

Cite this: *Chem. Sci.*, 2026, 17, 5029

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Deciphering the molecular origin of the 19.3 eV electronic excitation energy of  $\text{H}_3^+$ Josene M. Toldo,<sup>†ab</sup> Jakob K. Staab,<sup>†ac</sup> Eduard Matito,<sup>de</sup> Cina Foroutan-Nejad<sup>f</sup> and Henrik Ottosson<sup>ga</sup>

The trihydrogen cation,  $\text{H}_3^+$ , is unique in the Universe. It serves as the primary proton reservoir, driving essential astrochemical reactions, and it functions as a thermostat for giant gas planets.  $\text{H}_3^+$  has also a remarkably low photodissociation rate, explained by its exceptionally high first electronic excitation energy (19.3 eV), which is well above the ionization energy of the much more abundant monohydrogen (13.6 eV). Herein we reveal that the key factors behind the high excitation energy of  $\text{H}_3^+$ , and thus, its astrophotocatalytic inertness, are: (i) aromatic stabilization in its electronic ground state, (ii) antiaromatic destabilization in its first excited state, and (iii) a high nuclear-to-electronic charge ratio (+3 vs. -2). Through comparisons with analogous (isolobal)  $\pi$ -conjugated carbocations, we find that ground state aromatic stabilization plus excited state antiaromatic destabilization raise the excitation energy of  $\text{H}_3^+$  by 4.8–6.0 eV. This means that for  $\text{H}_3^+$ , the excited state antiaromatic character (which normally leads to high photoreactivity) contributes to its astrophotocatalytic inertness. Thus, only with the increase in excitation energy due to ground state aromaticity plus excited antiaromaticity can  $\text{H}_3^+$  act as a thermostat for giant gas planets and as a proton reservoir that drives astrochemical reactions, thereby fulfilling its unique role in space.

Received 19th November 2025  
Accepted 30th December 2025

DOI: 10.1039/d5sc09067a

rsc.li/chemical-science

## Introduction

Triangular  $\text{H}_3^+$  is the most abundant polyatomic ion in the interstellar medium, where it functions as the primary interstellar acid, initiating reactions that lead to more complex molecules (Fig. 1).<sup>1–3</sup> It further acts as a thermostat (coolant) in the upper atmospheres of giant gas planets,<sup>4</sup> and it has been postulated that it even could have functioned as a coolant in the primordial gas (though with a different mechanism than in the giant gas planets).<sup>5</sup> With three H atoms, it is the smallest molecule that exhibits aromaticity ( $\sigma$ -aromaticity),<sup>6–9</sup> a stabilizing molecular property.<sup>10</sup>

The first electronically excited singlet states of  $\text{H}_3^+$ , the doubly degenerate  $1^1\text{E}'$  states at the equilateral triangular structure ( $D_{3h}$  symmetric), are of exceptionally high vertical energy (19.3 eV, Fig. 2),<sup>11</sup> and they are dipole-allowed and

dissociative.<sup>12–14</sup> Despite this, astrochemical databases list a photodissociation rate of  $4 \times 10^{-13} \text{ s}^{-1}$  or lower,<sup>13,15</sup> whereby it is among the astrochemical species with lowest photodissociation rates.<sup>16,17</sup> The reason is that the much more

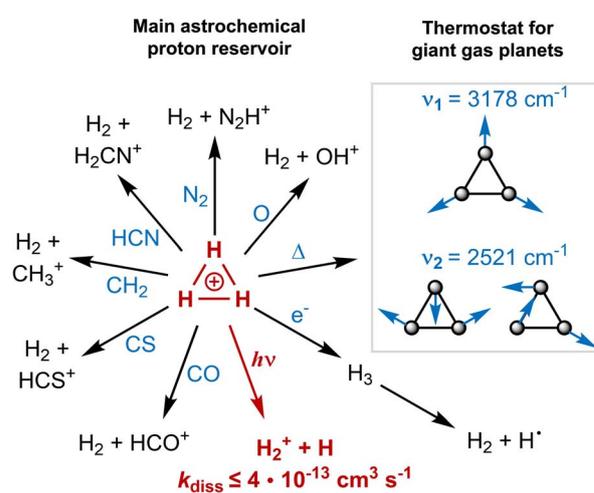


Fig. 1 A summary of the functions of  $\text{H}_3^+$  in space, with its role as (i) primary proton reservoir initiating a number of core astrochemical reactions (typical rate constants for these reactions are  $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ), and (ii) as a thermostat in the upper atmospheres of giant gas planets ensuring that their temperatures do not exceed a threshold.

