Nonadiabatic photodynamics of amantadine and cyanoadamantane cations: Departure from the energy gap law?

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Abstract

Cations of diamondoids and derivatives thereof have recently become the subject of experimental, spectroscopic studies due to their potential role in astrochemistry. In particular, their electronic spectra and photoinduced dynamics trigger great interest. Here, we report on computational investigations of two nitrogen-containing derivatives of the adamantane cation (Ada$^+$, C$_{10}$H$_{16}^+$), the amantadine cation (Ama$^+$, C$_{10}$H$_{15}$NH$_2^+$) and the cyanoadamantane cation (Ada-CN$^+$, C$_{10}$H$_{15}$CN$^+$). Specifically, we study electronic (vibrationally resolved) spectra and nonadiabatic molecular dynamics (modeled using the surface hopping approach based on semiempirical electronic structure theory) of these radical cations. The internal conversion time constants as well as reactive relaxation outcomes (cage-opening and hydrogen loss) are compared for the two derivatives and also with the case of Ada$^+$ [Roy et al., Theor. Chem. Acc. 2023, 142, 71]. Remarkably, we find a longer ground-state recovery time for Ada-CN$^+$ than for Ama$^+$ (for the same excitation energy window), despite a smaller excitation energy for the former. Thus, a static energy gap law cannot be used to rationalize nonadiabatic dynamics and excited-state lifetimes in this case: Dynamics and details of the couplings between several states play a decisive role.
1 Introduction

Diamondoids are the carbon cage molecular species which attract attention of researchers in various fields such as interstellar chemistry [1], nanotechnology [2], and medicinal chemistry [3]. The basic molecular unit of these is adamantane (Ada, C\textsubscript{10}H\textsubscript{16}) [4]. Ada and higher neutral diamondoids (diamantane, triamantane, etc.) as well as derivatives thereof have been extensively studied over decades, in particular with regard to their vibrational, electronic, and optical properties [5–15].

In astrochemistry, the open-shell (radical) cations of diamondoids are of special interest as they absorb lower energy photons in comparison to their neutral counterparts and may potentially be formed in interstellar medium by ionization with photons and/or cosmic rays [16]. Thus, several recent studies have targeted the optical spectra of radical cations of diamondoids [16–19]. Specifically, the optical spectrum of Ada\textsuperscript{+} has been obtained by electronic photodissociation (EPD) spectroscopy by Crandall \textit{et al.} [17] and helium-tagged electronic spectroscopy by Kappe \textit{et al.} [18]. In addition, the EPD study by Crandall \textit{et al.} [17] has provided insight into photoinduced fragmentation of Ada\textsuperscript{+}. The optical spectrum of the diamantane cation, Dia\textsuperscript{+}, has also been recently reported by the same group [19].

Besides the cations of pristine diamondoids consisting only of carbon and hydrogen, cations of nitrogen-containing adamantane derivates have received attention lately [16, 20]. In the context of astrochemistry, the interest stems from recent detection of aromatic nitriles in the interstellar medium [21–23]. Recently, the EPD optical spectrum and fragmentation pathways of the cyanoadamantane cation (Ada-CN\textsuperscript{+}) were reported by Crandall \textit{et al.} [16]. Another nitrogen-containing derivate cation which has gained interest is the amantadine cation (Ama\textsuperscript{+} or Ada-NH\textsubscript{2}\textsuperscript{+}), which has been studied by infrared photodissociation (IRPD) spectroscopy by the group of Dopfer [20, 24]. It was found that substitution of a hydrogen atom (of the adamantane cage) with the NH\textsubscript{2} group greatly facilitates opening of the adamantane cage [20,24]. The optical spectrum of Ama\textsuperscript{+} has not been reported so far though. We also note that an IRPD spectrum for Ada-CN\textsuperscript{+} was presented by the same group [25].

Computed excitation energies and oscillator strengths of vertical electronic transitions of Ada\textsuperscript{+} [17, 26–28] and Ada-CN\textsuperscript{+} [16] were reported in the literature. Besides vertical excitations, vibrationally resolved absorption [28, 29] and photoelectron [12,29,30] spectra of Ada\textsuperscript{+} and Ada, respectively, were also calculated. For Ada-CN\textsuperscript{+}, Crandall \textit{et al.} [16] calculated a vibrationally-resolved spectrum for a selected band (\(D_0 \rightarrow D_{11}\)). We note that the absence of vibrationally resolved spectra for other bands is caused by unsuccessful excited-state optimizations of cationic diamondoids when using time-dependent density functional theory [16,17,28,29]. Recently,
we have also simulated adiabatic and nonadiabatic dynamics of Ada$^+$ [29], providing insight into (ultra)fast electronic relaxation and fragmentation of the cation.

