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PAPER

Explicitly correlated coupled cluster calculations for the propargyl cation ($\text{H}_2\text{C}_3\text{H}^+$) and related species†

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The vibrations of the propargyl cation ($\text{H}_3\text{C}_3\text{H}^+$) have been studied by vibrational configuration interaction (VCI) calculations, using explicitly correlated coupled cluster theory at the CCSD(T*)-F12a level to determine the underlying 12-dimensional potential energy surface. The wavenumbers of the fundamental vibrations are predicted with an accuracy of *ca.* 5 cm^{-1} . Harmonic wavenumber shifts for three different energy minima of the complex $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ are combined with the corresponding VCI values in order to provide a comparison with recent infrared photodissociation (IRPD) spectra (A. M. Ricks *et al.*, *J. Chem. Phys.*, 2010, **132**, 051101). An excellent agreement between experiment and theory is obtained for bands ν_2 (symm. CH stretch), ν_3 (pseudoantisymm. CC stretch), and ν_4 (CH_2 scissoring). However, reassignments are suggested for the bands observed at 3238 cm^{-1} , the “doublets” around 3093 and 1111 cm^{-1} , and the band at 3182 cm^{-1} . The assignment of the latter to the asymmetric CH stretching vibration of *c*- $\text{C}_3\text{H}_3^+\cdot\text{Ar}$ is certainly wrong; the combination tone $\nu_3 + \nu_5$ of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ is a more likely candidate. Furthermore, accurate proton affinities are predicted for the carbenes H_2C_n with $n = 3-8$, thereby providing data of interest for interstellar cloud chemistry.

1. Introduction

Ions of formula C_3H_3^+ belong to the fundamental cations of organic chemistry. The most stable isomer thereof is the cyclopropenyl cation (*c*- C_3H_3^+), but a more reactive isomer, the propargyl cation ($\text{H}_2\text{C}_3\text{H}^+$ or *l*- C_3H_3^+), has also been known from mass spectrometric studies for about four decades.¹ According to early work by Lossing,² it is $1.1 \pm 0.1\text{ eV}$ higher in energy than the cyclic isomer. In 1987, Smith and Adams have shown by selected ion flow tube (SIFT) studies that both cations may be produced through rapid reaction of C_3H^+ and H_2 .³ This may be a way of interstellar synthesis of the cations, which will then further react to the well-known interstellar molecules *c*- C_3H_2 and *l*- C_3H_2 by dissociative attachment of an electron.⁴ In 1990, the 10.49-eV photoionization mass and photoelectron (PE) spectra of $\text{H}_2\text{C}_3\text{H}$, $\text{H}_2\text{C}_3\text{D}$, and $\text{D}_2\text{C}_3\text{H}$ were reported by Minsek and Chen.⁵ For the latter species, a significant structure was observed in the PE spectrum and assigned to vibrational excitation within the $\text{H}_2\text{C}_3\text{D}^+$ ion. A subsequent theoretical study, based on 5-dimensional

potential energy surfaces calculated by the coupled electron pair approximation (CEPA), could not reproduce these findings.⁶ Instead, the adiabatic peak was predicted to be clearly dominant, with less than 10% relative intensity calculated for all other peaks. The zero kinetic energy (ZEKE) spectrum of the propargyl radical was published in 2000, but was withdrawn later and is therefore not discussed further.^{7,8} First electronic and infrared spectra of $\text{H}_2\text{C}_3\text{H}^+$ and $\text{D}_2\text{C}_3\text{D}^+$, isolated in neon matrices at 5 K, were published by Wyss *et al.*⁹ These authors observed the $\tilde{\text{A}}^1\text{A}' \leftarrow \tilde{\text{X}}^1\text{A}_1$ electronic transition of both the normal as well as the perdeuterated species. In addition and of particular importance for the present work, the most intense IR vibrations of $\text{H}_2\text{C}_3\text{H}^+$ and $\text{D}_2\text{C}_3\text{D}^+$ were observed at $2079.9(1.0)$ and $1955.2(1.0)\text{ cm}^{-1}$, with uncertainties of the measurements being given in parentheses.

While no gas-phase IR spectrum has yet been published for the free propargyl cation, weakly bound complexes of $\text{H}_2\text{C}_3\text{H}^+$ with various ligands were studied in 2002 through infrared photodissociation (IRPD) spectroscopy by Dopfer and coworkers.¹⁰⁻¹² The most extensive spectroscopic information was obtained for the complex of a C_3H_3^+ cation with the N_2 molecule and spectroscopic signatures of both *c*- $\text{C}_3\text{H}_3^+\cdot\text{N}_2$ and $\text{H}_2\text{C}_3\text{H}^+\cdot\text{N}_2$ were observed.¹⁰ For the latter, a hydrogen-bonded structure was assumed on the basis of *ab initio* calculations at the MP2 level (second-order perturbation theory according to Møller and Plesset) and bands at 3139 , 3113 and 3001 cm^{-1} were assigned to ν_1 (acetylenic CH stretch),

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ν_2 (symmetric CH_2 stretch) and $2\nu_4$ (first overtone of CH_2 scissoring vibration), respectively. No definitive assignment could be given for two more peaks observed at 3243 and 3191 cm^{-1} . At almost the same positions, peaks were also found for the more weakly bound complexes $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ne}$ and $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$.¹² Again, their assignment remained unclear. Quite recently, the latter complex was investigated by Duncan and coworkers¹³ over the wide region between 800 and 4000 cm^{-1} . Eight single peaks and two “doublets” were assigned to vibrations of the propargyl cation. The pseudoantisymmetric CC stretching vibration (ν_3) was found 3 cm^{-1} lower than the above neon matrix value. The strongest band was observed at 3238 cm^{-1} , but one has to keep in mind that the power of the optical parametric oscillator (OPO) used in the laser IRPD study decreases strongly with increasing wavelength. This band was assigned to a hydrogen-bonded acetylenic CH stretching vibration and the assignment implies a complex of C_{2v} equilibrium structure in which the argon atom is closest to the acetylenic hydrogen atom of the propargyl cation. As we could show recently through state-of-the-art explicitly correlated coupled cluster calculations,¹⁴ the C_{2v} structure is only a local minimum on the potential energy surface of $\text{H}_2\text{C}_3\text{H}^+$ and a C_s structure is significantly lower in energy. This finding has important consequences for the interpretation of the existing IRPD spectra.