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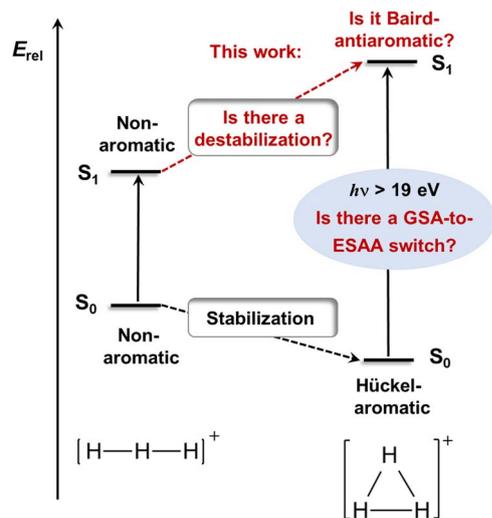


Fig. 2 Tentative changes from the nonaromatic character of linear  $H_3^+$  in its  $S_0$  and  $S_1$  states to the equilateral triangular  $H_3^+$  with a stabilizing Hückel-aromaticity in  $S_0$  (GSA = ground state aromaticity) and a destabilizing Baird-antiaromaticity in  $S_1$  (ESAA = excited state antiaromaticity). Factors related to our hypothesis and explored herein written in red, while known factors in black.

abundant H and  $H_2$ , with ionization and excitation energies at 13.1–15.4 eV,<sup>1,18</sup> shield  $H_3^+$  from high-energy irradiation in the interstellar medium (ISM).<sup>12,13,19,20</sup> In the ISM,  $H_3^+$  degrades unimolecularly only when exposed to electrons ejected from other molecules or atoms upon cosmic ray ionization.<sup>1,13</sup> Indeed, direct photodissociation only occurs when  $H_3^+$  is rovibrationally excited, whereby the electronic excitation energy decreases down to 4.9 eV.<sup>12,13</sup> Had it been more prone to photodissociate, this would have impaired its astrochemical and astrophysical functions, and thus, been detrimental to the development of the Universe as we presently know it. However, the molecular origins of its very high vertical excitation energy remain unknown and have never been addressed earlier. With such fundamental knowledge in hand it should also be possible to pinpoint other species of astrochemical relevance that may also exhibit unusually high first electronic excitation energies.

$H_3^+$  in its electronic ground state ( $S_0$ ) has a  $D_{3h}$  symmetric structure<sup>11,21–23</sup> with  $\sigma$ -aromatic character,<sup>6–9</sup> in line with Hückel's  $4n + 2$  rule ( $n = 0, 1, 2, \dots$ ) as it has two  $\sigma$ -electrons. We now hypothesize that the counter-concept, antiaromaticity,<sup>10</sup> is relevant for its first excited state of singlet multiplicity ( $S_1$ ), and thus, its excitation energy (Fig. 2). In this context, the analogous cyclic and fully  $\pi$ -conjugated hydrocarbons (*i.e.*, annulenes) in their lowest excited triplet states ( $T_1$ ) of  $\pi\pi^*$  character follow Baird's rule,<sup>24–28</sup> which tells that molecules with  $4n + 2$   $\pi$ -electrons are antiaromatic and destabilized in these states while those with  $4n$  are aromatic and stabilized. Although derived for the  $T_1$  state, the rule can often be extended to the lowest  $\pi\pi^*$  excited state of singlet multiplicity. Thus, the exceptionally high excitation energy of  $H_3^+$  may stem from  $\sigma$ -antiaromatic destabilization in  $S_1$  (Fig. 2) combined with  $\sigma$ -aromatic stabilization

in  $S_0$ , *i.e.*, a switch in character from ground state Hückel-aromaticity (GSA) to excited state Baird-antiaromaticity (ESAA), a GSA-to-ESAA switch in character.