In the present work, we report nonadiabatic, surface hopping molecular dynamics simulations for Ama$^+$ and Ada-CN$^+$ — the derivatives of Ada$^+$, containing an electron donating (NH$_2$) and an electron withdrawing (CN) groups, respectively. This way, systematic trends of replacing H with electron donors or acceptors on internal conversion and fragmentation dynamics can be evaluated. We also present vibrationally resolved absorption spectra of both cations computed under the vertical gradient approximation (described in the next section). The predicted spectra and observed ultrafast processes are compared for the two derivatives and also with the findings obtained for Ada$^+$ in our previous work [29].

2 Methods

The amantadine cation (Ama$^+$) and the cyanoadamantane cation (Ada-CN$^+$) have been optimized in the ground ($D_0$) state at the UB3LYP [31,32]/6-31G* [33,34] level of theory (Fig. 1).

![Figure 1: The structures of the (a) amantadine (Ama$^+$) and (b) cyanoadamantane (Ada-CN$^+$) cations optimized at the UB3LYP/6-31G* level of theory.](https://doi.org/10.26434/chemrxiv-2024-wb8xd)

To confirm the minimum nature of the obtained geometries, a normal mode analysis was performed for the optimized structures using the same level of theory, and no imaginary frequencies were found. Then, the vertical excitation energies of the $D_0 \rightarrow D_i$ transitions and the corresponding oscillator strengths were calculated at
the minimum geometries of the cations. To do so, linear response time-dependent
density functional theory (TD-DFT) [35] with two density functional approxima-
tions, namely TD-UB3LYP/6-31G* and TD-UCAM-B3LYP [36]/6-31G*, as well as
the semiempirical configuration interaction singles and doubles (CISD) method were
used. Specifically, the restricted open-shell OM3 method [37] was employed to gen-
erate molecular orbitals for CISD calculations. This method was also applied to study
nonadiabatic dynamics of the adamantane cation (Ada+) in our recent work [29].
The CISD calculations were performed in the restricted active space of \( x \) occupied
and \( y \) virtual frontier orbitals. Specifically, after test calculations of vertical spectra,
we set \( x = 9 \) and \( y = 10 \) for Ama+, and \( x = 12 \) and \( y = 10 \) for Ada-CN+. The
semiempirical method is thus termed ROOM3/CISD \((x \times y)\). DFT and TD-DFT
calculations were performed using Gaussian 16 [38], and the ROOM3/CISD \((x \times y)\)
calculations were done with the MNDO program [39].

Furthermore, vibrationally resolved absorption spectra of the cations were com-
puted at the (TD-)DFT level (UB3LYP/6-31G*) making use of the vertical gradient
(VG) approximation [40]. VG is a version of what is known as IMDHO, Independent
Mode Displaced Harmonic Oscillator — the model which does not include frequency
alteration and Duschinsky rotation [41] — with the geometry shift being calculated
without optimizing the excited state, but using instead the gradient of the excited
state potential energy surface at the minimum geometry of the ground state. A
higher level, e.g., adiabatic Hessian (AH), was not used because the TD-DFT ex-
cited state optimizations failed to converge. The vibrationally resolved spectra were
computed in the Franck–Condon approximation employing the time-dependent (TD)
formalism for spectroscopy (which is based on autocorrelation functions) as imple-
mented in Gaussian 16. The default Gaussian 16 parameters were mostly used. In
particular, a Gaussian broadening with half-width at half-maximum of 135 cm\(^{-1}\)
was applied. For Ama+, a smaller time step and a larger number of steps were used
[keywords TD=(2NStep=20,Time=1e-12)], since the default parameters resulted in
nonphysical negative intensities for some transitions. The spectra were computed for
temperature \( T = 0 \) K.

The nonadiabatic dynamics simulations were performed using Tully’s surface
hopping (SH) approach [42] with energy-based decoherence correction [43] as imple-
mented [44] in the MNDO program. The electronic structure of the cations was
described with the ROOM3/CISD \((x \times y)\) method. For Ada-CN+, two sets of SH
simulations were considered, corresponding to excitation of two lowest energy bands
recently observed experimentally by Crandall et al. [16]. For Ama+, for which no
experimental optical spectrum is available (to the best of our knowledge), excitation
to the lowest energy band was considered. Each set of SH simulations includes 1000
trajectories. The initial geometries and nuclear velocities for the SH trajectories were sampled using the Wigner function [45] at \( T = 0 \) K. The Wigner function was obtained under harmonic approximation following optimization and normal mode analysis (for the \( D_0 \) state) at the ROOM3/CISD\((x \times y)\) level. The initial electronic state for a given trajectory was chosen as the brightest state (i.e., the state with the largest oscillator strength) in a given excitation energy window. For Ama\(^+\), the energy window \([1,3]\) eV was considered; and for Ada-CN\(^+\), energy windows \([1,3]\) eV and \([3.5,5]\) eV were investigated. These choices are based on absorption spectra calculated at the initial geometries selected by Wigner sampling, as an alternative approach to the (harmonic) quantum approach using the VG approximation. These spectra were calculated as

\[
I(E) = \frac{1}{M} \sum_{i,\alpha} f_{i,\alpha} \exp \left( -\frac{1}{2\sigma^2} (E - E_{i,\alpha})^2 \right).
\]

