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

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The vibrations of the propargyl cation (H$_2$C$_3$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 H$_2$C$_3$H$^+$·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 $\nu_2$ (symm. CH stretch), $\nu_3$ (pseudoantisymm. CC stretch), and $\nu_4$ (CH$_2$ scissoring). However, reassigments 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-C$_3$H$_2$·Ar is certainly wrong; the combination tone $\nu_3 + \nu_5$ of H$_2$C$_2$H$^+$·Ar is a more likely candidate. Furthermore, accurate proton affinities are predicted for the carbenes H$_2$C$_n$ with $n = 3$–8, thereby providing data of interest for interstellar cloud chemistry.

1. Introduction

Ions of formula C$_3$H$_2^+$ belong to the fundamental cations of organic chemistry. The most stable isomer thereof is the cyclopropenyl cation (c-C$_3$H$_2^+$), but a more reactive isomer, the propargyl cation (H$_2$C$_3$H$^+$ or l-C$_3$H$_2^+$), has also been known from mass spectrometric studies for about four decades.$^1$ According to early work by Lossing,$^2$ it is 1.1 ± 0.1 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$_3$H$^+$ and H$_2$. This may be a way of interstellar synthesis of the cations, which will then further react to the well-known interstellar molecules c-C$_3$H$_2$ and l-C$_3$H$_2$ by dissociative attachment of an electron.$^3$ In 1990, the 10.49-eV photoionization mass and photoelectron (PE) spectra of H$_2$C$_3$H, H$_2$C$_3$D, and D$_2$C$_3$H were reported by Minsek and Chen.$^4$ For the latter species, a significant structure was observed in the PE spectrum and assigned to vibrational excitation within the H$_2$C$_3$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 H$_2$C$_3$H$^+$ and D$_2$C$_3$D$^+$, isolated in neon matrices at 5 K, were published by Wyss et al.$^9$ These authors observed the $A'A' \leftrightarrow X'A_1$ 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 H$_2$C$_3$H$^+$ and D$_2$C$_3$D$^+$ were observed at 2079.9(1.0) and 1955.2(1.0) 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 H$_2$C$_3$H$^+$ with various ligands were studied in 2002 through infrared photodissociation (IRPD) spectroscopy by Dopfer and coworkers.$^{10,11}$ The most extensive spectroscopic information was obtained for the complex of a C$_3$H$_3$ cation with the N$_2$ molecule and spectroscopic signatures of both c-C$_3$H$_2$N$_2$ and H$_2$C$_3$H$^+$·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 Möller and Plesset) and bands at 3139, 3113 and 3001 cm$^{-1}$ were assigned to $\nu_1$ (acetylenic CH stretch),
\( \nu_2 \) (symmetric CH\(_2\) stretch) and \( 2\nu_2 \) (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 H\(_2\)C\(_3\)H\(^+\)·Ne and H\(_2\)C\(_3\)H\(^+\)·Ar.\(^{12}\) Again, their assignment remained unclear. Quite recently, the latter complex was investigated by Duncan and coworkers\(^{16}\) 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 pseudoaxially symmetric CC stretching vibration (\( \nu_3 \)) was found 3 cm\(^{-1}\) lower than the above neon matrix value. The strongest band was observed at 4072 cm\(^{-1}\) over the 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\(_2\)v equilibrium structure in which the argon atom is closest to the acetylenic hydrogen atom of the propargyl cation. As we could recently through state-of-the-art explicitly correlated coupled cluster calculations,\(^{14}\) the C\(_2\)v structure is only a local minimum on the potential energy surface of H\(_2\)C\(_3\)H\(^+\) and a C\(_i\) 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/6-31G (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 H\(_2\)C\(_3\)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,\(^{10,11}\) the shifts in the intramolecular vibrational fundamentals of different structures of the complexes H\(_2\)C\(_3\)H\(^+\)·Ar and c-C\(_2\)H\(_5\)·Ar have been studied as well. In addition, accurate values will be predicted for the proton affinities of the H\(_2\)C\(_n\) species with \( n = 3-8 \). Such thermochemical data are of interest to astrochemistry, since three members of the H\(_2\)C\(_n\) series of molecules (H\(_2\)C\(_2\), H\(_2\)C\(_3\), and H\(_2\)C\(_4\)) 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\(_2\)C\(_n\) 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 3CFIX) 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 = D, T, and Q) basis sets of Peterson et al.\(^{21}\) In the following, they will be briefly denoted by VnZ-F12. For the C\(_n\)H\(_{n+1}\)·Ar complexes, the VTZ-F12 basis for C\(_4\)H\(_5\) was employed in conjunction with the aug-cc-pVQ+dZ 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 Weigend\(^{25}\) 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 H\(_2\)C\(_3\)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 \textit{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 H\(_2\)C\(_3\)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, \textit{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 \textit{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 (modal) 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 \( \nu_1 \) 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 \( \mu \)-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,\textsuperscript{16} it was recently applied to calculate IR spectra of $H_2$CCC and $D_2$CCC\textsuperscript{17} and photoelectron spectra for different isotopomers of the propargyl radical, $H_2C_3H$.\textsuperscript{18} The chosen approach makes use of a five-dimensional (5D) approximate vibrational Hamiltonian of the form (in atomic units)