Accordingly, we now investigated if the lowest excited states of  $H_3^+$  are antiaromatic and based this assessment on quantum chemical calculations of various (anti)aromaticity descriptors. Is ESAA the factor that leads to the very high excitation energy or are there other factors? Furthermore, can knowledge gained through this investigation impact on other parts of astrochemistry? The  $H_3^+$  cation has a 3-center 2-electron bond, a type of bonding it shares with nonclassical carbocations such as the vinyl ( $C_2H_3^+$ ) and ethyl ( $C_2H_5^+$ ) cations,<sup>29–37</sup> species which are also of astrochemical relevance.<sup>38,39</sup> One can thus argue that the findings herein can be useful to understand the astrophotochemical features of these species as well.

Computations of  $H_3^+$  were run at the EOM-CCSD level for all species, which for  $H_3^+$  corresponds to a full configuration interaction (FCI) calculation, *i.e.*, a numerically exact solution of the Schrödinger equation. These computations were performed using the aug-cc-pVTZ basis set of Dunning. For further computational details, see the Computational methods section and the SI.

## Results and discussion

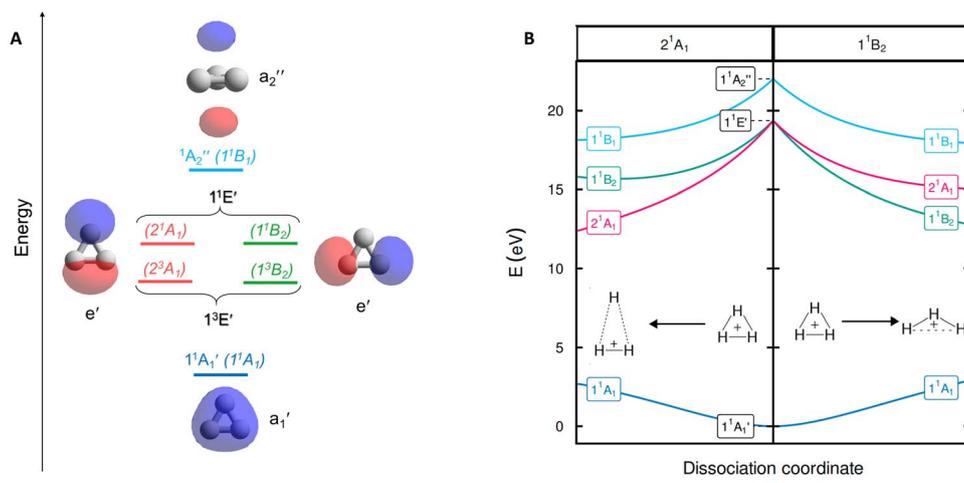
Herein, we first present and discuss results of the potential energy surfaces of the  $S_0$  and lowest few singlet excited states, followed by assessments of the (anti)aromatic characters of these states. This allows us to get a first tentative link between the excited state surface profiles and ESAA alleviation, yet, other factors that can impact on the lowest excitation energy of  $H_3^+$  are also identified and explored. Towards the end we compare with the analogous (isolobal) carbocations, which allows us to estimate the energetic component of a GSA-to-ESAA switch in character on the vertical excitation energy of  $H_3^+$ .

### Potential energy surfaces

According to our computations, the H–H distances of equilateral triangular  $H_3^+$  in  $S_0$  are 0.875 Å which is very close to the earlier computed value of 0.873 Å found with variational Born–Oppenheimer theory using explicitly correlated Gaussian functions.<sup>11</sup> The degenerate  $1^1E'$  states appear vertically 19.28 eV above the  $S_0$  state (Fig. 3A), again very similar to the reference value of 19.33 eV.<sup>11</sup> Expansion of the basis set beyond aug-cc-pVTZ has a negligible effect on the vertical excitation energy (19.2883 eV with FCI/aug-cc-pV5Z). The transition is symmetry allowed with an oscillator strength  $f = 0.562$ , yet, as it is well above the ionization energy of H (13.6 eV), the excitation has exceptionally low probability.

