

Theoretical study of multiphoton ionization of cyclohexadienes and unimolecular decomposition of their mono- and dications†

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Quantum chemical calculations of the geometric structure, vertical excitation energies, and ionization potentials for the isomeric pair of 1,3- and 1,4-cyclohexadienes and their mono- and dications have been performed employing a variety of theoretical methods and basis sets. The computed ionization potentials and electronic excitation energies are used to evaluate the range of internal energies available for fragmentation of the cations following multiphoton resonance ionization of the cyclohexadienes in intense laser field. The conditions governing the competition between multiple ionization and decomposition of the ions are also discussed. Calculations of stationary points on the potential energy surfaces for various fragmentation channels and relative product yields at different available internal energies are then utilized to analyze the trends in branching ratios of major dissociation products of the 1,4-cyclohexadiene²⁺ dication, which include $C_3H_3^+ + C_3H_5^+$, $C_2H_3^+ + C_4H_5^+$, and $C_4H_3^+ + C_2H_5^+$.

Introduction

When organic molecules are irradiated by intense-field femtosecond lasers, in some cases they mostly decompose to several ionized fragments and the yield of the parent cations is negligibly small, whereas in other occasions the parent cations dominate and the fragmentation is not significant.^{1–21} Here, the laser wavelength plays an important role. For example, it has been shown²² that the wavelength affects the behavior of benzene in the intense laser field; the dication $C_6H_6^{2+}$ was observed upon irradiation at 400 and 800 nm, however, the fragmentation was detected only at 400 nm. Fuß *et al.*²³ found predominance of parent cations for 1,3-cyclohexadiene (1,3-CHD) *versus* heavy fragmentation for 1,3,5-hexatriene upon their intense laser field irradiation. They explained this difference in terms of resonance between the energy of laser photons and the excitation wavelength of the cations. It has been noted¹⁰ that upon excitation by a femtosecond laser, a resonance between the laser wavelength and the cation's electronic excitation energy is the key factor required for ion fragmentation. In that study, two isomeric pairs of organic molecules, 2,3-dimethyl-1,3-butadiene and 2,5-dimethyl-2,4-hexadiene as well as 1,3-cyclohexadiene and 1,4-cyclohexadiene, were irradiated with a Ti:sapphire laser of 800 nm wavelength, with a pulse duration of 120 fs and intensity of 10^{14} W cm⁻². 1,4-Cyclohexadiene and 2,3-dimethyl-1,3-butadiene cations ex-

hibit resonance excitation at 800 nm, whereas 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene cations do not show significant absorption at this wavelength. As a result, only parent cations were observed for 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene, while for their structural isomers 1,4-cyclohexadiene and 2,3-dimethyl-1,3-butadiene the yield of the parent cations was negligibly small and profound fragmentation was detected, where the number and pattern of peaks in the mass spectra depended on the intensity and other laser parameters.²⁴ Another pair of molecules (though not isomeric) showing contrasting fragmentation patterns is pyridine and pyrazine.^{10,25,26}

According to the TOF mass spectra obtained upon irradiation of 1,3- and 1,4-CHD,¹⁰ only monocations were observed for the former and heavy fragmentation was found for the latter, with negligibly small signals from 1,4-CHD⁺ and 1,4-CHD²⁺. It was also found that the highest peak in the TOF spectra of 1,3-CHD was due to the parent monocation and the peak at m/z 40 was presumably due to the doubly charged parent ion. The formation of the 1,3-CHD⁺ monocation required 5–8 photons, while the formation of the dication 1,3-CHD²⁺ involved 15–20 photons; the monocations appeared earlier than the dications. Another work²³ using a 110-fs laser with a lower intensity of 2×10^{13} W cm⁻² and the same wavelength of 800 nm demonstrated that irradiated 1,3-CHD and *trans-cis-trans*-hexatriene (tct-HT) produce multiply charged cations from initially formed monocations and then the multi-cations can dissociate; fragmentation of hexatriene was much more profound than for 1,3-CHD. Nevertheless, the conditions of the latter experiment, such as shorter laser pulse duration, were apparently more conducive for the formation of 1,3-CHD dications.

Nakashima and Yatsushashi²⁷ have found that the use of shorter laser pulses leads to less fragmentation. Therefore, excitation at a non-resonant wavelength and/or with an ultimately short pulse could generate molecular ions as a

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dominant product from any type of molecules. Fragmentation in a high intensity laser field is complicated if it occurs and the mechanism has not been fully understood at the present stage.²⁸ Among the parameters affecting ionization and fragmentation, excitation wavelengths and pulse duration at fixed laser intensity have been found to drastically change ionization patterns. Intact molecular ions are produced when wavelengths are non-resonant with electronic levels of cations, whereas fragmentation proceeds to a large extent when the wavelength is resonant with electronic transitions. An ultimately short pulse should presumably lead to the formation of fragment-free ions because, as the time period between consecutive pulses is similar to the pulse duration, cations do not have enough time to undergo internal conversion to lower electronic states and thus the absorbed photon energy is not transformed to internal vibrational energy needed for dissociation. Instead, they absorb more and more photons, move up the ladder of excited electronic states, and eventually lose more electron(s) before they can decompose, *i.e.*, ionization of cations in these conditions should be preferable over their dissociation. As the time required for internal conversion of electronically excited cations was estimated to be in the range of 10–50 fs,²⁷ it was suggested that with sub ten fs pulse, intact molecular ion formation is possible for any molecule, even if the excitation wavelength is resonant with the cation absorption levels.

When a CHD molecule absorbs a UV photon, it is converted to an excited electronic state and then undergoes internal conversion back to the ground electronic vibrationally excited state; the open-chain *cis-cis-cis* hexatriene (ccc-HT also denoted as cZc-HT) is produced with quantum yield of 0.4.^{23,29–31} Multireference configuration interaction (MRCI) calculations of stationary points on the potential energy surfaces (PES) related to the transition of cyclohexadiene to hexatriene by ring opening have been reported.²⁹ According to these calculations, CHD is first excited to the 1^1B_u (S_2) electronic state, which rapidly (within 10–53 fs^{23,32–35}) relaxes to 2^1A_g (S_1), and the latter in turn converts to the ground 1^1A_g (S_0) state (within ~ 1 ps in solution^{33–35} or ~ 200 fs in the gas phase²³). Thereafter, the 1^1A molecule takes either CHD or ccc-HT configuration.