Here, \( I \) is the intensity, \( E \) the excitation energy, \( E_{i,\alpha} \) and \( f_{i,\alpha} \) are the calculated excitation energy and oscillator strength, respectively, for the \( D_0 \rightarrow D_i \) transition of snapshot \( \alpha \), \( \sigma \) is a broadening parameter (\( \sigma = 0.05 \) eV in this work), and \( M \) is a normalization factor (here, \( M \) is chosen to be the maximum intensity of the broadened spectrum in the considered energy interval). For Ama\(^+\) and Ada\(^+\), in the SH dynamics after excitation to the lowest energy band (corresponding to the first intense transition, see below), ten electronic states (the ground state and nine excited states) were taken into account. For Ada-CN\(^+\), excitation into the second, higher energy band was also considered, and twelve electronic states (the ground state and eleven excited states) were included in the SH simulations in this case. The trajectories were propagated for 1 ps with a nuclear time step of 0.1 fs and an electronic time step of 1 as. The SH calculations were performed with the MNDO program.

3 Results and Discussion

3.1 Electronically excited states and vibrationally resolved spectra of the cations

The vertical excitation energies and oscillator strengths for the cations were calculated with TD-UB3LYP/6-31G\(^*\), TD-UCAM-B3LYP/6-31G\(^*\), and ROOM3/CISD\( (9 \times 10) \) methods at the optimized UB3LYP/6-31G\(^*\) geometries. The results for the
brightest states of interest in this work are collected in Tab. 1. A detailed analysis including other states and the character of orbitals involved in transitions is presented in the SI (see sections S1 and S2 there).

Table 1: Excitation energies (in eV) and oscillator strengths (in parentheses) for the transitions to the bright states of interest (state labels are also provided).\textsuperscript{a}

<table>
<thead>
<tr>
<th>State</th>
<th>TD-UB3LYP/6-31G*</th>
<th>TD-UCAM-B3LYP/6-31G*</th>
<th>ROOM3/CISD\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ama\textsuperscript{+}</td>
<td>1.85 (0.03) $D_2$</td>
<td>2.48 (0.05) $D_2$</td>
<td>2.67 (0.11) $D_2$</td>
</tr>
<tr>
<td>Ada\textsuperscript{+}</td>
<td>1.83 (0.03) $D_3/D_4$</td>
<td>1.79 (0.04) $D_3/D_4$</td>
<td>2.00 (0.09) $D_3/D_4$</td>
</tr>
<tr>
<td>Ada-CN\textsuperscript{+}</td>
<td>1.25 (0.06) $D_2$</td>
<td>1.25 (0.06) $D_2$</td>
<td>1.98 (0.12) $D_3$</td>
</tr>
<tr>
<td></td>
<td>3.77 (0.05) $D_{11}$</td>
<td>3.82 (0.07) $D_{11}$</td>
<td>4.14 (0.12) $D_8$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculations were performed at the UB3LYP/6-31G* optimized geometries
\textsuperscript{b} Active spaces are $9 \times 10$ for Ama\textsuperscript{+} and Ada\textsuperscript{+}, and $12 \times 10$ for Ada-CN\textsuperscript{+}
\textsuperscript{c} TD-UB3LYP and ROOM3/CISD results from ref. [29]

The first bright state of Ama\textsuperscript{+} is $D_2$. The $D_0 \rightarrow D_2$ transition is predicted at 1.85 eV, 2.48 eV, and 2.67 eV at the B3LYP, CAM-B3LYP, and ROOM3/CISD($9 \times 10$) levels, respectively. This transition has the largest oscillator strength ($f$) among the lowest energy transitions, although the absolute $f$ values are small: 0.03, 0.05, and 0.11 for B3LYP, CAM-B3LYP, and ROOM3/CISD, respectively.

For Ada-CN\textsuperscript{+}, the brightest among low-lying states was found to be the $D_2$ state for B3LYP and CAM-B3LYP, while for the semiempirical CISD method, it is $D_3$. The excitation energies (and oscillator strengths) for this bright transition are 1.25 eV (0.06), 1.25 eV (0.06), and 1.98 eV (0.12) at the B3LYP, CAM-B3LYP, and ROOM3/CISD($12 \times 10$) level, respectively. Note that for the semiempirical calculations, in the case of Ada-CN\textsuperscript{+}, we changed the active space from $9 \times 10$ to $12 \times 10$. This choice was made by inspecting orbitals (in TD-DFT and semiempirical CISD calculations) involved in the higher energy bright transition corresponding to the second band in the experimental spectrum [16] ($D_{11}$ in the study of Cran dall \textit{et al.} [16]). This higher energy bright transition is also listed in Tab. 1. It is located at 3.77 eV, 3.82 eV, and 4.14 eV according to B3LYP, CAM-B3LYP, and ROOM3/CISD, respectively. The corresponding bright state is $D_{11}$ at the TD-DFT levels (in agreement with the recent TD-DFT calculations of Cran dall \textit{et al.} [16]) and $D_8$ at the ROOM3/CISD($12 \times 10$) level (at the optimized UB3LYP/6-31G* geometry). Here, we note that ROOM3/CISD($12 \times 10$) calculations at the optimized
ROOM3/CISD(12 × 10) geometry yield this bright state as \( D_{11} \) (as in the TD-DFT case).