To the authors' knowledge, only one full-dimensional study of anharmonic vibrational wavenumbers of $\text{H}_2\text{C}_3\text{H}^+$ is available in the literature. It made use of hybrid density functional theory at the B3LYP/6-311G (2df,p) level, molecular vibrations being treated by vibrational perturbation theory at second order (VPT2).¹⁵ A high-level theoretical study of the vibrations of the propargyl cation is thus clearly desirable. In the present work, explicitly correlated coupled cluster theory in conjunction with the vibrational configuration interaction (VCI) method is employed to calculate all fundamental vibrational wavenumbers of $\text{H}_2\text{C}_3\text{H}^+$ to an accuracy of *ca.* 5 cm^{-1} . The high efficiency and accuracy of such an approach was recently demonstrated by Rauhut *et al.*¹⁶ In order to allow for proper comparison with the IRPD spectra,^{10–13} the shifts in the intramolecular fundamental vibrations of different structures of the complexes $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ and $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$ have been studied as well. In addition, accurate values will be predicted for the proton affinities of the H_2C_n species with $n = 3\text{--}8$. Such thermochemical data are of interest to astrochemistry, since three members of the H_2C_n series of molecules (H_2C_3 , H_2C_4 , and H_2C_5) are known interstellar molecules and their synthesis may occur through dissociative recombination of the corresponding protonated species with an electron. To the authors' knowledge, no direct experimental determination of the proton affinities of H_2C_n species has yet been carried out and so the theoretical values from the present work will stand as predictions.

2. Details of calculations

The electronic structure calculations of the present work were mainly carried out by explicitly correlated coupled cluster theory at the CCSD(T*)-F12a level.^{17–19} Throughout, the fixed-amplitude approximation 3C(FIX) was employed in the underlying density-fitting MP2-F12 calculations.²⁰

The contributions of connected triple substitutions were scaled (T*) according to the recipe of Werner and coworkers.^{18,19} As atomic orbital (AO) basis sets for the species containing C and H atoms we chose the cc-pVnZ-F12 ($n = \text{D, T, and Q}$) basis sets of Peterson *et al.*²¹ In the following, they will be briefly denoted by VnZ-F12. For the $\text{C}_3\text{H}_3^+\cdot\text{Ar}$ complexes, the VTZ-F12 basis for C_3H_3^+ is employed in conjunction with the aug-cc-pV(Q+d)Z basis for argon,²² AVQZ for brevity. The combined basis set corresponds to the basis of the intermediate size used in our previous study of the cation–argon complexes.¹⁴ The optimized auxiliary basis sets of Yousaf and Peterson,^{23,24} termed VnZ-F12/OptRI or AVnZ/OptRI, were employed in the explicitly correlated coupled cluster calculations. Following the recommendation of the same authors, JKFIT and MP2FIT basis sets were taken from the work of Weigend²⁵ and Weigend *et al.*²⁶ Tight thresholds were employed in the construction of the complementary auxiliary basis set (CABS) such that no functions were deleted. The CABS singles correction^{18,19} was used to improve the Hartree–Fock reference energies. For the calculation of equilibrium structures and harmonic vibrational wavenumbers of $\text{H}_2\text{C}_3\text{H}^+$, standard CCSD(T)^{27–29} in conjunction with various Dunning-type basis sets (of the cc-pVnZ and cc-CVnZ family, briefly denoted by VnZ or CVnZ, respectively) was employed as well. The electronic structure calculations of the present work were carried out with version 2009.1 of the MOLPRO system of *ab initio* programs;³⁰ for the VCI calculations a development version thereof was employed.

For the determination of anharmonic frequencies the 12-dimensional potential energy surface (PES) of $\text{H}_2\text{C}_3\text{H}^+$ has been calculated by CCSD(T*)-F12a/VTZ-F12 making use of a multimode expansion in terms of normal coordinates up to 3rd order, *i.e.* including 3-mode couplings.³¹ In total 26 562 grid points have been determined. In a subsequent step the PES has been transformed to polynomials up to 9th order in each dimension. The accuracy of the fitted PES has been checked statistically by selecting 2390 arbitrary points on the surface and a comparison of the *ab initio* single point energies with energy values determined from the fit. The absolute mean deviation was as low as 7 cm^{-1} . One-mode wavefunctions (modals) have been obtained from state-specific vibrational self-consistent field theory (VSCF) based on a basis of 20 distributed Gaussians. In contrast to our previous work we used a mode-dependent basis, which we found to be more flexible and thus reliable than a constant basis for all modals. This leads, in particular, to an enhanced description of low lying vibrational states. Vibration correlation effects were accounted for by configuration-selective state-specific vibrational configuration interaction (VCI) theory based on Watson's Hamiltonian for non-linear molecules.³² For details see ref. 33 and 34. Different correlation spaces have been used to monitor the convergence of the states of interest. As the ν_1 stretching mode was found to be quite sensitive with respect to the excitation level, finally up to six modals were used for each oscillator in all calculations. Including single to quadruple excitations the initial correlation space comprises 450 575 configurations. Vibrational angular momentum terms were included based on the approximation of a constant μ -tensor.³⁵

The calculation of absolute IR intensities by full-dimensional VCI based on CCSD(T*)-F12a potential energy and electric dipole moment functions is still an arduous task. We have therefore adopted a simpler dimensionality-reduced approach, restricted to totally symmetric vibrational modes. Following its first application to molecules with equilibrium structures of C_{2v} symmetry,³⁶ it was recently applied to calculate IR spectra of H_2CCC and D_2CCC ³⁷ and photoelectron spectra for different isotopomers of the propargyl radical, H_2C_3H .³⁸ The chosen approach makes use of a five-dimensional (5D) approximate vibrational Hamiltonian of the form (in atomic units)

$$\hat{H}_{\text{vib}} = -1/2 \sum_{i=1}^5 \partial^2 / \partial Q_i^2 + V_{\text{anh}}(S_1, S_2, S_3, S_4, S_5) \quad (1)$$

where Q_i are the normal coordinates of the five totally symmetric vibrations. The anharmonic potential energy function (PEF) is represented in polynomial form according to

$$V_{\text{anh}} = \sum_{ijklm} C_{ijklm} S_1^i S_2^j S_3^k S_4^l S_5^m \quad (2)$$