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

(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

$$V_{\text{anh}} = \sum_{ijklm} C_{ijklm} S_i S_j S_k S_l S_m$$

(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 $\hat{H}_{\text{vib}}$ over a basis of harmonic oscillator product functions according to

$$H_{ii}(v_1, v_2, v_3, v_4, v_5) = H_0(v_1, v_2, v_3, v_4, v_5) + \sum_{i=1}^{5} A_i \left( v_i + \frac{1}{2} \right)$$

(3)

The five parameters $A_i$ are determined in an adjustment process to the results of VCI calculations for the wavenumbers of the five totally symmetric fundamentals ($\nu_{v_a}$–$\nu_{v_b}$) of $H_2C_3H$.\textsuperscript{18}

From the calculated vibrational wave functions and the analytical EDMF,\textsuperscript{17} integrated molar absorption intensities for vibrational transitions arising from the vibrational ground state are calculated according to the formula

$$A_m = \frac{\pi N_A}{M c \epsilon_0} \left| \mu_0 \right|^2$$

(4)

In eqn (4), $N_A$ is the Avogadro constant, $\hbar$ the Planck’s constant divided by $2\pi$, $\epsilon_0$ the speed of light in vacuum, $\nu_0$ the vibrational wavenumber, and $\mu_0$ 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 0.0005 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\textsuperscript{-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\textsuperscript{-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 molecules\textsuperscript{16} yielded a mean absolute deviation of only 4.0 cm\textsuperscript{-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 $\nu_{v_2}$ and amounts to 33 cm\textsuperscript{-1}. We predict the acetylenic CH stretching vibration $\nu_{v_1}$ at 3236 cm\textsuperscript{-1}. Its anharmonicity contribution $\Delta \nu_1 = \omega_1 - \nu_1$ is calculated to be 122 cm\textsuperscript{-1}, which appears to be a rather normal value. For comparison, the $\Delta \nu_1$ value for the corresponding radical ($H_2C_2H$) is estimated to be 128 cm\textsuperscript{-1} by combining the

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>$r_{1e}$/Å</th>
<th>$x_{v_1}^e$/°</th>
<th>$R_{1e}$/Å</th>
<th>$R_{2e}$/Å</th>
<th>$r_{2e}$/Å</th>
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</thead>
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<tr>
<td>CCSD(T*)-F12a\textsuperscript{b}</td>
<td>VDZ-F12</td>
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<td>1.07475</td>
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<td>119.33</td>
<td>1.34948</td>
<td>1.23101</td>
<td>1.07430</td>
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<tr>
<td>CCSD(T)\textsuperscript{b}</td>
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<td>1.34924</td>
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<td>V/6Z</td>
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<td>CVQZ\textsuperscript{c}</td>
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<tr>
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<td></td>
<td>CV/6Z</td>
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<td>1.34585</td>
<td>1.22762</td>
<td>1.07265</td>
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</table>