After excitation, in  $C_{2v}$  symmetry, the  $1^1E'$  states split into the  $2^1A_1$  and  $1^1B_2$  states (Fig. 3B), where  $2^1A_1$  as  $S_1$  dissociates to  $H_2^+ + H$  while  $1^1B_2$  as  $S_1$  leads to  $2H(1s) + H^+$ .<sup>14</sup> These dissociative forces can be understood as a result of the Jahn–Teller theorem.<sup>40</sup> Along  $D_{3h}$  symmetric geometries, the degenerate  $1^1E$  forms a conical intersection seam, which is lifted by symmetry-breaking nuclear distortions along a pair of E type vibrations, leading to electronic





**Fig. 3** (A) The three valence MOs ( $a_1'$  and  $e'$ ), the Rydberg orbital  $a_2''$ , and the labels of the electronic states within the  $D_{3h}$  (normal print) and  $C_{2v}$  (in parenthesis and italics) point groups. (B) Potential energy surface profiles of  $H_3^+$  from the  $D_{3h}$  symmetric  $S_0$  equilibrium geometry along the minimum energy path of the  $2^1A_1$  state keeping  $C_{2v}$  symmetry to an acute isosceles triangle (left), and along the minimum energy path of the  $1^1B_2$  state to an obtuse isosceles triangle (right).

stabilization. We recognize that extensive vibronic coupling effects influence the excited state spectrum and that these, as well as different conical intersections, strongly impact on photochemical dissociation dynamics of  $H_3^+$ , as has already been explored in previous studies based on highly accurate potential energy surfaces.<sup>13,41–46</sup> The current work, however, does not attempt to quantitatively model neither spectroscopic data nor photodissociation rates. Instead, the objective of our study is to elucidate the origin of the unusually high electronic excitation energy of  $H_3^+$ , which hitherto is totally unexplored.

The first triplet states (the degenerate  $1^3E'$ ) have vertical excitation energies of 14.87 eV (Table S1) and exhibit similar dissociative behaviors as  $1^1E'$ , in line with earlier findings.<sup>47</sup> Lastly, the higher energy  $1^1A_2''$  state in  $D_{3h}$  symmetry is a dissociative second-order saddle point with H–H distances of 1.620 Å. As this state involves an excitation from an  $a_1'$  orbital to a nonbonding Rydberg-type orbital  $a_2''$  (Fig. 3A), only one electron remains in a bonding molecular orbital (MO), which cannot counterbalance the electrostatic repulsion between three protons. For further results and discussions on this state, see Sections S1 and S2 of the SI.

### Probing excited state antiaromaticity

The aromatic or antiaromatic characters of the various electronic states were determined comprehensively through use of energetic, electronic, and magnetic (anti)aromaticity descriptors (for details see Section S3 or ref. 10). Thus, we analyze changes in three of the four aspects of aromaticity, with the geometric aspect being impossible to assess due to the dissociative nature of the excited states. The energetic aspect is determined through the extra cyclic resonance energy (ECRE).<sup>48,49</sup> To measure electron delocalization,<sup>50</sup> we use the two-center delocalization index (DI)<sup>51,52</sup> and the normalized multicentre index ( $MCI^{1/n}$ )<sup>53</sup> that reflect the aromatic character.

The magnetic response properties are explored by magnetically induced current densities (MICDs), and also by nucleus independent chemical shifts (NICSS).

Although assessed in earlier reports,<sup>6–9</sup> the values for  $\sigma$ -aromaticity of the  $S_0$  state are discussed briefly in order to contrast the antiaromatic character of the excited states (*vide infra*).  $H_3^+$  has two electrons and forms a 3-center 2-electron (3c–2e) bond, both in its linear and triangular structures. Therefore, the energy gain when going from the linear to the triangular structure (1.76 eV) represents the ECRE, reflecting an aromatic stabilization of cyclic  $H_3^+$  in  $S_0$  (Fig. 2). The topological analysis of the electron density also reveals a species that benefits from extensive 3c–2e bonding, manifested in the formation of a non-nuclear attractor (NNA) in the center (Fig. 4A), in agreement with previous works.<sup>7,8</sup> Large DI values between the hydrogen atoms and the large positive  $MCI^{1/n}$  of 0.62 (Fig. 4A)<sup>54</sup> are also consistent with  $\sigma$ -aromaticity in  $S_0$  (the  $MCI^{1/n}$  of benzene in  $S_0$  is 0.59 (ref. 55)). Finally,  $H_3^+$  in its  $S_0$  state displays a diatropic MICD of 4.39 nA T<sup>-1</sup>, in agreement with the NICS(0)<sub>zz</sub> value of –37.1 ppm, confirming the magnetic aromaticity of  $H_3^+$  in  $S_0$  (see further Section S3 of the SI).