An analogous expansion is made for the electric dipole moment function (EDMF). For the definition of the mass-independent symmetry coordinates S_1 – S_5 we refer to ref. 38. The 5D model is improved by taking the anharmonic interaction with the asymmetric vibrational modes of b_1 and b_2 symmetry into account in a crude implicit way. The corrections consist in a modification of the diagonal elements $H_{ii}(v_1, v_2, v_3, v_4, v_5)$ of \hat{H}_{vib} over a basis of harmonic oscillator product functions according to

$$\tilde{H}_{ii}(v_1, v_2, v_3, v_4, v_5) = H_{ii}(v_1, v_2, v_3, v_4, v_5) + \sum_{i=1}^5 \Delta_i \left(v_i + \frac{1}{2} \right) \quad (3)$$

The five parameters Δ_i are determined in an adjustment process to the results of VCI calculations for the wavenumbers of the five totally symmetric fundamentals (ν_1 – ν_5) of $H_2C_3H^+$.

From the calculated vibrational wave functions and the analytical EDMF, integrated molar absorption intensities for vibrational transitions arising from the vibrational ground state are calculated according to the formula

$$A_{f0} = \frac{\pi N_A}{3 \hbar c_0 \epsilon_0} \bar{\nu}_{f0} |\mu_{f0}|^2 \quad (4)$$

Table 1 Calculated equilibrium geometrical parameters for $H_2C_3H^+$

Method	Basis	$r_{1c}/\text{\AA}$	$\alpha_e/^\circ$	$R_{1e}/\text{\AA}$	$R_{2e}/\text{\AA}$	$r_{2c}/\text{\AA}$
CCSD(T*)-F12a ^b	VDZ-F12	1.08764	119.38	1.35074	1.23274	1.07475
	VTZ-F12 ^d	1.08745	119.33	1.34948	1.23101	1.07430
	VQZ-F12 ^d	1.08721	119.32	1.34894	1.23044	1.07411
CCSD(T) ^b	VQZ	1.08743	119.29	1.34995	1.23158	1.07444
	V5Z	1.08715	119.31	1.34924	1.23076	1.07407
	V6Z	1.08716	119.32	1.34899	1.23051	1.07404
	CVQZ ^e	1.08609	119.24	1.34679	1.22876	1.07319
CCSD(T) ^c	CV5Z	1.08575	119.28	1.34603	1.22789	1.07278
	CV6Z	1.08573	119.27	1.34585	1.22762	1.07265

^a HCH equilibrium angle. ^b Valence electrons correlated. ^c All electrons correlated. ^d Ref. 38. ^e Improved geometry optimization with respect to ref. 47.

In eqn (4), N_A is the Avogadro constant, \hbar the Planck's constant divided by 2π , c_0 the speed of light in vacuum, ϵ_0 the electric constant, $\bar{\nu}_{f0}$ the vibrational wavenumber, and μ_{f0} the corresponding vibrational transition dipole moment.

3. Results and discussion

3.1 Results for free $H_2C_3H^+$

Calculated equilibrium geometrical parameters for $H_2C_3H^+$, as obtained by CCSD(T*)-F12a (valence electrons correlated) and standard CCSD(T), are listed in Table 1. Almost identical results are obtained at levels CCSD(T*)-F12a/VQZ-F12 and CCSD(T)/V6Z, the largest difference in bond lengths amounting to 0.00006 Å. CCSD(T*)-F12a with the VTZ-F12 basis already yields results which differ from the CCSD(T)/V6Z values by at most 0.00053 Å. The last three rows of Table 1 report results of CCSD(T) calculations in which all electrons were correlated.

The basis set dependence of harmonic vibrational wavenumbers for $H_2C_3H^+$ is investigated in Table 2. Throughout, only the valence electrons were correlated in the underlying coupled cluster calculations. Standard CCSD(T)/V6Z and CCSD(T*)-F12a/VQZ-F12 yield differences which do not exceed 1 cm^{-1} . Likewise, very small differences are observed upon increasing the basis set from VTZ-F12 to VQZ-F12 in the explicitly correlated coupled cluster calculations.

Calculated anharmonic vibrational wavenumbers for the fundamental vibrations of $H_2C_3H^+$ are listed in Table 3. The present VCI results are expected to be accurate to *ca.* 5 cm^{-1} . This rather low estimate is believed to result from significant error compensation: inclusion of core–valence and core–core correlations usually increases vibrational wavenumbers while the consideration of higher-order correlation effects leads to a decrease. Comparable VCI/CCSD(T)-F12a calculations for 9 different test molecules¹⁶ yielded a mean absolute deviation of only 4.0 cm^{-1} . The agreement of the present VCI results with the previous VPT2 data (based on a B3LYP quartic force field) is quite good. The largest difference occurs for the in-plane CCC bending vibration ν_{12} and amounts to 33 cm^{-1} . We predict the acetylenic CH stretching vibration ν_1 at 3236 cm^{-1} . Its anharmonicity contribution $\Delta\nu_1 = \omega_1 - \nu_1$ is calculated to be 122 cm^{-1} , which appears to be a rather normal value. For comparison, the $\Delta\nu_1$ value for the corresponding radical (H_2C_3H) is estimated to be 128 cm^{-1} by combining the

Table 2 Calculated harmonic vibrational wavenumbers (in cm^{-1}) for $\text{H}_2\text{C}_3\text{H}^+$ ^a