Hexatriene is an important functional group in a variety of more complicated molecules. The C_6H_8 cation system is of great theoretical and chemical interest because it provides an opportunity to compare a relatively simple cation rearrangement with the well-characterized neutral hexatriene and cyclohexadiene structural isomers.^{29,36} Due to the interest in the $C_6H_8^+$ radical cations, a wide variety of experimental and theoretical techniques have been employed to study them. For instance, the ring-closing reaction of hexatriene radical cation $C_6H_8^+$ to 1,3-cyclohexadiene radical cation was investigated computationally at the B3LYP/6-31G* and QCISD(T)/6-311G**/QCISD/6-31G* levels of theory.³⁷ The electrocyclic ring opening of 1,3-cyclohexadiene under photochemical conditions has been studied in some detail by a variety of experimental techniques.³⁸ Condensation reaction between 1,3-butadiene radical cation and acetylene in the gas phase was also reported and *ab initio* molecular orbital calculations at the UMP2/6-311+G(d,p)//UMP2/6-31G(d) + ZPE level

for the $C_6H_8^+$ and ($C_6H_7^+ + H$) systems were performed.³⁹ The photoinduced ring-closure and ring-opening reactions that interconvert 1,3,5-hexatriene and 1,3-cyclohexadiene are models for more complicated ring-opening reactions, including that involved in the synthesis of vitamin-D.⁴⁰ Different rotamers of the hexatriene radical cation have been characterized both experimentally and computationally.⁴⁰ The energy order of various hexatriene (HT) radical cation rotamers was concluded to be *cis-cis-cis* (ccc) < *cis-trans-cis* (ctc) < *trans-cis-trans* (tct) < *trans-trans-trans* (ttt).^{41,42} A detailed matrix-isolation study of photochemical interconversions between different hexatriene cation rotamers as well as the ring opening of cyclohexadiene cation was also reported.⁴³ The only photodissociation process observed so far for the 1,3,5-hexatriene cation was $C_6H_8^+ \rightarrow C_6H_7^+ + H$.^{44,45}

In the present study we suggest a theoretical interpretation of the resonance ionization and fragmentation of 1,3- and 1,4-CHD and try to explain the observed mass spectra based on the analysis of the calculated potential energy surface. Our goal is to investigate the thermochemical and mechanistic aspects of the dissociation of the cyclohexadiene mono- and dications with the help of density functional and *ab initio* calculations.

Computational methods

Geometries of various isomers, transition states, and fragmentation products on PESs of 1,3- and 1,4-CHD and their mono- and dications have been optimized using the hybrid density functional B3LYP method^{46,47} and the standard 6-31G** basis set.⁴⁸ Vibrational frequencies calculated at the same B3LYP/6-31G** level of theory were used to characterize stationary points on PESs as local minima (the number of imaginary frequencies NIMAG = 0) or transition states (NIMAG = 1) and to compute zero-point vibrational energies (ZPE) as a half of the sum of all harmonic vibrational frequencies.⁴⁹ Unless mentioned otherwise, all relative energies discussed in the text include ZPE corrections. Minimal energy reaction paths from transition states down to corresponding local minima have been traced using the intrinsic reaction coordinate (IRC) method.⁵⁰ Energies of most important structures have been refined by single-point calculations utilizing the chemically accurate model chemistry G3(MP2,CCSD)//B3LYP/6-31G** approach.^{51,52} The computed data on the PESs and molecular parameters have been used for statistical calculations of energy-dependent rate constants of individual reaction steps employing RRKM theory.^{53–55} Then, the rate constants have been utilized to solve systems of kinetic equations to obtain relative yields of various fragmentation products.

A variety of quantum chemical methods including time-dependent density functional theory TD-B3LYP,^{56–58} outer-valence Green functions method OVGF,^{59,60} complete active space self-consistent field CASSCF,^{61,62} configuration interaction with single excitations CIS⁶³ and with single and double excitations CISD,^{64,65} and coupled-clusters with single and double excitations and perturbative treatment of triple excitations CCSD(T)^{66,67} (available in the MOLPRO 2002⁶⁸ and GAUSSIAN-03⁴⁸ program packages) with the standard

6-31G**, 6-311G*, 6-311+G*, and aug-cc-pvdz basis sets⁴⁸ were used for calculations of ionization potentials (IP) and electronic excitation energies (E_c).

Results and discussion

Multiphoton ionization

The results of our quantum chemical calculations of ionization and electronic excitation energies of 1,3- and 1,4-CHD are collected in the Supplementary Information in Tables S1–S4 and illustrated in Fig. S1–S3.† Most of calculations of excitation energies have been performed using the outer valence Green functions method (OVGF),^{59,60} which provides electronic correlation corrections to Koopmans' theorem. The method is based upon *ab initio* electron propagator theory, where propagator self-energies are expanded through third and fourth order in electronic interaction. The Hartree–Fock wavefunction in OVGF is used as a reference state, and then order by order corrections to Koopmans' theorem are generated. Thus, the OVGF approach is generally much more accurate than simple interpretation of transition energies based on the orbital energies (HOMO–LUMO) and it often provides agreement with experiment within 0.1 eV. Fig. S1 shows molecular orbital (MO) energy levels of 1,3-CHD and 1,4-CHD calculated at the HF/6-311+G* level and illustrates electronic density distribution for four highest occupied MOs. The calculated values and types of the most relevant ionization potentials involved in the formation of mono- and dications of the 1,3-CHD and 1,4-CHD molecules are presented in Fig. S2 and S3, respectively. Single ionization potentials from five highest occupied MOs and double ionization potentials where one electron is removed from HOMO and another from ten highest occupied orbitals computed at different theoretical levels at optimized geometries of neutral 1,3-CHD and 1,4-CHD (vertical IPs) are given in Table S1 in the Supplementary Information. Vertical IPs from the highest occupied level of radical cations 1,3-CHD⁺ and 1,4-CHD⁺ calculated at optimized geometries of these monocations are presented in Table S2. A comparison of the data in the two Tables shows that when ionization occurs from HOMO, due to a bonding character of this orbital, geometric relaxation of the monocations reduces their IPs by ~0.3 eV. Excitation energies and oscillator strengths for electronic transitions involving eleven doubly occupied and sixteen vacant MOs in mono- and dications are collected in Tables S3 and S4, respectively, in the Supplementary Information.

