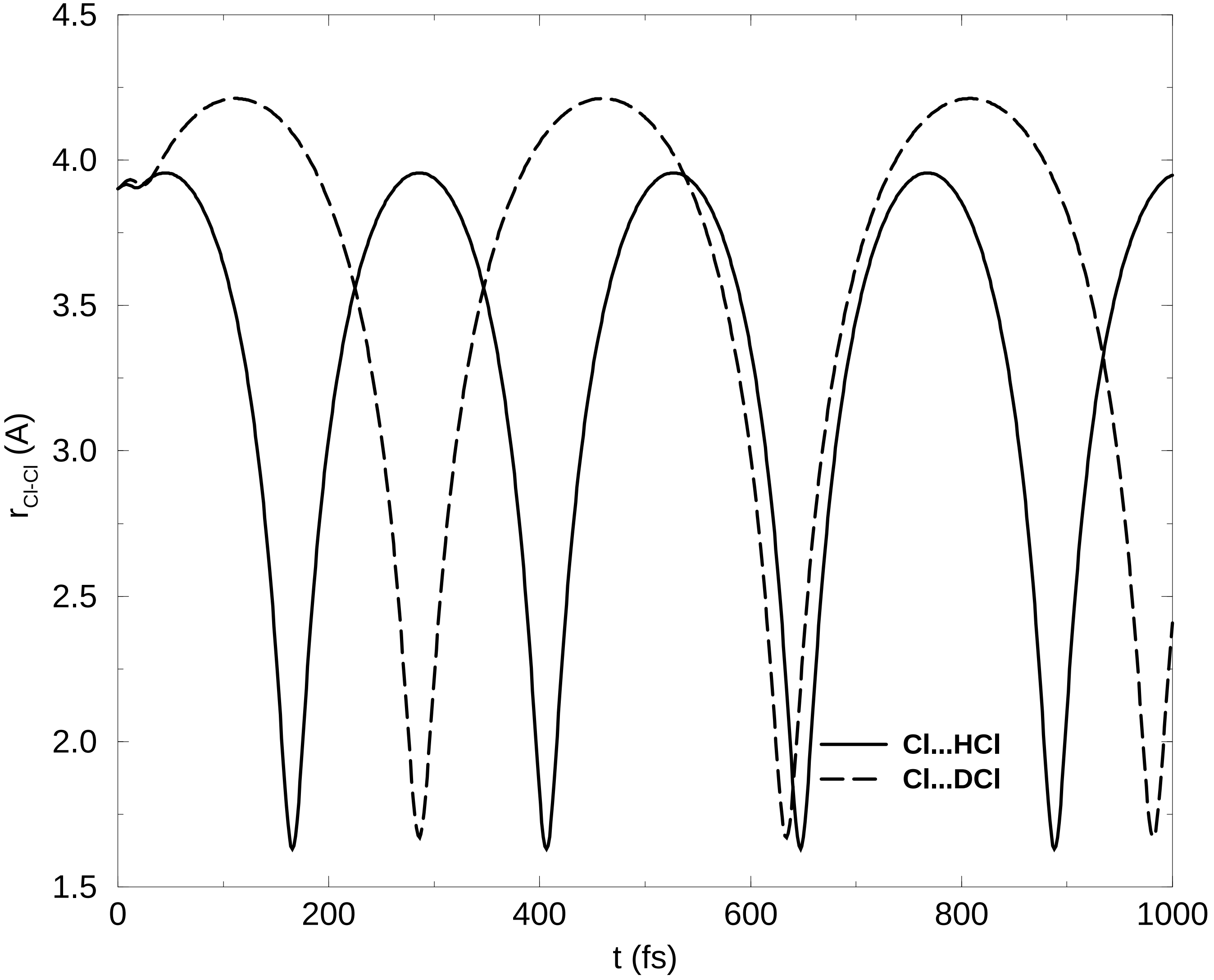
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