Vibration	CCSD(T)				CCSD(T*)-F12a		
	VTZ	VQZ	V5Z	V6Z	VDZ-F12	VTZ-F12	VQZ-F12
$\omega_1 (a_1)$	3360	3358	3360	3360	3354	3358	3359
$\omega_2 (a_1)$	3118	3118	3118	3118	3115	3115	3117
$\omega_3 (a_1)$	2118	2122	2123	2123	2116	2121	2123
$\omega_4 (a_1)$	1484	1481	1481	1481	1478	1479	1480
$\omega_5 (a_1)$	1130	1133	1134	1134	1129	1132	1134
$\omega_6 (b_1)$	1123	1122	1120	1120	1113	1117	1119
$\omega_7 (b_1)$	868	875	877	878	869	876	878
$\omega_8 (b_1)$	262	257	255	255	252	254	255
$\omega_9 (b_2)$	3225	3227	3227	3227	3225	3225	3226
$\omega_{10} (b_2)$	1038	1037	1037	1037	1037	1036	1036
$\omega_{11} (b_2)$	605	619	623	625	615	625	625
$\omega_{12} (b_2)$	284	288	289	289	280	287	288
ZPE ^b	9307	9319	9327	9324	9292	9313	9320

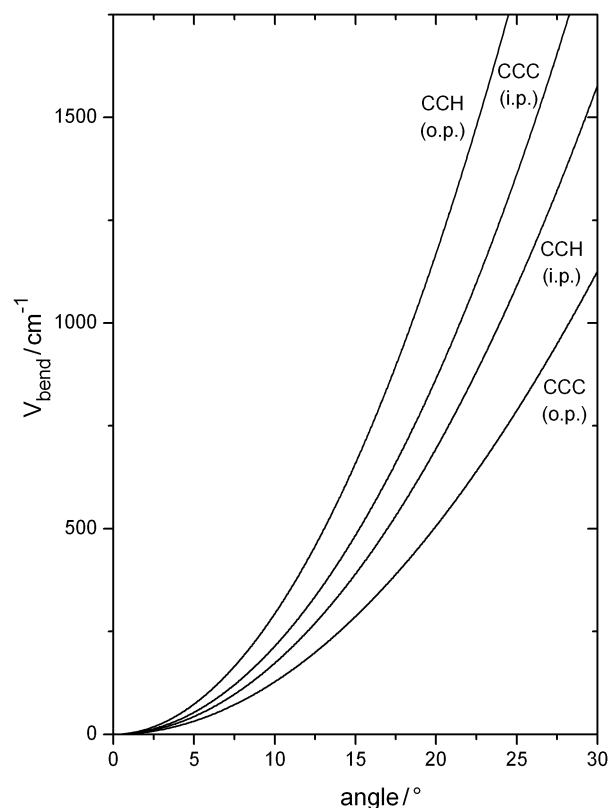
^a Valence electrons are correlated in coupled cluster calculations.^b Harmonic zero-point vibrational energy.**Table 3** Calculated anharmonic vibrational wavenumbers (in cm^{-1}) for $\text{H}_2\text{C}_3\text{H}^+$

Vibration	B3LYP ^a	CCSD(T*)-F12a
	6-311G(2df,p)	VTZ-F12
$\nu_1 (a_1)$	3226	3236
$\nu_2 (a_1)$	2976	2990
$\nu_3 (a_1)$	2089	2080
$\nu_4 (a_1)$	1440	1446
$\nu_5 (a_1)$	1139	1123
$\nu_6 (b_1)$	1113	1099
$\nu_7 (b_1)$	899	872
$\nu_8 (b_1)$	278	264
$\nu_9 (b_2)$	3059	3080
$\nu_{10} (b_2)$	1014	1017
$\nu_{11} (b_2)$	618	615
$\nu_{12} (b_2)$	331	298
ZPE (anh.) ^b		9208

^a ref. 15. ^b Anharmonic zero-point vibrational energy.

UCCSD(T*)-F12a/VTZ-F12 harmonic value from ref. 38 with the precise experimental value of 3322.3 cm^{-1} .⁴² For the methylenic CH stretches we obtain $\Delta\nu_2$ (symm. CH stretch) = 125 cm^{-1} and $\Delta\nu_9$ (asymm. CH stretch) = 145 cm^{-1} . Rather similar values of 133 and 139 cm^{-1} were recently obtained for H_2C_3 from analogous VCI/CCSD(T*)-F12a calculations.³⁷ The present gas-phase wavenumber prediction for ν_3 , the pseudo-antisymmetric CC stretching vibration, coincides with the neon matrix value of Wyss *et al.*⁹ One may well expect that such an inert matrix has only a very small effect on a vibration of small amplitude like ν_3 . Vibrational anharmonicity lowers this vibration by 41 cm^{-1} . The CH_2 scissoring vibration ν_4 is calculated at 1446 cm^{-1} , 33 cm^{-1} below the harmonic value. The recommended gas-phase value for the propargyl radical ν_4 is $1440 \pm 15 \text{ cm}^{-1}$ ⁴³ and thus very similar. A small anharmonicity contribution of only 9 cm^{-1} is calculated for the pseudo-symmetric CC stretching vibration ν_5 , the band origin of which is predicted at 1123 cm^{-1} .

The out-of-plane bending vibration with highest wavenumber (ν_6) is mostly CH_2 wagging in character and is calculated at 1099 cm^{-1} , 101 cm^{-1} above the corresponding value for H_2CCC . Its anharmonicity contribution amounts to only 18 cm^{-1} .

**Fig. 1** Variation of the CCSD(T*)-F12a/VTZ-F12 energy for $\text{H}_2\text{C}_3\text{H}^+$ with the CCH and CCC angles, with the other geometrical parameters kept fixed at their equilibrium values.