The calculated single and double ionization energies for 1,3-CHD, 8.20 and 22.9 eV (Table S1), are close to the experimental values of 8.25 and 23.1 eV,¹⁰ respectively. The computed energies for the lowest electronic transitions in the 1,3-CHD⁺ and 1,4-CHD⁺ monocations are 2.81 and 1.17 eV (Table S3), respectively, also in good accord with the experimental values of 2.58 and 1.22 eV.⁶⁹ This indicates that our results should be generally reliable.

Some of the calculated IP values are resonant with the laser wavelength of 800 nm used in most experiments described in the Introduction. For instance, as seen in Table S1, the 1,3-cyclohexadiene monocation 1,3-CHD⁺ can be produced by

resonance ionization of the neutral molecule from the orbital HOMO-1 (Fig. S1 in Supplementary Information) with the calculated IP of 10.90 eV. A resonance exists between the energy of seven laser photons (the energy of one photon is equal to 1.55 eV) and the computed IP. Then 1,3-CHD⁺ is produced in an excited electronic state (Fig. S2). Next, the electronically excited monocation can relax to the ground state by transferring an electron from HOMO to HOMO-1. If this process occurs radiationlessly, *i.e.*, *via* internal conversion, the monocation acquires internal (vibrational) energy equal to the difference of the calculated IPs from HOMO-1 (10.90 eV) and HOMO (8.20 eV). An indirect indication that such internal conversion is feasible is a large oscillator strength computed for this electronic transition (Table S3), which corresponds to a high transition dipole moment between the two states. As a result, the ground state monocation 1,3-CHD⁺ will be obtained with internal energy of 2.5–3.1 eV depending on the level of theoretical calculations. Note that the experimental transition energy for this case is 2.58 eV and thus the direct excitation from the monocation is not in resonance with the laser wavelength (1.7 times photon energy). This energy may be sufficient for the ring opening and H detachment from the monocation.²³

The further fate of the monocation in intense laser field can be twofold: it can either undergo further excitation or ionization from the excited electronic state or first relax to vibrationally hot ground electronic state and then be ionized or excited. If the removal of the first electron from HOMO-1 is immediately followed by the second ionization from HOMO, the energy required for the elimination of a second electron is estimated as the energy of 9.2 laser photons (Table S1). In this case, the 1,3-CHD²⁺ dication is formed in an excited electronic state, 2.25 eV above the ground state at the vertical geometry according to OVGF/6-311+G* calculations (Table S1). The fact that the observed TOF mass spectra¹⁰ mostly contain the peak corresponding to 1,3-CHD⁺ and a small 1,3-CHD²⁺ peak indicate that this scenario was unlikely under the experimental conditions. This means that before the monocation can be ionized, it undergoes fast internal conversion to the ground state from which both absorption of a single 800 nm photon and multiphoton resonance ionization are not very probable—see absorption spectra of 1,3-CHD⁺.¹⁰ According to its excitation energies shown in Table S3, the monocation can be excited by five laser photons (HOMO-1 → LUMO+1) but, since the monocation survives in the experimental conditions, apparently, the intensity of this transitions is not high enough.

If ionization of the monocation takes place from the ground electronic state, the most likely process is removal of two electrons in 1,3-CHD from HOMO, for which the required energy is close to a resonance with the energy of fifteen photons. However, internal energy acquired in this case by the dication produced would be too low and not sufficient for fragmentation (see the subsequent section). According to our calculations, there is a resonance between the HOMO-3 → LUMO intense excitation in 1,3-CHD²⁺ and the energy of three photons (Table S4). However, the corresponding IP of 1,3-CHD⁺ where one electron is removed from HOMO and another from HOMO-4 cannot be strictly assigned as

resonant. The calculated IP value equals to 17.2 times the photon energy, but considering that the calculated values are underestimated 0.05–0.37 eV as compared to experiment (0.03–0.24 times the photon energy), the experimental energy required for this transition should be even further away from resonance than the calculated value. The experimental study where the dications were observed²³ was carried out with shorter laser pulses and therefore with a broader distribution of photon energies. This could have made resonance multiphoton ionization of 1,3-CHD⁺ and 1,3-CHD²⁺ somewhat more probable.

For 1,4-CHD, the calculated ionization energies from HOMO and HOMO-3 are in resonance with six and eight photons, respectively (Table S1). The excited electronic state of 1,4-CHD⁺ formed in this case lies 3.39 eV above the vertical ground state. It is also seen in Table S3 that the energies of two electronic transitions in 1,4-CHD⁺, HOMO → LUMO+1 and HOMO-3 → HOMO, are close to resonance with three photons. If these transitions would occur and be followed by internal conversion to 1,4-CHD⁺ in the ground electronic state, the acquired internal energy should be sufficient for the H loss from the cation because, according to our calculations, the energy required for this process is only 3.3 eV. Indeed, small peaks corresponding to C₆H₇⁺ and C₆H₆⁺ were observed in the experimental mass spectra.¹⁰ Otherwise, excited 1,4-CHD⁺ is able to absorb another 800 nm (1.55 eV) photons and thus acquire extra energy. This explains why only a small peak corresponding to 1,4-CHD⁺ was observed in experiment. Double ionization with formation of the dication 1,4-CHD²⁺ is in resonance with the energy of fifteen or eighteen photons if two electrons are removed from HOMO or one from HOMO and another from HOMO-4, respectively (see Table S1 and Fig. S3). If the electronically excited state is produced first, it can undergo internal conversion to the ground state providing the molecule with internal vibrational energy of 4.2 eV, estimated as a difference of IPs given in Table S1. Alternatively, assuming that the ground state dication is produced first, it may absorb two extra

photons (HOMO-2 → LUMO) if its two-photon absorption cross section is high enough and then be subjected to internal conversion. In both cases, the internal energy of the ground-state dication should be sufficient for its fragmentation.