Evaluation of the potential antiaromaticity in the  $1^1E'$  states of  $D_{3h}$  symmetric  $H_3^+$  is more challenging from computational perspectives, requiring separate characterizations of the two states, the  $2^1A_1$  and  $1^1B_2$  states in  $C_{2v}$  symmetry. Indeed, our investigation offers a first exploration of whether the concept of excited-state antiaromaticity is applicable to doubly degenerate first excited states. Notably, we find that in the lowest excited state, going from the linear ( $D_{\infty h}$ ) to the triangular geometry of  $H_3^+$  (which is the equilibrium geometry in  $S_0$ ) results in a destabilization in the lowest vertically excited singlet states by 4.19 eV (Fig. 4B). This reveals a negative ECRE indicating antiaromaticity. Thus, the stabilization in  $S_0$  plus destabilization in  $1^1E'$  ( $S_1$ ) upon cyclization have implications for the vertical





from dia- to paratropicity, or *vice versa*,<sup>57</sup> related to the orbital degeneracies at highly symmetric structures.<sup>58</sup> Now, by following the  $C_{2v}$  symmetric dissociation paths of  $H_3^+$ , and thus, the  $2^1A_1$  and  $1^1B_2$  states, we observe gradually diminishing paratropic ring currents (Fig. 4C), in line with antiaromaticity relief. Also the NICS(0)<sub>zz</sub> values computed along these paths reveal antiaromaticity, with values of 77.1 and 84.7 ppm at two  $C_{2v}$  symmetric structures distorted by a factor 1.5, leading to, respectively, acute and obtuse isosceles triangular structures as exemplified in Fig. 3B (see further Section S3).

### Protons-to-electrons ratios and impacts

Having established the antiaromaticity of the  $1^1E'$  states of  $H_3^+$ , the question is if the GSA-to-ESAA switch in character (Fig. 2) explains the unusually high vertical excitation energy of this cation. From computations of light atoms, molecules and ions with only two electrons such as He,  $Li^+$ ,  $HHe^+$  and  $He_2^{2+}$  (Table S3), we see that high vertical excitation energies are characteristic of these species, which mostly cannot exhibit aromaticity as they are acyclic. Many of these ions are also found in space, *e.g.*,  $Li^+$  and  $HHe^+$ .<sup>59</sup> Indeed, it has been argued that  $HHe^+$  was the first molecule of the Universe,<sup>60,61</sup> and it produces  $H_2^+$  upon collision with atomic H, which in turn can produce  $H_3^+$  in a reaction with  $H_2$ .<sup>62</sup>

The excitation energies are higher for more positively charged species, and is highest when the protons are concentrated in one nucleus (He,  $Li^+$  and  $Be^{2+}$ ). Hence, in the  $3p,2e$  series,  $Li^+$  and  $HHe^+$  feature higher vertical  $E(S_1)$  than  $H_3^+$  by, respectively, 41.16 and 6.91 eV, and similar for the vertical  $E(T_1)$  (Table S3). For the  $2e$  species He,  $Li^+$  and  $Be^{2+}$ , with protons-to-electrons ratios of 1.0, 1.5 and 2.0, respectively, the first excitation energy goes up dramatically from 20.94 eV to 60.44 eV and 121.26 eV as the excitation implies a gradually larger loss in the electrostatic attraction between electrons and nuclei.

Next, to estimate the impact of the protons-to-electrons ratio on the excitation energies, we explored the  $\pi$ -conjugated and  $S_0$  aromatic cyclopropenium cation,  $c-C_3H_3^+$ , which has an equilateral triangular structure and a near-unit ratio of 1.05 between total nuclear and electronic charges (+21 *vs.* -20) (Sections S4 and S5).<sup>63-65</sup> Indeed,  $c-C_3H_3^+$  is isolobal with  $H_3^+$ , *i.e.*, its  $\pi$ -orbitals are analogous to the  $\sigma$ -orbitals of  $H_3^+$ .<sup>66</sup> Thus, this cation helps us decipher the relative contributions of the protons-to-electrons ratio *versus* the GSA-to-ESAA switch to the 19.28 eV excitation energy of  $H_3^+$ .