For the CH_2 rocking vibration (ν_{10}), the difference between $\text{H}_2\text{C}_3\text{H}^+$ and H_2CCC is small (-14 cm^{-1}), with the smaller value calculated for the neutral species. Vibrations ν_7 and ν_{11} of $\text{H}_2\text{C}_3\text{H}^+$ may be described as CCH out-of-plane bending and CCH in-plane bending, respectively. Their wavenumbers (872 and 615 cm^{-1}) are substantially different. This may be traced back to the CCH bending potentials which are displayed in Fig. 1. The potential curve for out-of-plane bending is much steeper than that for in-plane bending. The figure also shows the CCC bending potentials for which, like for H_2CCC (see Fig. 2 of ref. 37), the opposite behaviour is observed.

Results of the dimensionality-reduced (5D) calculations for $\text{H}_2\text{C}_3\text{H}^+$ are listed in Table 4. The underlying PEF and EDMF are supplied as ESI† (Tables S1 and S2). Anharmonicity effects on the intensities of the fundamentals ν_3 , ν_4 , and ν_5 are very small. On the other hand, significant reductions are calculated for the ν_2 band (-13%) and the ν_1 band (-17%). In the former case, the reduction results from reasonably strong Fermi resonance between ν_2 and $2\nu_4$, the first overtone of the CH_2 scissoring vibration. In the latter case, the ν_1 band borrows some intensity to the $\nu_3 + \nu_5$ band. The intensity of this combination tone is sizeable and amounts to as much as 81% of the intensity calculated for the ν_2 fundamental.

3.2 CCSD(T*)-F12a calculations for $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ complexes

In extension of our previous work,¹⁴ full dimensional geometry optimizations have been carried out for $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ complexes, using CCSD(T*)-F12a in conjunction with basis

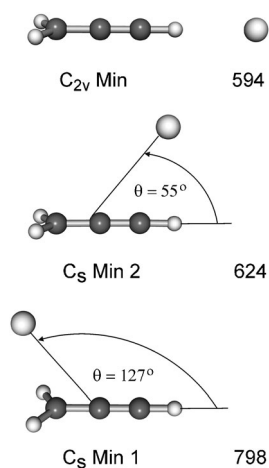
Table 4 Wavenumbers and absolute IR intensities for vibrations of $\text{H}_2\text{C}_3\text{H}^+$ involving totally symmetric modes^a

Vibration	$\bar{\nu}/\text{cm}^{-1}$	$A^b/\text{km mol}^{-1}$
ν_5	1123	18.7 (18.8)
ν_4	1446	12.4 (11.8)
ν_3	2080	371 (378)
$2\nu_5$	2245	6.7
$\nu_4 + \nu_5$	2567	0.2
$2\nu_4$	2866	3.6
ν_2	2990	25.0 (28.6)
$\nu_3 + \nu_5$	3185	20.2
ν_1	3236	93.4 (112)

^a From 5D approximation with corrections for the anharmonic interaction with the b_1 and b_2 modes (see the text). Correction parameters (in cm^{-1}), obtained through adjustment to the underlined values (VCI values from Table 3) are: $\Delta_1 = -15$, $\Delta_2 = -78$, $\Delta_3 = -14$, $\Delta_4 = -15$, and $\Delta_5 = 1$. ^b Values from “double-harmonic” approximation are given in parentheses.

set combination (VTZ-F12, AVQZ). Three energy minima were found; they are termed “ C_s Min 1”, “ C_s Min 2” and “ C_{2v} min” and are graphically displayed in Fig. 2. The corresponding nuclear cartesian coordinates are listed in Table S3 of ESI.† Compared to our previous calculations with rigid cations, the changes in equilibrium geometrical parameters are very minor. The equilibrium dissociation energies D_e (in cm^{-1}) for structures C_s Min 1, C_s Min 2 and C_{2v} are 798.4(792.6), 624.3(620.6) and 593.9(592.1), respectively, where the previous values for rigid cations (see Table 1 of ref. 14) are given in parentheses. Consideration of non-rigidity effects thus increases the D_e values by less than 6 cm^{-1} .

Harmonic vibrational wavenumbers for the three energy minima are supplied as ESI† (see Table S4). The wavenumber shifts with respect to free $\text{H}_2\text{C}_3\text{H}^+$, which are more important for the present work, are listed in Table 5. For the most stable structure C_s Min 1, the CH stretching vibrations are slightly blue-shifted by 5–6 cm^{-1} . On the other hand, a red-shift of -43 cm^{-1} is predicted for the C_{2v} structure. This is a rather normal value for a very weak hydrogen bond.

**Fig. 2** Equilibrium structures and dissociation energies D_e (in cm^{-1}) for complexes $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ calculated by CCSD(T*)-F12a with basis set (VTZ-F12, AVQZ).**Table 5** CCSD(T*)-F12a harmonic wavenumber shifts (in cm^{-1}) for intramolecular vibrations of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ complexes

Vibration ^a	C_s Min 1	C_s Min 2	C_{2v}
ν_1	4.9	6.1	-43.4
ν_2	6.0	1.0	1.0
ν_3	0.7	3.6	-4.5
ν_4	0.1	0.1	0.9
ν_5	-3.7	2.4	1.6
ν_6	-2.5	-5.1	-1.2
ν_7	-5.2	-3.4	21.6
ν_8	16.6	15.1	4.0
ν_9	6.4	0.6	0.4
ν_{10}	0.4	-0.4	1.0
ν_{11}	3.1	-1.6	34.2
ν_{12}	3.7	1.6	2.0

^a Numbering for the free cation (see Table 3) is employed.

The C_{2v} structure exhibits blue shifts of 22 and 34 cm^{-1} in the out-of-plane (ν_7) and in-plane (ν_{11}) CCH bending vibrations, respectively. As has been shown previously for complexes of type $\text{HCCH}\cdot\text{L}$ ($\text{L} = \text{NH}_3$, Cl^- , Br^- and I^-),^{39–41} such blue shifts are quite typical for hydrogen-bonded acetylenic groups. The largest shifts calculated for the two C_s energy minima of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ refer to the low-lying out-of-plane vibration ν_8 . It lies in the far-IR region of the spectrum and is thus not accessible to current IRPD spectroscopy.