\textsuperscript{a} HCH equilibrium angle. \textsuperscript{b} Valence electrons correlated. \textsuperscript{c} All electrons correlated. \textsuperscript{d} Ref. 38. \textsuperscript{e} Improved geometry optimization with respect to ref. 47.
### Table 2: Calculated harmonic vibrational wavenumbers (in cm⁻¹) for H₂C₃H⁺

<table>
<thead>
<tr>
<th>Vibration</th>
<th>CCSD(T) VTZ</th>
<th>CCSD(T*)-F12a VTZ</th>
<th>CCSD(T*)-F12a VQZ</th>
<th>CCSD(T*)-F12a V5Z</th>
<th>CCSD(T*)-F12a V6Z</th>
<th>CCSD(T*)-F12a VDZ-F12</th>
<th>CCSD(T*)-F12a VTZ-F12</th>
<th>CCSD(T*)-F12a VQZ-F12</th>
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<td>3358</td>
<td>3360</td>
<td>3360</td>
<td>3354</td>
<td>3358</td>
<td>3359</td>
<td></td>
</tr>
<tr>
<td>ω₂ (a₂)</td>
<td>3118</td>
<td>3118</td>
<td>3118</td>
<td>3118</td>
<td>3115</td>
<td>3115</td>
<td>3117</td>
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<tr>
<td>ω₃ (a₃)</td>
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<td>2123</td>
<td>2123</td>
<td>2116</td>
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<td>2123</td>
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<tr>
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<td>1133</td>
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<tr>
<td>ω₆ (b₁)</td>
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<td>1120</td>
<td>1120</td>
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<tr>
<td>ω₁₀ (b₅)</td>
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<td>1036</td>
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<tr>
<td>ω₁₂ (b₇)</td>
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<td>288</td>
<td>289</td>
<td>289</td>
<td>280</td>
<td>287</td>
<td>288</td>
<td></td>
</tr>
</tbody>
</table>

ZPE (anh.)

- Valence electrons are correlated in coupled cluster calculations.
- Harmonic zero-point vibrational energy.

### Table 3: Calculated anharmonic vibrational wavenumbers (in cm⁻¹) for H₂C₃H⁺

<table>
<thead>
<tr>
<th>Vibration</th>
<th>B3LYP 6-311G(2df,p)</th>
<th>CCSD(T*)-F12a VTZ-F12</th>
</tr>
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<tbody>
<tr>
<td>ν₁ (a₁)</td>
<td>3226</td>
<td>3236</td>
</tr>
<tr>
<td>ν₂ (a₂)</td>
<td>2976</td>
<td>2990</td>
</tr>
<tr>
<td>ν₃ (a₃)</td>
<td>2089</td>
<td>2089</td>
</tr>
<tr>
<td>ν₄ (a₄)</td>
<td>1440</td>
<td>1446</td>
</tr>
<tr>
<td>ν₅ (a₅)</td>
<td>1139</td>
<td>1123</td>
</tr>
<tr>
<td>ν₆ (b₁)</td>
<td>1113</td>
<td>1099</td>
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<tr>
<td>ν₇ (b₂)</td>
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</tr>
<tr>
<td>ν₈ (b₃)</td>
<td>278</td>
<td>264</td>
</tr>
<tr>
<td>ν₁₀ (b₅)</td>
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<td>3080</td>
</tr>
<tr>
<td>ν₁₁ (b₆)</td>
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<tr>
<td>ν₁₂ (b₇)</td>
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<td>615</td>
</tr>
<tr>
<td>ν₁₃ (b₈)</td>
<td>331</td>
<td>298</td>
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</table>

ZPE (anh.)