Based on the above consideration of ionization potentials of 1,3-CHD and 1,4-CHD and their resonance with the photon energy, we find that the internal energy acquired by these molecules upon irradiation in intense 800 nm laser field and multiphoton ionization is generally much lower for 1,3-CHD than for 1,4-CHD. The amount of available energy for the 1,4-CHD²⁺ dication can be estimated as the energy of 2–3 photons, *i.e.*, 70–110 kcal/mol. Hence, in our calculations of rate constants for isomerization and fragmentation reactions of 1,4-CHD²⁺ we used available internal energies of 75, 85, and 105 kcal/mol. Now we can address dissociation mechanisms of C₆H₈⁺ and C₆H₈²⁺ in more detail.

Dissociation mechanisms

Monocations

Fig. 1 and Table S5 in Supplementary Information† show optimized structures and relative energies of various species along rearrangement and dissociation channels of cyclohexadiene monocations calculated at the G3MP2//B3LYP/6-31G** level of theory. One can see in Table S5 that decomposition of C₆H₈⁺ is a rather difficult process, which requires significant energy. Even the most energetically favorable dissociation channels, elimination of an H₂ molecule, C₆H₈⁺ → H₂ + C₆H₆⁺, and atomic hydrogen, C₆H₈⁺ → H + C₆H₇⁺, are endothermic by 50.9 and 41.3 kcal/mol, respectively. Splitting of the H⁺, H₂⁺, C₂H₃⁺, and C₄H₆⁺ cations is more unfavorable, with endothermicities varying between 70 and 210 kcal/mol. At the G3(MP2)//B3LYP/6-31G** level, no exit barrier was found for the atomic hydrogen elimination channel and a tiny (~0.05 kcal/mol) barrier was located at B3LYP/6-31G**. This result somewhat differ from that obtained at the UMP2/6-311+G**//UMP2/6-31G* level,³⁹ where a distinct

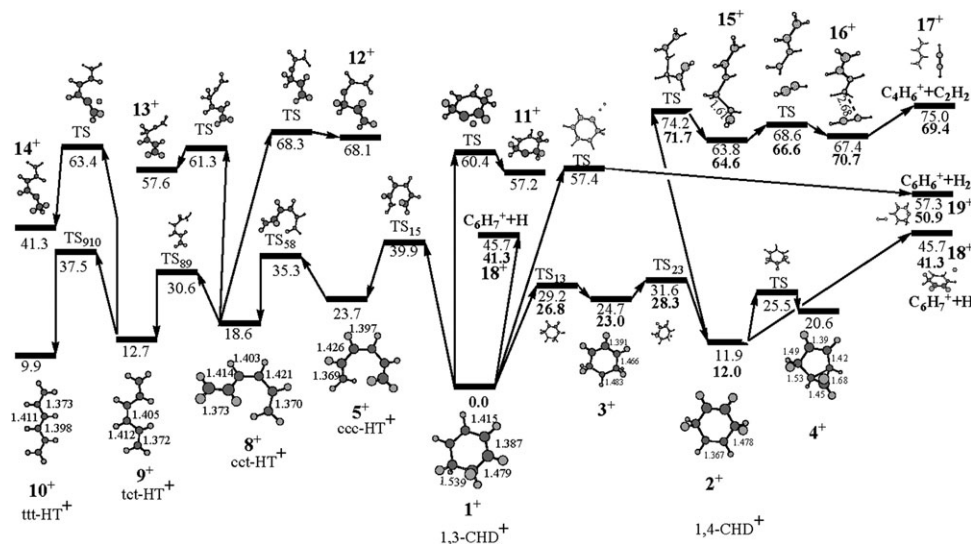


Fig. 1 Potential energy diagram for various reaction channels of isomerization and dissociation of the CHD⁺ monocation calculated at the B3LYP/6-31G** + ZPE and G3MP2// B3LYP/6-31G** (shown in bold) levels. Relative energies of various species are given in kcal/mol.

transition state for the H loss was found and the exit barrier was evaluated to be in the range of 6.3–10.6 kcal/mol. As UMP2 calculations usually tend to overestimate barrier heights, we expect that the present G3(MP2)//B3LYP/6-31G** result should be more reliable.

Within the energy range available from absorption of one laser photon, 35.7 kcal/mol, H atom elimination from 1,4-CHD⁺ as well as several intramolecular rearrangements are possible (see Fig. 1). The 1,4-CHD⁺ isomer (**2**⁺) lies 12.0 kcal/mol higher in energy than 1,3-CHD⁺ (**1**⁺) and therefore **2**⁺ is less stable and can lose hydrogen easier. **1**⁺ and **2**⁺ can be obtained from one another by two consecutive H migrations, and **3**⁺, the intermediate between them, resides 23.0 kcal/mol above the most stable isomer **1**⁺ and is separated from **1**⁺ and **2**⁺ by small barriers of 3.8 and 5.3 kcal/mol, respectively. Structure **2**⁺ can be transformed, overcoming a barrier of 13.6 kcal/mol, into isomer **4**⁺ lying 8.7 kcal/mol above **2**⁺ and containing adjoining five- and three-member rings.

The energy required to open the cyclohexadiene ring appears to be higher than that needed for the H shifts. In particular, isomerization of the most stable isomer 1,3-CHD⁺ **1**⁺ to the open-chain structure ccc-hexatriene (ccc-HT, **5**⁺), which resides 23.7 kcal/mol higher in energy than **1**⁺, occurs *via* transition state TS₁₅ overcoming a barrier of 39.9 kcal/mol at the B3LYP/6-31G** + ZPE level. At the QCISD(T)/6-311G**//QCISD/6-31G* level, the barrier height at TS₁₅ was calculated as 36.7 kcal/mol,³⁷ whereas in experiment it was estimated for similar compounds as 7–16.5 kcal/mol,^{70,71–75} although these measurements may concern ring opening in the dication. Considering different conformations of the hexatriene cation, we find that their energies decrease as the number of *trans* fragments increases (see Tables S5 and S6 in the Supplementary Information† and Fig. 1). For instance, *cis-cis-trans*-hexatriene (cct-HT, **8**⁺), is 5.1 kcal/mol more stable than ccc-HT (**5**⁺), tct-HT (**9**⁺) is 5.9 kcal/mol more favorable than cct-HT (**8**⁺), and ttt-HT (**10**⁺) lies 2.8 kcal/mol lower in energy than tct-HT (**9**⁺). The barriers separating these conformations and corresponding to rotations around CC bonds are calculated to be 11.6 (**5**⁺–**8**⁺), 12.0 (**8**⁺–**9**⁺), and 24.8 kcal/mol (**9**⁺–**10**⁺).