3.3 On the assignment of the IRPD spectra of $\text{C}_3\text{H}_3^+\cdot\text{Ar}$ complexes

The peak with highest wavenumber found in the IRPD spectra of Roth and Dopfer¹² and Ricks *et al.*¹³ occurs at 3239 and 3238 cm^{-1} , respectively. Combining the present VCI wavenumber for the acetylenic CH stretching vibration ν_1 of free $\text{H}_2\text{C}_3\text{H}^+$ with the harmonic shift for the energetically most favourable structure of the argon complex (C_s Min 1), we arrive at 3241 cm^{-1} , very close to the experimental values. For the hydrogen-bonded structure of C_{2v} symmetry we predict $\nu_1 = 3236 - 43 = 3193 \text{ cm}^{-1}$. Within the double harmonic approximation, this vibration is predicted to have a large IR intensity of 290 km mol^{-1} , a factor of 2.6 higher than for free $\text{H}_2\text{C}_3\text{H}^+$. The presence of isomer C_{2v} Min in the CH stretching region of an IRPD spectrum should thus predominantly show up close to 3193 cm^{-1} .

Rather surprisingly, Ricks *et al.*¹³ assigned the band observed at 3182 cm^{-1} to the asymmetric CH stretching vibration of $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$, “based on its position, its predicted intensity and its behaviour with ion source conditions.” The first argument appears to be rather peculiar. In a neon matrix at 5 K, ν_4 ($c\text{-C}_3\text{H}_3^+$) was observed at 3130.4 cm^{-1} .⁹ Roth and Dopfer¹² reported very similar values of 3130 and 3136 cm^{-1} for the complexes $c\text{-C}_3\text{H}_3^+\cdot\text{Ne}$ and $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$, respectively. VCI calculations of Bartlett and coworkers yielded $\nu_4 = 3138 \text{ cm}^{-1}$ for the free cyclopropenyl cation.⁴⁴ Like for $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$, we calculated the harmonic vibrational wavenumbers for $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$ by CCSD(T*)-F12a with the basis set combination (VTZ-F12, AVQZ). For the most stable complex of C_s symmetry, the ν_4 band is split into two components which are blue-shifted with respect to free $c\text{-C}_3\text{H}_3^+$ by 3.7 and 1.1 cm^{-1} , respectively. For the higher-lying complex with

C_{2v} symmetry, the calculated shifts are 0.5 and -19.6 cm^{-1} . Combining the harmonic shifts with the neon matrix value for ν_4 ($c\text{-C}_3\text{H}_3^+$), we predict no peak for $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$ which has a wavenumber higher than 3135 cm^{-1} . We may thus safely rule out $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$ as the carrier of the band at 3182 cm^{-1} . From the experimental side,¹² this statement is further supported by the observation of peaks at 3184, 3182, and 3191 cm^{-1} , which were found in the IRPD spectra of $\text{C}_3\text{H}_3^+\cdot\text{L}$ with $\text{L} = \text{Ne}, \text{Ar},$ and N_2 , respectively. The close coincidence of the peaks points to a common origin. According to the data presented in Table 4, we suggest the $\nu_3 + \nu_5$ band to be a suitable candidate. Since only small-amplitude CC stretching vibrations are involved in this combination tone, it will hardly experience a substantial shift upon complex formation and the change in IR intensity with respect to free $\text{H}_2\text{C}_3\text{H}^+$ is expected to be small as well. For free $\text{H}_2\text{C}_3\text{H}^+$ (see Section 3.1), the intensity ratio $A(\nu_3 + \nu_5)/A(\nu_2)$ was calculated to be as large as 0.81. We thus expect that the $\nu_3 + \nu_5$ band should show up in the IRPD spectrum of Ricks *et al.* These authors found the band at 3182 cm^{-1} to grow substantially under more extreme discharge conditions (see ESI of ref. 13). Under such conditions, the less stable H-bound isomer of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ might gain a higher population in the molecular beam. As a result, the $\nu_3 + \nu_5$ and ν_1 (H-bound) bands might overlap and form a broader and stronger joint band.

According to Ricks *et al.*, peaks observed at 3075 and 3107 cm^{-1} were attributed to the $\Delta K = \pm 1$ subbands of the asymmetric CH stretching vibration ν_9 . Such an assignment is only meaningful for a H-bound complex of C_{2v} symmetry, however. For the most stable complex of C_s symmetry we calculate $\nu_9 = 3080 + 6 = 3086\text{ cm}^{-1}$, not too far from the lower component of the “doublet” of Ricks *et al.* No definitive assignment is possible for the upper component, but the a_1 -component of ν_4 ($c\text{-C}_3\text{H}_3^+$) or the combination tone $\nu_3 + \nu_{10}$ might be suitable candidates.

The present calculations predict the symmetric CH stretching vibration of the most stable complex of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ at $\nu_2 = 2990 + 6 = 2996\text{ cm}^{-1}$. This is in good agreement with the assignment of Ricks *et al.* who attributed a peak at 3004 cm^{-1} to this vibration. Likewise, an excellent agreement between theory and experiment exists for ν_3 (2081 vs. 2077 cm^{-1}) and ν_4 (1446 vs. 1445 cm^{-1}). As noted earlier,³⁸ the assignment of the band observed at 1222 cm^{-1} to the pseudosymmetric CC stretching vibration ν_5 appears to be incorrect. We predict the ν_5 band of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$ (C_s Min 1) to occur at 1119 cm^{-1} . This is close to the upper component of the “doublet” observed around 1111 cm^{-1} , which was assigned to “the perpendicular band contour of the ν_6 CH_2 out-of-plane wag”.¹³ Again, this assignment requires a H-bound complex of C_{2v} symmetry. For the ν_6 band of C_s Min 1, the present calculations yield a wavenumber of 1097 cm^{-1} . We therefore suggest to assign the two peaks of the “doublet” to the close-lying fundamentals ν_5 and ν_6 of the most stable complex.

3.4 Proton affinities at 0 K for H_2C_n species ($n = 3\text{--}8$)

Combining the results of the present CCSD(T*)-F12a/VQZ-F12 calculations with the earlier ones for H_2CCC ,³⁷ we calculate an equilibrium proton affinity (PA_e) of 917.1 kJ mol^{-1} for H_2CCC .