- ref. 15
- 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. For the methylene CH stretches we obtain Δν₂ (symm. CH stretch) = 125 and Δν₃ (asymm. CH stretch) = 145 cm⁻¹. Rather similar values of 133 and 139 cm⁻¹ were recently obtained for H₂C₃ from analogous VCI/CCSD(T*)-F12a calculations. The present gas-phase wavenumber prediction for ν₃, the pseudo-antisymmetric CCC stretching vibration, coincides with the neon matrix value of Wyss et al. One may well expect that such an inert matrix has only a very small effect on a vibration of small amplitude like ν₃. Vibrational anharmonicity lowers this vibration by 41 cm⁻¹. The CH₂ scissoring vibration ν₄ is calculated at 1446 cm⁻¹, 33 cm⁻¹ below the harmonic value. The recommended gas-phase value for the propargyl radical ν₄ is 1440 ± 15 cm⁻¹ and thus very similar. A small anharmonicity contribution of only 9 cm⁻¹ is calculated for the pseudo-symmetric CC stretching vibration ν₅, the band origin of which is predicted at 1123 cm⁻¹.

### 3.2 CCSD(T*)-F12a calculations for H₂C₃H⁺-Ar complexes

In extension of our previous work, full dimensional geometry optimizations have been carried out for H₂C₃H⁺-Ar complexes, using CCSD(T*)-F12a in conjunction with basis...
Table 4  Wavenumbers and absolute IR intensities for vibrations of H$_2$C$_3$H$^+$ involving totally symmetric modes$^a$

<table>
<thead>
<tr>
<th>Vibration</th>
<th>$\tilde{\nu}$ (cm$^{-1}$)</th>
<th>$\tilde{A}$ (km mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_5$</td>
<td>1123</td>
<td>18.7 (18.8)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1446</td>
<td>12.4 (11.8)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>2080</td>
<td>371 (378)</td>
</tr>
<tr>
<td>$2\nu_5$</td>
<td>2245</td>
<td>6.7</td>
</tr>
<tr>
<td>$2\nu_4$</td>
<td>2567</td>
<td>2.2</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>2866</td>
<td>3.6</td>
</tr>
<tr>
<td>$\nu_3$ + $\nu_5$</td>
<td>3185</td>
<td>20.2</td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>3236</td>
<td>93.4 (112)</td>
</tr>
</tbody>
</table>

$^a$ 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: $A_1 = -15$, $A_2 = -78$, $A_3 = -14$, $A_4 = -15$, and $A_5 = 1$. $^b$ Values from “double-harmonic” approximation are given in parentheses.

set combination (VTZ-F12, AVQZ). Three energy minima were found; they are termed “C$_1$ Min 1”, “C$_1$ Min 2” and “C$_{2v}$ min” and are graphically displayed in Fig. 2. The corresponding nuclear cartesian coordinates are listed in Table S3 of ESL.$^+$ 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$_1$ Min 1, C$_1$ Min 2 and C$_{2v}$ are 798.4(792.6), 624.3(620.6) and 593.9(592.1), respectively, which are blue-shifted with respect to free H$_2$C$_3$H$^+$, where the previous values for rigid cations (see Table 1 of ref. 14) are: $D_e$ = 990.0 cm$^{-1}$, $D_e$ = 881.5 cm$^{-1}$, and $D_e$ = 621.8 cm$^{-1}$, respectively. VCI calculations of Bartlett and coworkers yielded $D_e$ = 3138 cm$^{-1}$ for the C$_{2v}$ structure, which is blue-shifted by 5–6 cm$^{-1}$ with respect to C$_1$ Min 1, a factor of 2.6 higher than for free H$_2$C$_3$H$^+$. This compares equally well with previous calculations and supports our earlier findings that C$_{2v}$ is the most stable complex for H$_2$C$_3$H$^+$. For the argon complex (C$_1$ Min 1), the CH stretching vibrations are slightly blue-shifted by 5–6 cm$^{-1}$.