Notably, dominant molecular orbitals characterizing the lowest energy intense transitions involve contributions of substituents (see Fig. S1 and S2). We also note that no degenerate states were found for Ama\(^+\) and Ada-CN\(^+\) in contrast to Ada\(^+\) [29]. For Ada\(^+\), the lowest-energy excited states were pairwise degenerate (e.g. \( D_1/D_2 \) and \( D_3/D_4 \)) [29], due to the higher symmetry.

From Tab. 1, we see that the ROOM3/CISD excitation energies are larger than the TD-DFT excitation energies. However, all three methods predict the same trend when comparing the excitation energies of the first intense transition for different cations: Ama\(^+\) > Ada\(^+\) > Ada-CN\(^+\). At that, the difference between Ama\(^+\) and Ada\(^+\) is very small at the B3LYP level (~0.02 eV), as also is the difference between Ada\(^+\) and Ada-CN\(^+\) at the ROOM3/CISD level.

Further, the vibrationally resolved absorption spectra of Ama\(^+\) and Ada-CN\(^+\) were calculated at the TD-UB3LYP/6-31G* level and using the VG approximation. They are shown in Fig. 2 together with the VG TD-UB3LYP/6-31G* spectrum of Ada\(^+\) reported in ref. 29.

For Ama\(^+\), three structureless bands are observed in the total spectrum (in the energy range up to 6 eV), with the major contributions stemming from \( D_2, D_8, \) and \( D_9 \) (Fig. 2a). Notably, none of the ten transitions exhibit vibronic fine structure. This is in contrast to Ada\(^+\) [29], for which some transitions show the fine structure (Fig. 2b). Also the Ada-CN\(^+\) absorption spectrum shows fine structure (see Fig. 2c and the discussion below). Unfortunately, no experimental optical spectrum has been reported for Ama\(^+\) (unlike Ada\(^+\) [17] and Ada-CN\(^+\) [16]); therefore, a comparison with experiment for Ama\(^+\) is so far not possible.

For Ada-CN\(^+\), the spectrum consists of two bands (in the considered energy range, up to 6 eV), which is in agreement with the recently reported experimental spectrum [16]. The first, lower energy band (at 0.7–3 eV) is mainly made up of transitions to \( D_2 \) and \( D_5 \) states. At that, the \( D_0 \rightarrow D_5 \) transition shows vibronic progression, whereas the \( D_0 \rightarrow D_2 \) transition is structureless. The second band (at 3–5.5 eV) comprises transitions to \( D_{11} \) and \( D_{14} \), and weaker transitions to \( D_{12} \) and \( D_{15} \). Here, the \( D_0 \rightarrow D_{11} \) transition demonstrates some vibronic progression. Overall, the spectrum is in semi-quantitative agreement with the experimental EPD spectrum [16].

When comparing the total absorption spectra of Ama\(^+\), Ada\(^+\), and Ada-CN\(^+\) in Fig. 2, we see that the latter two are overall similar (both in their two-peak appearance and the observed vibrational fine structure), while the spectrum of Ama\(^+\) is quite distinct (three main peaks, no fine structure). For the maxima of the first
intense low-energy bands in the spectra, there is a clear trend towards lower excitation energies with the electron-withdrawing ability of the “ligands”, with Ama$^+$ $\sim$ 1.9 eV, Ada$^+$ $\sim$ 1.8 eV, and Ada-CN$^+$ $\sim$ 1.2 eV.

Figure 2: Absorption spectra of (a) Ama$^+$, (b) Ada$^+$ (from ref. [29]), and (c) Ada-CN$^+$ in the VG approximation (shown are the individual $D_0 \rightarrow D_i$ contributions and their sum). Calculations are done at the (TD-)UB3LYP/6-31G* level of theory.
3.2 Surface Hopping Calculations

We then modeled the nonadiabatic dynamics using the surface hopping approach in combination with ROOM3/CISD(9 × 10) for Ama⁺ and ROOM3/CISD(12 × 10) for Ada-CN⁺, to obtain excited state lifetimes and to characterize possible photofragmentations or rearrangements.

3.2.1 Absorption spectra from Wigner sampling

First, however, vertical absorption spectra were computed with the respective ROOM3/CISD methods for the initial geometries sampled from the Wigner distribution. The individual stick spectra and the total broadened spectra are shown in Fig. 3.

We note here that the “fine structure” present in these spectra should not be compared with the vibronic progression resulting from the quantum-mechanical calculation (like for the transitions to $D_5$ and $D_{11}$ of Ada-CN⁺ in Fig. 2c), since nuclei are treated classically in this case.