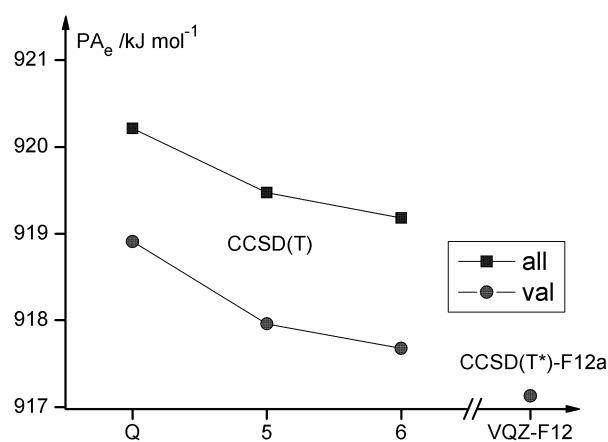


Fig. 3 Dependence of the equilibrium proton affinity for H_2CCC on the basis set.

An almost identical value of 917.0 kJ mol^{-1} is obtained when the smaller VTZ-F12 basis is employed. These values are slightly smaller than the result of standard CCSD(T) calculations with the V6Z basis set (917.7 kJ mol^{-1}). The valence correlation contribution to PA_e is calculated to be -21.6 kJ mol^{-1} by CCSD(T*)-F12a/VQZ-F12 and -21.1 kJ mol^{-1} by CCSD(T)/V6Z. Thereof, connected triple substitutions make up a contribution of only -4.2 kJ mol^{-1} . Correlating all electrons in standard coupled cluster calculations (CV6Z basis) increases PA_e by 1.5 kJ mol^{-1} . Fig. 3 shows the variation of PA_e with the size of the basis set for calculations with and without inclusion of core correlation. At the basis set limit, the CCSD(T) result (all electrons correlated) is estimated to be $\text{PA}_e = 918.9\text{ kJ mol}^{-1}$. Higher-order correlation effects and relativistic effects are expected to play a minor role and will hardly change the PA_e value by more than 2 kJ mol^{-1} . The harmonic zero-point vibrational contribution to the proton affinity, termed ΔZPE (harm.), is calculated to be $-30.93\text{ kJ mol}^{-1}$ (VQZ-F12 basis) and $-30.95\text{ kJ mol}^{-1}$ (VTZ-F12 basis). The anharmonicity contribution, calculated with the smaller basis set, amounts to only 0.42 kJ mol^{-1} . Combined with the PA_e estimate, we thus arrive at a proton affinity at 0 K of PA_0 (H_2CCC) = 888.4 kJ mol^{-1} , with an estimated uncertainty of 2 kJ mol^{-1} .

The proton affinities of the larger H_2C_n species up to $n = 8$ have been calculated by CCSD(T*)-F12a with the VTZ-F12 basis set. Results of the geometry optimizations are shown in Fig. 4, which reports the equilibrium geometrical parameters for the cations $\text{H}_2\text{C}_n\text{H}^+$ and the differences with respect to the corresponding unprotonated species H_2C_n . Compared with the recommended equilibrium bond lengths established previously for cumulene carbenes (see Fig. 10 of ref. 45), the present values show differences in the CC distances of $0.0029\text{--}0.0037\text{ \AA}$ (average: 0.0034 \AA). The difference in r_{1c} (methylenic CH distance) is practically constant with a mean value of 0.0016 \AA .

In an attempt to arrive at rather accurate equilibrium structures for the protonated species $\text{H}_2\text{C}_n\text{H}^+$, we subtract the above average deviations from the CCSD(T*)-F12a equilibrium bond lengths given in Fig. 4. The results are supplied as ESI.† In the following, PA_e values for the larger

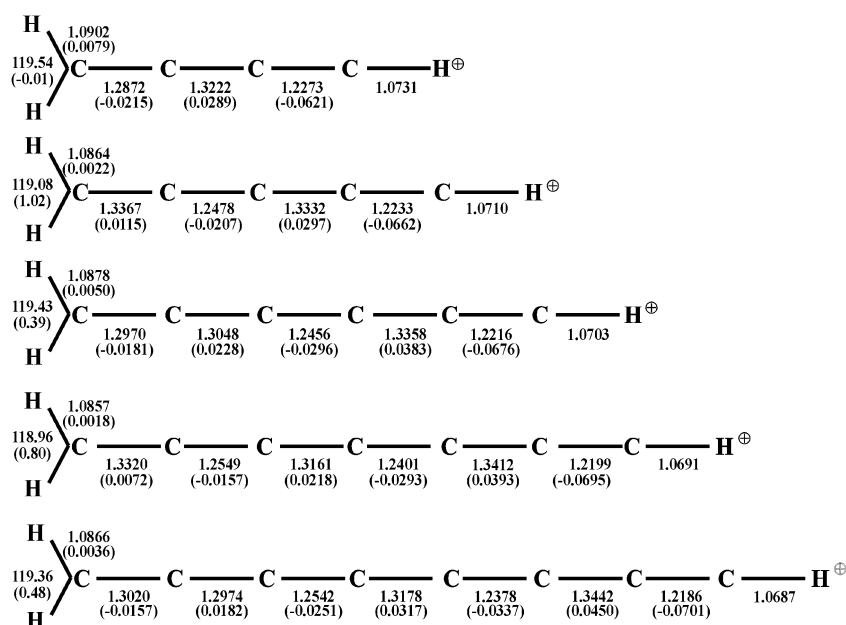


Fig. 4 CCSD(T*)-F12a/VTZ-F12 equilibrium structures for cations of type $H_2C_nH^+$. Differences with respect to neutrals H_2C_n are given in parentheses.