The $C_{2v}$ structure exhibits blue shifts of 22 and 34 cm$^{-1}$ in the out-of-plane ($\nu_7$) and in-plane ($\nu_{11}$) CCH bending vibrations, respectively. As has been shown previously for complexes of type HCCH-L (L = NH$_3$, Cl$^-$, Br$^-$, and I$^-$),$^{30-44}$ such blue shifts are quite typical for hydrogen-bonded acetylenic groups. The largest shifts calculated for the two C$_{2v}$ energy minima of H$_2$C$_3$H$^+$·Ar refer to the low-lying out-of-plane vibration $\nu_7$, which is 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 C$_3$H$_5$·Ar complexes

The peak with highest wavenumber found in the IRPD spectra of Roth and Dopfer$^{12}$ and Ricks $et$ $al.$,$^{13}$ occurs at 3239 and 3238 cm$^{-1}$, respectively. Combining the present VCI wavenumber for the acetylenic CH stretching vibration $\nu_1$ of free H$_2$C$_3$H$^+$ with the harmonic shift for the energetically most favourable structure of the argon complex (C$_1$ 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 $\nu_1 = 3236 - 43 = 3193$ cm$^{-1}$, which is 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 H$_2$C$_3$H$^+$. The presence of isomer C$_3$, Min 1 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-C$_3$H$_5$·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, $\nu_4$ (c-C$_3$H$_5$) was observed at 3130.4 cm$^{-1}$.$^{12}$ Roth and Dopfer$^{12}$ reported very similar values of 3130 and 3136 cm$^{-1}$ for the complexes c-C$_3$H$_5$·Ne and c-C$_3$H$_5$·Ar, respectively. VCI calculations of Bartlett and coworkers yielded $\nu_4 = 3138$ cm$^{-1}$, for the free cycloprenyl cation.$^{44}$ Like for H$_2$C$_3$H$^+$·Ar, we calculated the harmonic vibrational wavenumbers for c-C$_3$H$_5$·Ar by CCSD(T*)-F12a with the basis set combination (VTZ-F12, AVQZ). For the most stable complex of C$_{2v}$ symmetry, the $\nu_4$ band is split into two components which are blue-shifted with respect to free c-C$_3$H$_5$ by 3.7 and 1.1 cm$^{-1}$, respectively. For the higher-lying complex with

Table 5  CCSD(T*)-F12a harmonic wavenumber shifts (in cm$^{-1}$) for intramolecular vibrations of H$_2$C$_3$H$^+$·Ar complexes

<table>
<thead>
<tr>
<th>Vibration$^a$</th>
<th>$C_1$ Min 1</th>
<th>$C_1$ Min 2</th>
<th>$C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>4.9</td>
<td>6.1</td>
<td>-43.4</td>
</tr>
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<td>$\nu_2$</td>
<td>6.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>$\nu_3$</td>
<td>0.7</td>
<td>3.6</td>
<td>-4.5</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>-3.7</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>-2.5</td>
<td>-5.1</td>
<td>-1.2</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>-5.2</td>
<td>-3.4</td>
<td>21.6</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>16.6</td>
<td>15.1</td>
<td>4.0</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>6.4</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>0.4</td>
<td>-0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>3.1</td>
<td>-1.6</td>
<td>34.2</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>3.7</td>
<td>1.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^a$ Numbering for the free cation (see Table 3) is employed.
Combining the harmonic shifts with the neon matrix value for ν4 (c-C3H5+), we predict no peak for c-C3H5+·Ar which has a wavenumber higher than 3135 cm⁻¹. We may thus safely rule out c-C3H5+·Ar as the carrier of the band at 3182 cm⁻¹. From the experimental side, 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 C3H7⁺·L with L = Ne, Ar, and N2, respectively. The close coincidence of the peaks points to a common origin. According to the data presented in Table 4, we suggest the ν3 + ν6 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 H2C3H+ is expected to be small as well. For free H2C3H+ (see Section 3.1), the intensity ratio A(ν3 + ν6)/A(ν2) was calculated to be as large as 0.81. We thus expect that the ν3 + ν6 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 H2C3H+·Ar might gain a higher population in the molecular beam. As a result, the ν3 + ν5 and ν1 (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 ΔK = ±1 subbands of the asymmetric CH stretching vibration ν9. Such an assignment is only meaningful for a H-bound complex of C2v symmetry, however. For the most stable complex of C3 symmetry we calculate ν9 = 3080 + 6 = 3086 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 a1-component of ν4 (c-C3H5+) or the combination tone ν3 + ν10 might be suitable candidates.