The formation of the high-lying isomer **11**⁺, 57.2 kcal/mol above **1**⁺, from the latter requires a 60.4 kcal/mol barrier and involves H migration along the ring leaving one carbon atom without a hydrogen. Similarly high barriers of 68.3 and 61.3 kcal/mol are calculated for H migrations in hexatriene leading from cct-HT **8**⁺ to isomers **12**⁺, 68.1 kcal/mol above **1**⁺, and **13**⁺, 57.6 kcal/mol higher than **1**⁺, respectively. An H shift in tct-HT **9**⁺ occurs *via* a barrier of 50.7 kcal/mol and leads to the formation of structure **14**⁺, 41.3 kcal/mol, which has a terminal CH₃ group. However, these processes are significantly less favorable as compared to the H loss from cyclohexadienes, ring opening, and conformational changes of hexatriene.

Since the C₆H₈⁺ → H + C₆H₇⁺ reaction is the most preferable dissociation channel of cyclohexadiene cations, we also considered various scenarios of secondary decomposition of C₆H₇⁺ (see Fig. 2 and 3 and Table S5 in the Supplementary Information†). The H loss reaction C₆H₇⁺ → H + C₆H₆⁺ is calculated to be endothermic by 76.4 kcal/mol, whereas the

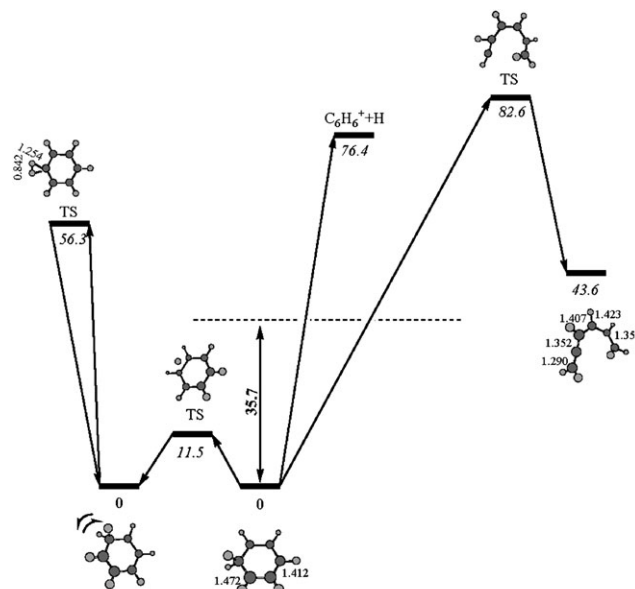


Fig. 2 Potential energy diagram for various reaction channels of isomerization and dissociation of the C₆H₇⁺ monocation calculated at the B3LYP/6-31G** + ZPE level. Relative energies of various species are given in kcal/mol.

ring opening has endothermicity of 43.6 kcal/mol and goes *via* a barrier of 82.6 kcal/mol. We can see that these values are about twice as high as those for the analogous processes in C₆H₈⁺. Fig. 3 shows relative energies of various structural isomers of C₆H₇⁺. According to the present calculations, the six-member ring structure is the most favorable, followed by planar five-member ring isomers (11–33 kcal/mol), and then by open chains and structures containing four-member rings and deformed five-member cycles (39–59 kcal/mol). The two least stable isomers are a six-member ring with a bare (hydrogen-less) carbon atom (100 kcal/mol) and a structure containing a three-member cycle (121 kcal/mol).

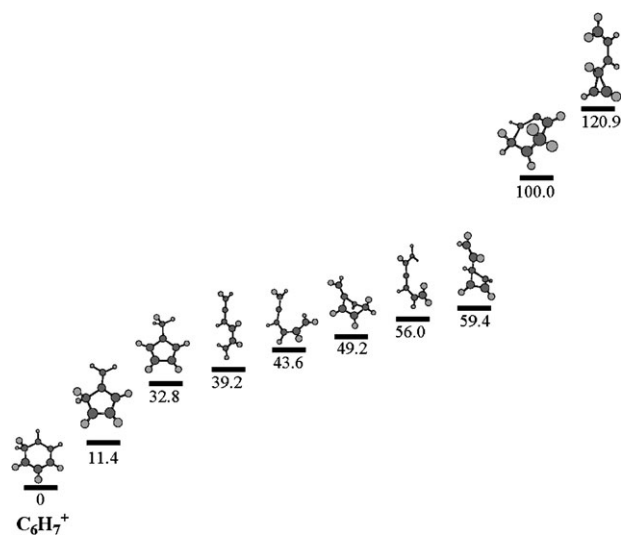


Fig. 3 Potential energy diagram of various isomers of the C₆H₇⁺ monocation calculated at the B3LYP/6-31G** + ZPE level. Relative energies of various species are given in kcal/mol.