The broadened spectrum for Ama⁺ (Fig. 3a) displays two bands in contrast to the vibrationally resolved spectrum in the VG approximation, which shows three bands (Fig. 2a). The first band includes mostly contributions of $D_1$, $D_2$, and $D_3$ in agreement with the VG spectrum, whereas $D_4$ and higher states compose the second band (Fig. 3a). The lowest energy band was used to select initial states for the SH calculations. Specifically, we set an energy window of [1,3] eV to select the initial states.

For Ada-CN⁺, three bands are observed in the energy range up to 7 eV (Fig. 3c), while the vibrationally resolved spectrum in Fig. 2c displays two bands. The first two bands (of the broaden spectrum calculated at the initial geometries) bear similarity to the experimental spectrum [16] as well as to the VG spectrum presented above (Fig. 2c). Two excitation energy windows were considered in the case of Ada-CN⁺, [1,3] eV and [3.5,5] eV, corresponding to the first and the second bands, respectively.

When comparing the maxima ($E_{\text{max}}$) of the lowest-energy intense bands of the broadened spectra (Fig. 3), we see now the following order: Ama⁺ > Ada-CN⁺ > Ada⁺ (see the second column in Tab 2). Thus, Ada-CN⁺ and Ada⁺ switch places in comparison with the ordering of Tab. 1. It should be noted though that there the difference between Ada-CN⁺ and Ada⁺ is very small, ~0.02 eV, at the ROOM3/CISD level (see the last column of Tab. 1) as mentioned above.
Figure 3: Spectra for initial conditions for 1000 trajectories for (a) Ama\(^+\), (b) Ada\(^+\) (results from ref. [29]), and (c) Ada-CN\(^+\), computed at the ROOM3/CISD(9 \(\times\) 10), ROOM3/CISD(9 \(\times\) 10), and ROOM3/CISD(12 \(\times\) 10), respectively. The bands marked by symbols were used to select initial state for SH calculations: An energy window of [1,3] eV (*) was used for Ama\(^+\), and energy windows of (*) [1,3] eV and (\(\Delta\)) [3.5,5] eV for Ada-CN\(^+\) (see text for further details). For Ada\(^+\), excitation to the D\(_3\)/D\(_4\) states (*) was considered.
3.2.2 Excited state lifetimes: Violation of the energy gap law?

Electronic state populations obtained from surface hopping calculations for excitation into the first intense bands are shown in Fig. 4. It is seen there that (ultra)fast internal conversion to the cation ground state ($D_0$) takes place. Using a single exponential to fit the rise of the $D_0$ population, $P_{D_0} = 1 - \exp(-t/\tau)$, we obtain ground state recovery times ($\tau$) of $\sim 25$ fs for Ama$^+$, and $\sim 120$ fs for Ada-CN$^+$. For Ada$^+$, in our previous work [29], the corresponding ground state recovery times were between 10 fs (when exciting into the $D_1/D_2$ band) and 100 fs (when exciting into high-energy band $D_8$ at $\sim 3.8$ eV, cf. Fig. 3b). Upon excitation of Ada$^+$ to the first intense band ($D_3/D_4$), $\tau \approx 39$ fs (this case is presented for comparison in Fig. 4b).

In more detail, in the case of Ama$^+$, for the considered excitation energy window of [1,3] eV, the major part of the initial population is in $D_2$ (0.5) and $D_1$ (0.3), and a smaller fraction (0.2) in $D_3$ (Fig. 4a). The $D_2$ and $D_3$ states decay very fast, giving rise to $D_1$ population rise at short times. The $D_1$ state, in turn, decays to $D_0$ again very quickly, resulting in the recovery of the ground state ($D_0$) with the time constant $\tau \approx 25$ fs. This time is comparable to the corresponding time constants for Ada$^+$, obtained for initial excitation energies <$ 3 $ eV, which are between 10 fs and 40 fs [29].

For Ada-CN$^+$, for the lower energy window of [1,3] eV, the initial population goes mainly into $D_3$ ($P_{D_3}(0) \approx 0.86$). The $D_3$ state decays with a time constant of 69 fs (obtained using a monoexponential fit $P_{D_3}(t) = P_{D_3}(0) \exp(-t/\tau)$). The $D_2$ and $D_1$ populations increase, reaching maxima at 35 fs and 75 fs, respectively, after which they decay. And the $D_0$ population rises, with a time constant of $\sim 120$ fs as mentioned above.