The present calculations predict the symmetric CH stretching vibration of the most stable complex of H2C3H+·Ar at ν2 = 2990 + 6 = 2996 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 ν3 (2081 vs. 2077 cm⁻¹) and ν4 (1446 vs. 1445 cm⁻¹). As noted earlier, the assignment of the band observed at 1222 cm⁻¹ to the pseudosymmetric CC stretching vibration ν9 appears to be incorrect. We predict the ν5 band of H2C3H+·Ar (C3v, 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 ν6 CH3 out-of-plane wag”. Again, this assignment requires a H-bound complex of C2v symmetry. For the ν6 band of C3v, 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 ν5 and ν6 of the most stable complex.

### 3.4 Proton affinities at 0 K for H2Cn species (n = 3–8)

Combining the results of the present CCSD(T*)-F12a/VQZ-F12 calculations with the earlier ones for H2CCC, we calculate an equilibrium proton affinity (PAe) of 917.1 kJ mol⁻¹ for H2CCC. 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 PAe 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 PAe by 1.5 kJ mol⁻¹. Fig. 3 shows the variation of PAe 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 PAe = 918.9 kJ mol⁻¹. Higher-order correlation effects and relativistic effects are expected to play a minor role and will hardly change the PAe 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 kJ mol⁻¹ (VQZ-F12 basis) and −30.95 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 PAe estimate, we thus arrive at a proton affinity at 0 K of PA0 (H2CCC) = 888.4 kJ mol⁻¹, with an estimated uncertainty of 2 kJ mol⁻¹.

The proton affinities of the larger H2Cn 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 H2CnH⁺ and the differences with respect to the corresponding unprotonated species H2Cn. 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 0.0029–0.0037 Å (average: 0.0034 Å). The difference in rcc (methylene CH distance) is practically constant with a mean value of 0.0016 Å.

In an attempt to arrive at rather accurate equilibrium structures for the protonated species H2CnH⁺, 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, PAe values for the larger
H$_2$C$_n$ 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$_2$C$_n$ 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 the longer carbon chains. On the other hand, the contribution from core correlation remains almost constant. A similar

**Table 6** CCSD(T*)-F12a/VTZ-F12 harmonic vibrational wavenumbers and zero-point energies (ZPEs) for H$_2$C$_n$ and H$_2$C$_n$H$^+$ species ($n = 4 - 6$)

<table>
<thead>
<tr>
<th>Species</th>
<th>Sym.</th>
<th>Harmonic vibrational wavenumbers/cm$^{-1}$</th>
<th>ZPE/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$C$_4$</td>
<td>$a_1$</td>
<td>3148, 2106, 1701, 1387, 901</td>
<td>7707</td>
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<tr>
<td></td>
<td>$b_1$</td>
<td>775, 482, 190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_2$</td>
<td>3244, 953, 393, 132</td>
<td></td>
</tr>
<tr>
<td>H$_2$C$_4$H$^+$</td>
<td>$a_1$</td>
<td>3369, 3079, 2129, 1810, 1312, 902</td>
<td>10084</td>
</tr>
<tr>
<td></td>
<td>$b_1$</td>
<td>846, 625, 454, 200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_2$</td>
<td>3173, 861, 846, 389, 174</td>
<td></td>
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<tr>
<td>H$_2$C$_5$</td>
<td>$a_1$</td>
<td>3125, 2145, 1925, 1501, 1348, 749</td>
<td>8827</td>
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<tr>
<td></td>
<td>$b_1$</td>
<td>938, 538, 246, 111</td>
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</tr>
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<td></td>
<td>$b_2$</td>
<td>3216, 1029, 413, 236, 134</td>
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<tr>
<td>H$_2$C$_5$H$^+$</td>
<td>$a_1$</td>
<td>3387, 3120, 2188, 2062, 1500, 1353, 742</td>
<td>11450</td>
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<tr>
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<td>$b_1$</td>
<td>1054, 803, 563, 273, 128</td>
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</tr>
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<td></td>
<td>$b_2$</td>
<td>3225, 1021, 639, 424, 277, 140</td>
<td></td>
</tr>
<tr>
<td>H$_2$C$_6$</td>
<td>$a_1$</td>
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<td>9738</td>
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<td>$b_1$</td>
<td>809, 458, 446, 221, 99</td>
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<td></td>
<td>$b_2$</td>
<td>3235, 973, 538, 364, 196, 89</td>
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<tr>
<td>H$_2$C$_6$H$^+$</td>
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<tr>
<td></td>
<td>$b_1$</td>
<td>857, 652, 429, 390, 221, 101</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_2$</td>
<td>3197, 894, 782, 514, 377, 225, 86</td>
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</table>