Table 6 CCSD(T*)-F12a/VTZ-F12 harmonic vibrational wavenumbers and zero-point energies (ZPEs) for H_2C_n and $H_2C_nH^+$ species ($n = 4-6$)

Species	Sym.	Harmonic vibrational wavenumbers/cm ⁻¹						ZPE/cm ⁻¹		
H_2C_4	a_1	3148	2106	1701	1387	901		7707		
	b_1	775	482	190						
	b_2	3244	953	393	132					
$H_2C_4H^+$	a_1	3369	3079	2129	1810	1312	902	10 084		
	b_1	846	625	454	200					
	b_2	3173	861	846	389	174				
H_2C_5	a_1	3125	2145	1925	1501	1348	749	8827		
	b_1	938	538	246	111					
	b_2	3216	1029	413	236	134				
$H_2C_5H^+$	a_1	3387	3120	2188	2062	1500	1353	742	11 450	
	b_1	1054	803	563	273	128				
	b_2	3225	1021	639	424	277	140			
H_2C_6	a_1	3142	2130	2055	1726	1422	1193	641	9738	
	b_1	809	458	446	221	99				
	b_2	3235	973	538	364	196	89			
$H_2C_6H^+$	a_1	3395	3101	2153	2103	1837	1381	1194	632	12 261
	b_1	857	652	429	390	221	101			
	b_2	3197	894	782	514	377	225	86		

H_2C_n species ($n = 4-8$) will be calculated at these recommended equilibrium structures. The zero-point vibrational contributions to the proton affinities are computed from the harmonic vibrational wavenumbers as given in Table 6. The effects of core correlation on the PA_e values have been investigated by standard CCSD(T) using basis sets CV5Z (for $n = 4-6$) and CVQZ (for $n = 7, 8$) in the correlated all-electron calculations and basis sets V5Z or VQZ, when only the valence electrons are correlated.

Calculated proton affinities for H_2C_n species are listed in Table 7. PA_e values are reported at the CCSD-F12a and CCSD(T*)-F12a levels. Version b of explicitly correlated coupled cluster theory delivers values which are only 0.1 kJ mol⁻¹ larger. The contribution of connected triple substitutions increases significantly with increasing chain length. This may mean that the accuracy of CCSD(T*)-F12a becomes worse for

Table 7 Calculated proton affinities for H_2C_n species ($n = 4-8$)^a

n	PA_e				
	CCSD-F12a ^b	CCSD(T*)-F12a ^b	ΔE (core) ^c	ΔZPE ^d	PA_0^f
4	941.5	933.5	2.0	-28.4	907.1
5	990.2	981.3	1.9	-31.4	951.7
6	1010.5	997.4	2.2	-30.2	969.4
7	1041.0	1027.2	2.0	(-31) ^e	998
8	1059.6	1041.9	2.2	(-31) ^e	1013

^a All values in kJ mol⁻¹. ^b VQZ-F12 basis. ^c From standard CCSD(T) calculations with (C)V5Z basis sets ($n = 4-6$) or (C)VQZ basis sets ($n = 7, 8$). ^d Harmonic contribution using data from Table 6. ^e Assumed. ^f Proton affinity at 0 K; see the text.

the longer carbon chains. On the other hand, the contribution from core correlation remains almost constant. A similar

situation applies for the change in harmonic ZPE. We therefore assume constant values of -31 kJ mol^{-1} for the larger species with $n = 7$ and 8, for which no harmonic vibrational wavenumbers have been calculated. The last column of Table 7 lists PA_0 values, obtained by adding the ΔZPE and $\Delta E(\text{core})$ values to the CCSD(T*)-F12a results for PA_e .

4. Conclusions

Despite several efforts, no high-resolution spectroscopic study of the fundamental propargyl cation has yet been successful. Therefore, the present paper reports results of state-of-the-art electronic structure calculations at the CCSD(T*)-F12a level of theory in conjunction with large-scale vibrational configuration interaction. On the basis of previous applications to related molecules,^{16,37,46} for which reliable spectroscopic data are available, the accuracy obtained for the fundamentals of $\text{H}_2\text{C}_3\text{H}^+$ is expected to be *ca.* 5 cm^{-1} . Owing to large predicted absolute IR intensities of 371 and 93 km mol^{-1} , the bands at 2079 cm^{-1} ($\sim\text{CC}$ antisymm. stretch) and 3236 cm^{-1} ($\sim\text{acetylenic CH}$ stretch) are most promising for forthcoming IR spectroscopic studies.

Without the help of reliable theoretical work, the correct interpretation of IRPD spectra of cation–argon complexes is often not an easy matter. The possible presence of isomers of the cation as well as different structures of the complexes may complicate the assignment process. The present and previous calculations¹⁴ have shown that the system $\text{H}_2\text{C}_3\text{H}^+ + \text{Ar}$ exhibits a pronounced absolute energy minimum of C_s symmetry ($C_s \text{ Min } 1$), which is well separated from two other local minima. We therefore expect that $C_s \text{ Min } 1$ dominates the IRPD spectra at low temperatures. Indeed, the most pronounced spectroscopic feature found in the IRPD spectrum of Ricks *et al.*¹³ is compatible with structure $C_s \text{ Min } 1$, but not with the higher-lying H-bound structure of C_{2v} symmetry. We actually see no indication of the latter structure in the IRPD spectrum at mild discharge conditions and therefore suggest reassignment of two “doublets”, claimed to arise from the specific rotational structure which only exists for complexes with C_{2v} symmetry.

A weak feature found in the IRPD spectrum of Ricks *et al.* at 1293 cm^{-1} may be due to the complex $c\text{-C}_3\text{H}_3^+\cdot\text{Ar}$. However, assignment of the band at 3182 cm^{-1} to the same species has no sound basis. Both previous spectroscopic work^{9–12} as well as the present theoretical study present strong arguments against that assignment. A likely candidate for the noted band is the combination tone $\nu_3 + \nu_5$ of $\text{H}_2\text{C}_3\text{H}^+\cdot\text{Ar}$, which is estimated to have a remarkably large IR intensity of 20 km mol^{-1} .

Ongoing theoretical studies at Göttingen concern the complexes of $\text{H}_2\text{C}_3\text{H}^+$ and $c\text{-C}_3\text{H}_3^+$ with N_2 , CO_2 , and O_2 and will be the subject of a forthcoming publication.

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