Remarkably, internal conversion to the ground state is slower for Ada-CN$^+$ than for Ama$^+$, $\sim 120$ fs vs. $\sim 25$ fs, despite a smaller initial excitation energy (see Tab. 2). Specifically, the mean excitation energy calculated at the initial geometries is 2.57 eV for Ama$^+$ and 2.36 eV for Ada-CN$^+$. Thus, the observed situation violates the well-known energy-gap law which predicts a faster rate for internal conversion due to nonadiabatic couplings with a decreasing energy gap between states [46]. Moreover, when comparing all three cations, we see that Ama$^+$ exhibits the fastest excited-state decay, while possessing the largest initial excitation energy at the same time. However, the energy-gap-law argument qualitatively holds when comparing Ada$^+$ to Ada-CN$^+$ (Tab. 2).
Figure 4: Adiabatic electronic state populations as a function of time for (a) Ama$^+$, (b) Ada$^+$ (results from ref. [29]), and (c) Ada-CN$^+$. For Ama$^+$ and Ada-CN$^+$, the excitation energy window of [1,3] eV is used. And Ada$^+$ is excited to the $D_3/D_4$ states [29].

Table 2: Initial energy gaps, dominant initial states, and ground-state recovery times for the studied cations.

<table>
<thead>
<tr>
<th>cation</th>
<th>$E_{\text{max}}$ (eV)$^a$</th>
<th>$\langle E \rangle$ (eV)$^b$</th>
<th>$\tau$ (fs)$^c$</th>
<th>window$^d$</th>
<th>states$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ama$^+$</td>
<td>2.54</td>
<td>2.57</td>
<td>25</td>
<td>[1,3] eV</td>
<td>$D_1/D_2$</td>
</tr>
<tr>
<td>Ada$^+ f$</td>
<td>2.17</td>
<td>2.01</td>
<td>39</td>
<td>$D_3/D_4$</td>
<td>$D_3/D_4$</td>
</tr>
<tr>
<td>Ada-CN$^+$</td>
<td>2.30</td>
<td>2.36</td>
<td>120</td>
<td>[1,3] eV</td>
<td>$D_3$</td>
</tr>
</tbody>
</table>

$^a$ Maxima of the broadened spectra shown in Fig. 3 (lowest-energy intense bands)
$^b$ Mean excitation energy calculated at the initial geometries for the SH trajectories
$^c$ Ground-state recovery time obtained from the monoexponential fit $P_{D_0}(t) = 1 - \exp(-t/\tau)$
$^d$ Energy window
$^e$ Dominant initial states used in the SH simulations
$^f$ Results from ref. [29]
To analyze the departure from the energy-gap law observed when comparing Ama$^+$ with Ada-CN$^+$, we calculated energy gaps and nonadiabatic coupling terms (scalar products $\mathbf{d}_{ij} \cdot \dot{\mathbf{R}}$ with $\mathbf{d}_{ij}$ being the nonadiabatic, first-derivative coupling vector between states $i$ and $j$, and $\dot{\mathbf{R}}$ nuclear velocities) between selected states. Specifically, in Fig. 5a, we plot the $D_3$ population for Ada-CN$^+$ and the $D_1$ and $D_2$ populations for Ama$^+$, i.e., for those states which are initially populated the most when selecting the [1,3] eV excitation window (cf. Tab. 2). The corresponding energy gaps expected to be most relevant for the relaxation to the ground state $D_0$ are the $D_0-D_1$ energy gaps for both cations as well as the $D_1-D_2$ energy gap for Ama$^+$ and the $D_2-D_3$ energy gap for Ada-CN$^+$ (Fig. 5b). For two of these pairs we also show the nonadiabatic coupling terms, i.e., those between states $D_1$ and $D_2$ for Ama$^+$ and between states $D_2$ and $D_3$ for Ada-CN$^+$ (Fig. 5c). The shown curves are averages over the swarm of trajectories. In the case of the nonadiabatic coupling, the absolute values were averaged.

From these curves we see that for the initial stage of photodynamics ($t \lesssim 6$ fs), the $D_1-D_2$ energy gap for Ama$^+$ ($\sim 0.4$ eV) is smaller than the $D_2-D_3$ energy gap for Ada-CN$^+$ ($\sim 0.5$ eV), see Fig. 5b. Moreover, for these short-time dynamics, the $D_1-D_2$ nonadiabatic coupling term for Ama$^+$ is larger than the $D_2-D_3$ nonadiabatic coupling term for Ada-CN$^+$ (for $t \lesssim 7$ fs), see Fig. 5c. Therefore, a faster decay of $D_2$ of Ama$^+$ can be expected in comparison to the $D_3$ decay for Ada-CN$^+$.

In addition, for Ama$^+$, the $D_1$ population is initially rather large ($\sim 0.3$) and the $D_0-D_1$ energy gap steeply decreases within the first 12 fs — this should facilitate $D_1 \rightarrow D_0$ transitions in Ama$^+$. Overall, the recovery of the ground state occurs faster for Ama$^+$ than for Ada-CN$^+$, considering the same energy window of [1,3] eV.

General inspection of Fig. 5 shows that gaps and couplings are rapidly varying with time, also changing the order between the two cations along the time axis. Therefore, the application of the gap law relying on static energy gaps alone, typically between the ground and first excited state only, must be taken with care. If the observed (partial) violation of the gap law as demonstrated here survives experimental investigation and / or higher-level theory remains to be seen, however, the statement that often several states, details of the couplings and, most of all, dynamics can play decisive roles is expected to be of quite general nature.