The vertical transition to the lowest  $\pi\pi^*$  states ( $1^1E''$ ) of  $c-C_3H_3^+$  requires 9.71 eV. This is only half that of the transition to the  $\sigma\sigma^*$  states of  $H_3^+$  but significantly higher than the lowest  $\pi\pi^*$  states of any other  $\pi$ -bonded hydrocarbon, *e.g.*, 7.11 eV for ethylene.<sup>67</sup> Thus,  $c-C_3H_3^+$  has its lowest  $\pi\pi^*$  states at an unusually high excitation energy despite its near-unit protons-to-electrons ratio. Interestingly, there are several  $\sigma\pi^*$  and  $\pi\sigma^*$  states below the first  $\pi\pi^*$  state. Therefore, the high excitation energy of the lowest  $\pi\pi^*$  transition of  $c-C_3H_3^+$  is not caused by a drastically diminished electrostatic attraction upon excitation. Instead, it should arise from the stabilization in the  $S_0$  state due to aromaticity plus destabilization in the  $\pi\pi^*$  states due to antiaromaticity, and this

applies also to the lowest triplet states. From this, one can estimate that the additional energy (9.57 eV) to reach the excitation energy of  $H_3^+$  is caused by the electrostatic effect.

Also  $Li_3^+$ , valence isoelectronic to  $H_3^+$ , is an equilateral triangle at its global minimum in the  $S_0$  state, but it is nonaromatic and best described as the smallest triatomic molecule with metallic bonding.<sup>8</sup> We now find its lowest singlet excited states, the degenerate  $^1E$  states, at an energy of merely 2.70 eV. In line with the nonaromatic  $S_0$  state, these states are also nonaromatic (see Table S3 and Section S6 in the SI). Compression to a triangle with half the Li-Li distance leads to no substantial changes in neither the singlet excitation energy nor the electron-nucleus attraction contributions (Table S3). Among the two possible mixed Li and H monocations ( $H_2Li^+$  and  $HLi_2^+$ ),  $H_2Li^+$  has an acute triangular structure with Li-H and H-H distances of 2.049 and 0.752, respectively (Fig. S7).  $HLi_2^+$ , on the other hand, has a linear structure<sup>68</sup> and was therefore not further considered here as it is nonaromatic.

Finally,  $H_2He^{2+}$  is also interesting in this context as it provides an electronegativity perturbation compared to the isoelectronic  $H_3^+$ ,<sup>59</sup> although our computations reveal that this dication is not a minimum on the  $S_0$  PES. However, when kept at the geometry which is optimal for  $H_3^+$  but with one H<sup>+</sup> exchanged to  $He^{2+}$ , we find that it is nonaromatic in both its  $S_0$  state and lowest singlet excited states (Fig. S10). Accordingly, there is no GSA-to-ESAA switch in character upon the excitation of  $H_2He^{2+}$ . In line with this, there is no significant increase in excitation energy (+0.24 eV) when going from  $HHe^+$  to  $H_2He^{2+}$ , in contrast to what is observed when going from  $H_2$  to  $H_3^+$  (+6.56 eV, see Table S3 and Section S6 for further discussion).

### Comparisons to analogous carbocations

Further analysis of the  $c-C_3H_3^+$  cation, a molecular ion which also is of astrochemical importance,<sup>29</sup> enables us to show that the very high first excitation energy of  $H_3^+$  is due to both stabilization by GSA plus destabilization by ESAA and the high protons-to-electrons ratio. Among the (anti)aromaticity aspects, we thus first explore the energetic aspect before the electronic and magnetic ones. The isomerization stabilization energy (ISE)<sup>69</sup> of  $c-C_3H_3^+$  in  $S_0$ , computed as the reaction energy for the 1,3-hydrogen shift from a nonaromatic isomer to the  $S_0$  aromatic methylcyclopropenium cation (Fig. 5A), is -2.03 eV with CCSD. This reveals a stronger aromatic character than that of benzene in  $S_0$  (-1.34 eV with CCSD/aug-cc-pVDZ). In contrast, the lowest vertically excited singlet and triplet  $\pi\pi^*$  states exhibit large positive ISE values of 2.66 and 2.78 eV with EOM-CCSD, corresponding to strong excited state antiaromatic destabilization. Accordingly, the  $S_0$  stabilization plus excited state antiaromatic destabilizations of  $c-C_3H_3^+$  are 4.69 and 4.81 eV, respectively, and these should represent lower bounds for the analogous energies in  $H_3^+$ .