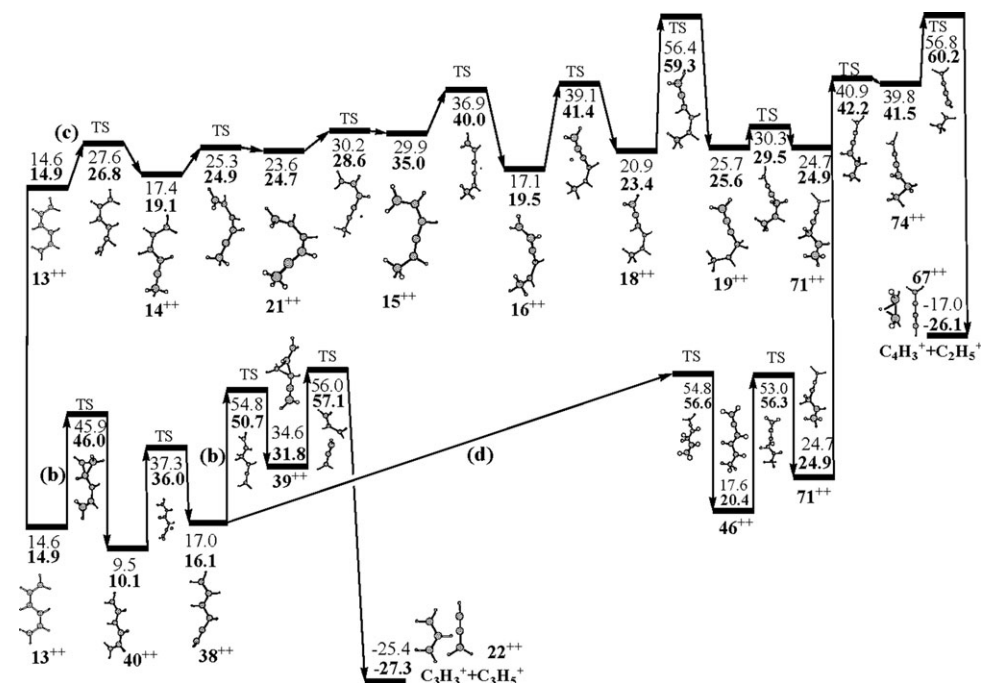


Fig. 5 Potential energy diagram for pathways (b), (c), and (d) of isomerization and dissociation of the CHD^{2+} dication calculated at the B3LYP/6-31G**+ZPE and G3MP2//B3LYP/6-31G** (in bold) levels. Relative energies of various species are given in kcal/mol.

Pathway (c) involves only H migrations and conformational changes and goes *via* chain intermediates: $13^{++} \rightarrow 14^{++} \rightarrow 21^{++} \rightarrow 15^{++} \rightarrow 16^{++} \rightarrow 18^{++} \rightarrow 19^{++} \rightarrow 71^{++} \rightarrow 74^{++} \rightarrow 67^{++}$. Isomers 14^{++} , 21^{++} , 15^{++} , 16^{++} , 18^{++} , 19^{++} , 71^{++} , and 74^{++} lie 4.2, 9.8, 20.1, 4.6, 8.5, 10.7, 10.0, and 26.6 kcal/mol higher in energy than 13^{++} , respectively,

and relative energies of transition states along this pathway are 26.8, 24.9, 28.6, 40.0, 41.4, 59.3, 29.5, 42.2, and 60.2 kcal/mol (Fig. 5). Pathway (d) proceeds from isomer 38^{++} through 46^{++} to the structure 71^{++} . The relative energy of isomer 46^{++} is 20.4 kcal/mol and those of transition states along the $38^{++} \rightarrow 46^{++} \rightarrow 71^{++}$ pathway are 56.6 and 56.3 kcal/mol.

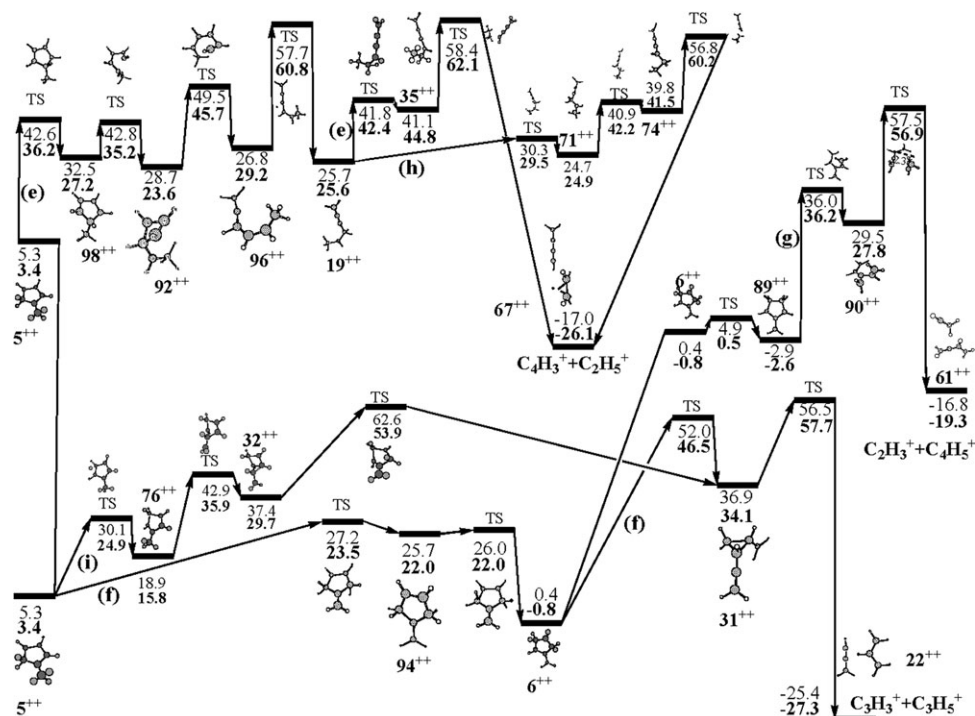


Fig. 6 Potential energy diagram for pathways (e), (f), (g), (h), and (i) of isomerization and dissociation of the CHD^{2+} dication calculated at the B3LYP/6-31G**+ZPE and G3MP2//B3LYP/6-31G** (in bold) level. Relative energies of various species are given in kcal/mol.