Last, for Ada-CN$^+$ we also considered excitation to the higher energy window of [3.5,5] eV (Fig. S3). In this case, the most populated states at $t = 0$ are $D_{10}$ (0.34) and $D_{11}$ (0.31), and next most populated states are $D_8$ (0.18) and $D_9$ (0.10). $D_{10}$ and $D_{11}$ decay giving rise to growth of the $D_8$ and $D_9$ populations, which, in turn, decrease after 86 fs and 25 fs, respectively. The lower states are slightly populated, e.g., a maximum in the $D_3$ population of 0.17 is observed at 176 fs, and the $D_1$
population reaches the maximal value of 0.13 at 222 fs. Eventually, the $D_0$ state is populated with the time constant of $\sim 300$ fs as already stated above.

Figure 5: Selected (a) populations $P_{D_1}$ (Ama$^+$), $P_{D_2}$ (Ama$^+$), $P_{D_3}$ (Ada-CN$^+$), (b) energy gaps $\Delta E_{01}$ (Ama$^+$), $\Delta E_{12}$ (Ama$^+$), $\Delta E_{01}$ (Ada-CN$^+$), $\Delta E_{23}$ (Ada-CN$^+$) and (c) absolute values of nonadiabatic coupling terms $|d_{12} \cdot \dot{R}|$ (Ama$^+$) and $|d_{23} \cdot \dot{R}|$ (Ada-CN$^+$) for Ama$^+$ and Ada-CN$^+$, for short-time dynamics.
3.2.3 Fragmentation and rearrangement reactions

In addition to the discussed electronic state populations, we analyzed nuclear dynamics for possible reactions. Specifically, a dissociation reaction of H loss and intramolecular bond-breaking rearrangement reactions were found. Fig. 6a shows the H loss yield for the three considered SH batches (one for Ama+ and two for Ada-CN+). The H loss yield, defined as the ratio of the number of trajectories showing hydrogen dissociation to the total number of trajectories and expressed in %, is plotted against initial excitation energy using bars centered at the mean excitation energy and having the width of twice standard deviation. For Ama+ and energy window [1,3] eV, the H loss yield is low, \( \sim 0.11 \% \). This value is smaller than the corresponding H loss yield for Ada+, \( \sim 1–2 \% \) for excitation energies \( \sim 1–2.5 \) eV [29].

The hydrogen dissociation in the case of Ama+ was observed for the H atoms of the cage (not the amino group).

![Figure 6: (a) H loss yield and (b) rearrangement as a function of excitation energy for Ama+ and Ada-CN+. Results for Ada+ upon excitation to \( D_3/D_4 \) are also shown. The bars are centered at the mean excitation energy and have a width of twice the standard deviation.](image)

For Ada-CN+, the H loss yield is larger than for Ama+ (Fig. 6a). Specifically, we find \( \sim 0.8 \% \) for energy window [1,3] eV and \( \sim 3.1 \% \) for energy window [3.5,5] eV. The former value is comparable to that for Ada+ (\( \sim 1–2 \% \)) for the similar excitation energy. For the higher energies (window [3.5,5] eV), we find a higher H loss yield of \( \sim 3.1 \% \). This is somewhat smaller than the H loss yield for Ada+ after excitation to \( D_8 \) (\( \sim 3.5–4.0 \) eV), 7.8 %, found in ref. [29].

No further fragments were found in our simulations with exception of one trajec-
tory for Ama\(^+\), which demonstrated an NH\(_2\) loss. We note that other fragmentation channels were observed in the experiment for Ada-CN\(^+\) (notably HCN loss) [16], which presumably require a (much) longer time to be realized.

Further, in addition to the H loss dissociation reaction, we have also observed intramolecular bond-breaking and rearrangement of the carbon cage. To do so, we compared initial bond lengths with the final distances (for the same pairs of atoms) and counted a reactive event if the final distance was more than 1.5 times larger than the initial one. The percentage of the trajectories showing rearrangement, calculated as 100 \(\times\) \(N_{\text{rearr}}/(N_{\text{tot}} - N_{\text{H-loss}})\) (here, \(N_{\text{rearr}}\) is the number of trajectories showing intramolecular bond breaking, \(N_{\text{tot}}\) is the number of all trajectories, and \(N_{\text{H-loss}}\) is the number of trajectories showing H loss), is presented in Fig. 6b, for the three sets of the SH simulations. Remarkably, in the case of Ama\(^+\), \(~87\) % of parent ion trajectories undergo rearrangement. Examples of the rearranged structures are shown in Fig. S4. The high rearrangement percentage is in agreement with the recent reports by George and Dopfer [20, 24], who observed Ama\(^+\) cage-opening by means of infrared photodissociation spectroscopy and also calculated a lower barrier for this reaction in the case of Ama\(^+\) in comparison with Ada\(^+\). For Ada\(^+\), the rearrangement percentage is \(~\leq 2\) % for excitation energies \(~\leq 3\) eV (and \(~\leq 7\) % when considering higher excitation energies). [We note that these values are slightly larger than those reported in ref. [29] because there we used the factor of 2 instead of 1.5 (used here, see above) to judge on the rearrangement event.] In the case of Ada-CN\(^+\), much less trajectories demonstrated rearrangement in comparison to Ama\(^+\), 2.5 % for the energy window of \([1,3]\) eV and 6.3 % for \([3.5,5]\) eV. Thus, Ada-CN\(^+\) behaves more similar to Ada\(^+\) in this respect.