A comparison of the various energies of the linear  $H_3^+$  with the corresponding ones of the allyl cation ( $H_2CCHCH_2^+$ ) allows for a second estimate of the impact of the high protons-to-electrons ratio of  $H_3^+$ . The two species are isolobal and nonaromatic in  $S_0$ , yet, have different protons-to-electrons counts (3 : 2 *vs.* 23 : 22). For the allyl cation, with a near-unit protons-to-





states well above the ionization energy of monohydrogen, and thus, provides  $\text{H}_3^+$  with its astrophotocatalytic persistence.

## Conclusions

Herein, we decipher the main causes of the very high electronic excitation energy of  $\text{H}_3^+$ , which enables its functions in space. This is achieved through a comparison of triangular  $\text{H}_3^+$  and linear  $\text{H}_3^+$  with two analogous  $\pi$ -conjugated hydrocarbon ions, the cyclopropenium cation ( $c\text{-C}_3\text{H}_3^+$ ) and the allyl cation ( $\text{CH}_2\text{-CHCH}_2^+$ ). Had the vertical excitation energy been lower (closer to the photoionization of the much more abundant monohydrogen),  $\text{H}_3^+$  would have been more prone to photodissociate in space. We reveal that three factors contribute to the high excitation energy; (i) the change from a stabilizing aromatic character to (ii) a destabilizing antiaromatic character upon excitation from  $S_0$  to the lowest excited states (present also in  $c\text{-C}_3\text{H}_3^+$ ), and (iii) the high ratio between total nuclear and electronic charges (which is present also in small cations). These three factors together provide the origin of the astrophotocatalytic inertness of  $\text{H}_3^+$ . Without this photostability,  $\text{H}_3^+$  could not have had the functions it has in the Universe, which would have led to a Universe different from the one we know. Furthermore, it may also impact on the photostability of species with similar 3-center-2-electron bonding characteristics as the  $\text{H}_3^+$  ion, such as the vinyl and ethyl cations ( $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_5^+$ , respectively),<sup>29–31,70</sup> as well as the  $S_0$  state aromatic  $c\text{-C}_3\text{H}_3^+$  and derivatives, which are all of astrochemical importance.<sup>29,70</sup> The excited state dynamics of these carbocationic species are not extensively explored but it can be an important direction for future research in astrochemistry.

We show for the first time that excited state antiaromaticity is a molecular electronic structure property with crucial astrochemical influence that also has astrophysical implications. In a broader sense, our findings point to the roles of excited state aromaticity and antiaromaticity as important new concepts for interpretation in astrochemistry. We anticipate that these effects impact on a number of photochemical processes in space.

## Computational methods

### Geometry and energy calculations

Geometry optimizations and energy calculations were performed with Gaussian 16 revision C.01.<sup>71</sup> The electronic singlet ground state and lowest excited triplet state were calculated using CCSD while singlet excited states were computed with EOM-CCSD. For  $\text{H}_3^+$ , this level is equivalent to full configuration interaction (FCI), and we referred to it as FCI in the manuscript. Frequency calculations were performed at the same level of theory to probe if the structures were minima or saddle points on the potential energy surfaces. In all cases, the aug-cc-pVTZ valence triplet-zeta of Dunning and co-workers<sup>72</sup> was used as the basis set. For wavefunction analysis we employed 6d 10f functions for the latter basis set. To obtain  $T_2$  state the orbital order was altered by usage of the guess = alter keyword in Gaussian. Calculations of electron-nucleus attraction contribution include core electrons for all molecules (see Table S3).