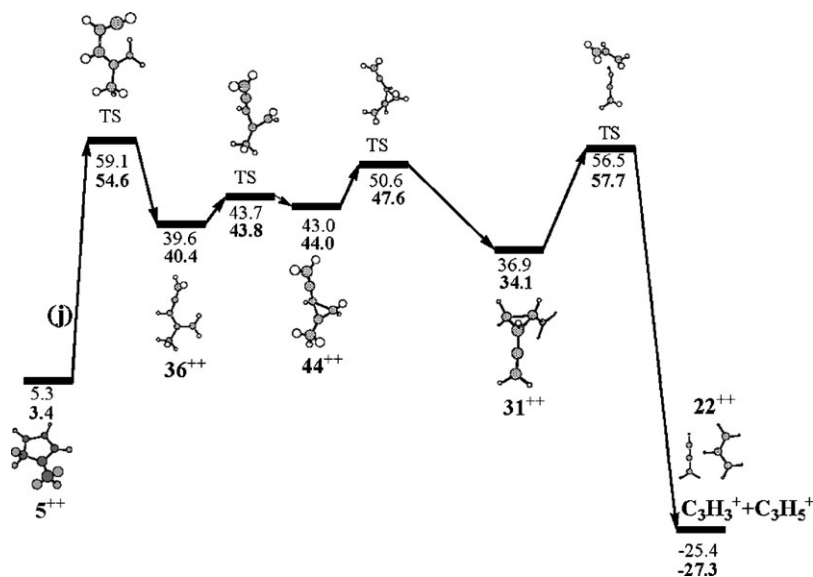


Fig. 7 Potential energy diagram for pathway (j) of isomerization and dissociation of the CHD²⁺ dication calculated at the B3LYP/6-31G**+ZPE and G3MP2//B3LYP/6-31G** (in bold) level. Relative energies of various species are given in kcal/mol.

Fig. 6 shows the most preferable dissociation channels, which pass *via* the five-member ring isomer **5⁺⁺** lying 9.1 kcal/mol above the most stable structure **3⁺⁺** and separated from it by a 20.8 kcal/mol barrier (Fig. 4). Three reaction channels are possible starting from **5⁺⁺**, (e), (f) and (i). Pathway (e), C₆H₈⁺⁺ (**5⁺⁺**) → C₄H₃⁺ + C₂H₅⁺ (**67⁺⁺**) involves open-chain isomers and structures containing four- and five-member rings: **5⁺⁺** → **98⁺⁺** → **92⁺⁺** → **96⁺⁺** → **19⁺⁺** → **35⁺⁺** → **67⁺⁺**. Relative energies of these intermediates and the product with respect to **1⁺⁺** are 3.4, 27.2, 23.6, 29.2, 25.6, 44.8, and -26.1 kcal/mol, and transition states have energies of 36.2, 35.2, 45.7, 60.8, 42.7, and 62.1 kcal/mol. Pathway (f) leads from **5⁺⁺** to isomer **94⁺⁺**, 18.6 kcal/mol above the former, *via* a barrier of 20.1 kcal/mol, and then to isomer **6⁺⁺** overcoming a tiny barrier of 0.1 kcal/mol. **6⁺⁺** is

0.8 and 4.2 kcal/mol more stable than **1⁺⁺** and **5⁺⁺**, respectively. Two dissociation channels exist starting from **6⁺⁺**, continuation of pathway (f), **6⁺⁺** → **31⁺⁺** → **22⁺⁺** leading to the C₃H₃⁺ and C₃H₅⁺ fragments, and pathway (g), **6⁺⁺** → **89⁺⁺** → **90⁺⁺** → **61⁺⁺** resulting in C₂H₃⁺ + C₄H₅⁺. The calculated exothermicity of the C₆H₈⁺⁺ (**1⁺⁺**) → C₂H₃⁺ + C₄H₅⁺ (**61⁺⁺**) reaction is 19.3 kcal/mol. Isomer **89⁺⁺** is 2.6 kcal/mol more stable than **1⁺⁺**, whereas **31⁺⁺** and **90⁺⁺** are less favorable than **1⁺⁺** by 34.1 and 27.8 kcal/mol, respectively. The barriers needed to be overcome are 47.3 and 23.6 kcal/mol on pathway (f) and 1.3, 38.8, and 29.1 kcal/mol along pathway (g).

Pathway (h) goes from isomer **19⁺⁺** *via* intermediates **71⁺⁺** and **74⁺⁺** to the C₄H₃⁺ + C₂H₅⁺ (**67⁺⁺**) fragmentation products (Fig. 6). Relative energies of the isomers are 24.9

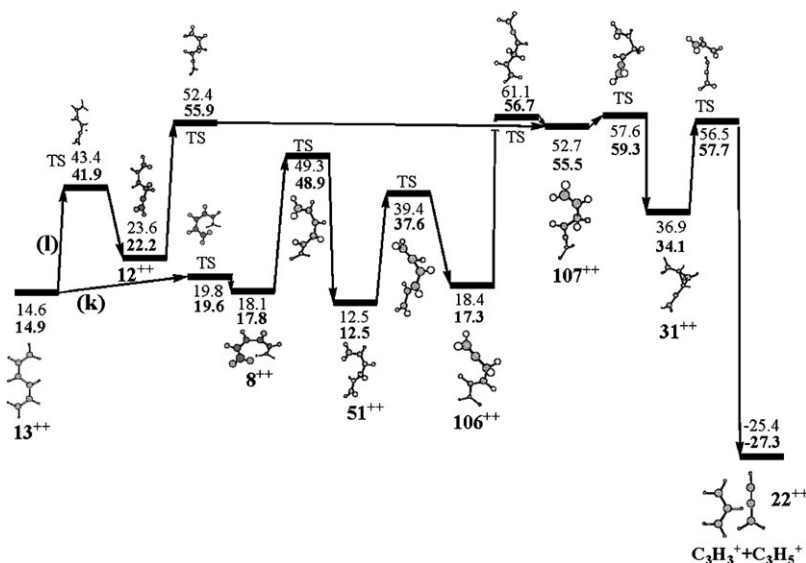


Fig. 8 Potential energy diagram for pathways (k) and (l) of isomerization and dissociation of the CHD²⁺ dication calculated at the B3LYP/6-31G**+ZPE and G3MP2//B3LYP/6-31G** (in bold) level. Relative energies of various species are given in kcal/mol.