4 Summary and Conclusions

We performed nonadiabatic molecular dynamics simulations for the derivatives of the adamantane cation, namely the amantadine cation (Ama\(^+\)) and the cyanoadamantane cation (Ada-CN\(^+\)), using Tully’s surface hopping approach combined with the semiempirical ROOM3/CISD electronic structure method. In addition, excited states and vibrationally resolved electronic absorption spectra of the cations (under the vertical gradient approximation) were investigated at the TD-DFT level (with B3LYP and CAM-B3LYP functionals).

We observed that the substituents (–NH\(_2\) and –CN) cause changes in absorption spectra. In particular, the lowest energy intense transitions are affected because of participation of the substituents in the molecular orbitals involved in these transitions. Moreover, the changes in the excitation energy are somewhat method-dependent,
with B3LYP predicting $\text{Ama}^+ \approx \text{Ada}^+ > \text{Ada-CN}^+$, CAM-B3LYP $\text{Ama}^+ > \text{Ada}^+ > \text{Ada-CN}^+$, and ROOM3/CISD $\text{Ama}^+ > \text{Ada}^+ \approx \text{Ada-CN}^+$. In addition, the vibronic spectra show differences between the cations—no fine structure was found for $\text{Ama}^+$ in contrast to $\text{Ada}^+$ and $\text{Ada-CN}^+$.

The photoinduced dynamics of $\text{Ama}^+$ after excitation in the first (lowest energy) band (located at 1–3 eV) of the computationally predicted absorption spectrum were considered. We found ultrafast internal conversion in the manifold of the cationic doublet states with the time constant for ground-state ($D_0$) recovery of $\sim 25$ fs. This time is similar to those obtained for $\text{Ada}^+$ in our preceding work [29], $\sim 10$–40 fs for initial excitation energies < 3 eV. Regarding the ultrashort timescale for the internal conversion, we note that the $D_1 \rightarrow D_0$ relaxation in the ethylene cation was measured to occur with a time constant of 7 fs [47].

In the case of $\text{Ada-CN}^+$, photodynamics after excitations to the first two lowest energy bands (also observed in the recent experiment by Crandall et al. [16]) were investigated. The corresponding ground-state recovery times are $\sim 120$ fs for excitation energy window of [1,3] eV and $\sim 300$ fs for window [3.5,5] eV. Thus, internal conversion is slower for $\text{Ada-CN}^+$ than for $\text{Ama}^+$ and $\text{Ada}^+$ (for the latter, a time constant of $\sim 100$ fs was obtained for initial excitation energy of 3.5–4 eV [29]).

Remarkably, when comparing $\text{Ama}^+$ and $\text{Ada-CN}^+$ in the case of the lower energy window of [1,3] eV, a departure from the well-known and celebrated energy gap-law is observed. Namely, $\text{Ada-CN}^+$ decays slower to the ground state than $\text{Ama}^+$ despite the lower initial excitation energy for the former. An analysis of the nonadiabatic dynamics reveals the dynamic nature of involved energy gaps and nonadiabatic coupling terms responsible for this situation. In summary, the application of the energy-gap law based on static energy gaps alone, typically between ground and first excited state only, appears to be insufficient. We expect that this statement will also hold if the dynamics are computed at a higher level as here, and it should not only apply to the cations considered in this work. In fact, a similar conclusion was made for another radical cation in ref. [48].

Both substituted cations ($\text{Ama}^+$ and $\text{Ada-CN}^+$) demonstrated a relatively low yield of ultrafast H loss happening within 1 ps of simulations ($\lesssim 3\%$), which is comparable to the case of $\text{Ada}^+$ ($< 8\%$). In addition, only one trajectory for $\text{Ama}^+$ showed NH$_2$ loss and no other fragments were found for both cations within 1 ps. Remarkably, for $\text{Ama}^+$, majority of the parent ion trajectories ($\sim 87\%$) evinced intramolecular rearrangement (cage opening) in agreement with low energy barriers reported by George and Dopfer [24]. In contrast to $\text{Ama}^+$, rearrangement percentage was found to be much lower for $\text{Ada-CN}^+$ ($\lesssim 6\%$), which is similar to that for $\text{Ada}^+$ ($\lesssim 7\%$).
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References


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