**Table 7** Calculated proton affinities for H$_2$C$_n$ species ($n = 4 - 8$)

<table>
<thead>
<tr>
<th>$n$</th>
<th>CCSD-F12a$^b$</th>
<th>CCSD(T*)-F12a$^b$</th>
<th>$\Delta E$ (core)$^c$</th>
<th>$\Delta$ZPE$^d$</th>
<th>PA$_0$$^f$</th>
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<tbody>
<tr>
<td>4</td>
<td>941.5</td>
<td>933.5</td>
<td>2.0</td>
<td>-28.4</td>
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<tr>
<td>5</td>
<td>990.2</td>
<td>981.3</td>
<td>1.9</td>
<td>-31.4</td>
<td>951.7</td>
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<tr>
<td>6</td>
<td>1010.5</td>
<td>997.4</td>
<td>2.2</td>
<td>-30.2</td>
<td>969.4</td>
</tr>
<tr>
<td>7</td>
<td>1041.0</td>
<td>1027.2</td>
<td>2.0</td>
<td>(-31)$^e$</td>
<td>998</td>
</tr>
<tr>
<td>8</td>
<td>1059.6</td>
<td>1041.9</td>
<td>2.2</td>
<td>(-31)$^e$</td>
<td>1013</td>
</tr>
</tbody>
</table>

$^a$All values in kJ mol$^{-1}$. $^b$VQZ-F12 basis. $^c$From standard CCSD(T) calculations with (C)VSZ 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.
situation applies for the change in harmonic ZPE. We therefore assume constant values of \(-31 \text{ kJ mol}^{-1}\) 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 \(P_{A_0}\) values, obtained by adding the \(\Delta ZPE\) and \(\Delta E(\text{core})\) values to the CCSD(T\(^*\))-F12a results for \(P_{A_c}\).

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 \(\text{H}_2\text{C}_2\text{H}^+\) is expected to be \(ca.\ \text{5 cm}^{-1}\). Owing to large predicted absolute IR intensities of 371 and 93 km mol\(^{-1}\), the bands at 2079 cm\(^{-1}\) (\(\sim\) CC antisymm. stretch) and 3236 cm\(^{-1}\) (\(\sim\) 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 calculations\(^{14}\) have shown that the system \(\text{H}_2\text{C}_2\text{H}^+ + \text{Ar}\) exhibits a pronounced absolute energy minimum of \(C_5\) symmetry (\(C_5\ \text{Min 1}\)), which is well separated from two other local minima. We therefore expect that \(C_5\ \text{Min 1}\) 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 \(C_5\ \text{Min 1}\), 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 \(c\text{-C}_3\text{H}_2\text{H}^+\text{Ar}\). However, assignment of the band at 3182 cm\(^{-1}\) to the same species has no sound basis. Both previous spectroscopic work\(^{8-12}\) as well as the present theoretical study present strong arguments against that assignment. A likely candidate for the noted band is the combination tone \(\nu_3 + \nu_4\) of \(\text{H}_2\text{C}_2\text{H}^+\text{Ar}\), which is estimated to have a remarkably large IR intensity of 20 km mol\(^{-1}\).

Ongoing theoretical studies at Göttingen concern the complexes of \(\text{H}_2\text{C}_2\text{H}^+\) and \(c\text{-C}_3\text{H}_2\text{H}^+\) with \(\text{N}_2\), \(\text{CO}_2\), and \(\text{O}_2\) and will be the subject of a forthcoming publication.

Acknowledgements

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References


44 R. Bartlett, as cited in ref. 13.