and 41.5 kcal/mol and those of transition states along the pathway $19^{++} \rightarrow 71^{++} \rightarrow 74^{++} \rightarrow 67^{++}$ are 29.5, 42.2, and 60.2 kcal/mol. Pathways (i) and (j) lead from structure 5^{++} to 31^{++} via intermediates 76^{++} and 32^{++} (Fig. 6, (i)) and via 36^{++} and 44^{++} (Fig. 7, (j)). For pathway (i) the relative energies of the isomers are 15.8 and 29.7 kcal/mol and the energies of transition states along $5^{++} \rightarrow 76^{++} \rightarrow 32^{++} \rightarrow 31^{++}$ are 24.9, 35.9, and 53.9 kcal/mol. For pathway j, $5^{++} \rightarrow 36^{++} \rightarrow 44^{++} \rightarrow 31^{++}$, the relative energies of the isomers and transition states are 40.4, 44.0, 54.6, 43.8, and 47.6 kcal/mol, respectively. Pathways (k) and (l) shown on Fig. 8 proceed from isomer 13^{++} to 31^{++} via consecutive intermediates 8^{++} (17.8 kcal/mol), 51^{++} (12.5 kcal/mol), 106^{++} (17.3 kcal/mol), and 107^{++} (55.5 kcal/mol) (channel (k)) and 12^{++} (22.2 kcal/mol) and 107^{++} (channel (l)). The highest barrier on pathway (l), 55.9 kcal/mol, is 0.8 kcal/mol lower than that on pathway (k). Isomer 107^{++} is separated from 31^{++} by a barrier of 3.8 kcal/mol, while the barrier for the last fragmentation step on this pathway being 1.6 kcal/mol lower than that for the preceding step (relative to 1^{++}). Finally, Fig. 4 shows less favorable fragmentation channels, such as elimination of H^+ and molecular hydrogen, which are not expected to give a significant contribution.

Relative yields of various fragmentation products of the CHD^{2+} dication calculated for available internal energies of 75, 85, and 105 kcal/mol are collected in Table 1. As mentioned above, the chosen sequence of internal energies covers the range of 2–3 photon energies, determined from the analysis of resonance multiphoton ionization caused by intense laser field with wavelength of 800 nm. It follows from the data shown in Table 1 that for the dication at all used internal energy values the fragmentation to $C_3H_3^+ + C_3H_5^+$ and $C_2H_3^+ + C_4H_5^+$ is preferable, where the former channel is favorable at lower energies and the latter at higher energies. As the available energy increases from 75 to 105 kcal/mol, the relative yield of $C_3H_3^+ + C_3H_5^+$ decreases from 48 to 31%, whereas the branching ratio of $C_2H_3^+ + C_4H_5^+$ increases from 39 to 42%. Meanwhile, the percentage yield of the $C_4H_3^+ + C_2H_5^+$ fragmentation grows by more than a factor of 2, from 13 to 27%. The calculated branching ratios are consistent with the experimental mass spectra,¹⁰ and the best agreement between the theoretical values and experiment is seen for the internal energy of 75 kcal/mol. It should be noted, however, that due to the complexity of the multiphoton ionization process, the dications in experiment may be formed with different internal energies and we do not deal here with a molecular ensemble with the same internal energy, like in the case of simple one-photon photodissociation.

Interestingly, the proton elimination from the dications is of minor importance, despite that the H loss is the dominant

Table 1 Relative yields of fragmentation products of $C_6H_8^{2+}$ (in %) calculated using the steady-state approximation for the internal energy values of 75, 85, and 105 kcal/mol

Internal energy	75 kcal/mol	85 kcal/mol	105 kcal/mol	Expt. ¹⁰
$C_3H_3^+ + C_3H_5^+$	48	39	31	45
$C_2H_3^+ + C_4H_5^+$	39	40	42	31
$C_4H_3^+ + C_2H_5^+$	13	21	27	24

process for the neutral molecules and monocations. This can be attributed to the reaction energetics. First, dissociation of dications to two monocations with separation of charge is more favorable than to a dication fragment and neutral H atom. Second, the elimination of H^+ is highly endothermic whereas dissociation to two heavy hydrocarbon monocations is exothermic (see Fig. 4 and Table S5 in the Supplementary Information†), which is a consequence of the very high ionization potential of the hydrogen atom (13.6 eV). As a result of the unfavorable reaction energy, the proton elimination from CHD^{2+} is not preferable kinetically.

Concluding remarks

Using the isomeric pair of 1,3-CHD and 1,4-CHD as an example, we have demonstrated that for the case of multiphoton resonance ionization followed by fragmentation one can evaluate the range of internal energies available for fragmentation of the cations through calculations of ionization potentials and electronic excitation energies. Calculations of PESs for various fragmentation channels and relative product yields at different available internal energies allowed us to analyze the trends in branching ratios for the major dissociation products of the 1,4- CHD^{2+} dication, including $C_3H_3^+ + C_3H_5^+$, $C_2H_3^+ + C_4H_5^+$, and $C_4H_3^+ + C_2H_5^+$. A comparison of theoretical results with experiment also shows that a pure presence of resonance between the laser wavelength and a certain ionization potential is not sufficient for fragmentation of the ion to occur. In addition, efficient internal conversion to the ground electronic state should be feasible and, if internal vibrational energy generated in this case from the energy of electronic excitation is high enough, fragmentation should then take place and TOF mass spectra should produce peaks corresponding to charged molecular fragments, as in the case of 1,4-cyclohexadiene. However, if this energy is not sufficient or internal conversion to the ground electronic state is too slow on the timescale of a particular experiment, the resonance fragmentation would not take place and mass spectra would mostly show parent ions produced by multiphoton ionization, as in the case of 1,3-cyclohexadiene.

It should be also noted that multiphoton resonance ionization is not the only mechanism, which can lead to the formation of multi-charged ions in intense laser fields. It is well established in the literature that other mechanisms may occur under fs laser fields at relatively moderated intensities. For instance, it has been shown that within the first laser period after ionization, the extracted electron is likely to return to the vicinity of the ion with high kinetic energy and such re-collision can bring about further autoionization of this ion.^{77,78} In this case, the resulting internal energy and hence the fragmentation pattern of the multi-charged ion produced can differ from those ensuing resonance multi-ionization.

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