### Aromaticity assessment

Results of the multicentre index (MCI)<sup>53</sup> were computed by usage of AIMAll,<sup>73</sup> APOST-3D, and ESI-3D<sup>56,74</sup> packages. Due to the presence of a non-nuclear attractor (NNA) in some of the species, we consider a different partition of the molecular space to compute the delocalization indices (DI(F))<sup>51,52</sup> and the MCI. Some of us have previously found that Becke-rho's atomic partition provides similar values to partitions based on quantum theory of atoms in molecules (QTAIM),<sup>75</sup> a theory which uses a topological approach to define an atom in a molecule. Becke's partition employs the position of the bond critical points (BCP) between atoms to define the atomic radii in the original Becke's partition.<sup>76</sup> This multicentre integration technique assigns weights to atoms in the molecule. The calculation of the DI for correlated wavefunctions employed the so-called Fulton approximation,<sup>77</sup> which provides very good agreement with the actual DI.

Isomerization stabilization energies (ISE) were computed at (EOM)-CCSD/cc-pVTZ optimized geometries but for the energy values reported we used the aug-cc-pVTZ basis set.

The magnetically induced ring current density (MICD) was calculated by employing complete active space self-consistent field (CASSCF) method (with all electrons, and occupied and virtual orbitals included in the active space, corresponding to an FCI calculation) and aug-cc-pVTZ basis set, using a development version of Dalton Program 2020.<sup>78,79</sup> In order to compute the ring current passing through the bonds of the triangular  $\text{H}_3^+$ , the MICD was integrated in a plane perpendicular to the bond, spanning from the centre of mass of the molecule 20 bohr at opposite sides of the plane (along vectors normal to the ring plane and cutting through the bond) using 200 subdivisions in the Gauss-Lobatto quadrature.<sup>80</sup>

## Author contributions

Conceptualization: HO; methodology: HO, CFN, EM; investigation: JMT, JKS; visualization: JMT, JKS; funding acquisition: HO; project administration: HO; supervision: HO; analysis: JMT, JKS; writing – original draft: JMT; writing – review & editing: JMT, JKS, EM, CFN, HO.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data underlying this study are openly available in the published article and its supplementary information (SI), and also openly available in zenodo at <https://doi.org/10.5281/zenodo.15713452>. The data supporting this article have been included as part of the SI. Supplementary information: Section S1: energies and geometries of  $\text{H}_3^+$ ; Section S2: aromaticity of  $\text{H}_3^+$ , electronic properties; Section S3: aromaticity of  $\text{H}_3^+$ , magnetic properties; Section S4: protons-to-electrons ratios; Section S5: cyclopropenium cation ( $\text{C}_3\text{H}_3^+$ );



Section S6:  $\text{Li}_3^+$ ,  $\text{H}_2\text{Li}^+$  and  $\text{H}_2\text{He}^{2+}$ ; Section S7: supplementary references; Section S8: Cartesian coordinates, absolute energies, and imaginary frequencies for all calculated structures. See DOI: <https://doi.org/10.1039/d5sc09067a>.

## Acknowledgements

We thank Dr Radovan Bast for extensive help with the magnetically induced current density calculations, Mr Hannes Gustafsson and Dr Lucia Corti for involvement in preliminary calculations. We also thank Prof. Jochen Autschbach, Prof. Paul Barklem, Prof. Eszter Borbas, Prof. em. Bengt Gustafsson, Prof. Martin Rahm, Prof. Philippe Wernet, and Prof. Judy Wu for discussions on the project at various stages. The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) and the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Center (NSC), Linköping, Sweden, through grant agreements 2022/5-378, 2023/5-335 and 2024/5-422. The Foundation Olle Engkvist Byggmästare is greatly acknowledged for a postdoctoral fellowship to J. M. T. (grant 184-390). H. O. thanks the Swedish Research Council for financial support (grants 2019-05618 and 2023-04179), and J. M. T. thanks the University Claude Bernard Lyon 1 for the funding provided through AAP Accueil EC. E. M. is grateful for the funding and technical support provided by the Donostia FEDER Una manera de hacer Europa International Physics Center (DIPC), and grant PID2022-140666NB-C21 funded by MCIN/AEI/10.13039/501100011033 and “FEDER Una manera de hacer Europa”. C. F.-N. thanks National Science Centre, Poland 2020/39/B/ST4/02022 for funding.

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