Descendant of the X-ogen carrier and a ‘mass of 69’: infrared action spectroscopic detection of HC$_3$O$^+$ and HC$_3$S$^+$

Sven Thorwirth $^{a,}$, Michael E. Harding $^{b,}$, Oskar Asvany $^{a,}$, Sandra Brünken $^{c,}$, Pavol Jusko$^{a,}$, Kin Long Kelvin Lee $^{d,}$, Thomas Salomon $^{a,}$, Michael C. McCarthy $^{d}$ and Stephan Schlemmer $^{a,}$

$^a$I. Physikalisches Institut, Universität zu Köln, Köln, Germany; $^b$Institut für Physikalische Chemie, Abteilung für Theoretische Chemie, Karlsruher Institut für Technologie (KIT), Karlsruhe, Germany; $^c$Institut für Moleküle und Materialien, FELIX Laboratory, Radboud University, Nijmegen, The Netherlands; $^d$Center for Astrophysics – Harvard & Smithsonian, Cambridge, MA, USA

ABSTRACT
The carbon chain ions HC$_3$O$^+$ and HC$_3$S$^+$ – longer variants of the famous ‘X-ogen’ line carrier HCO$^+$ – have been observed for the first time using two cryogenic 22-pole ion trap apparatus (FELion, Coltrap) and two different light sources: the Free Electron Laser for Infrared eXperiments (FELIX), which was operated between 460 and 2500 cm$^{-1}$, and an optical parametric oscillator operating near 3200 cm$^{-1}$; signals from both experiments were detected by infrared predissociation action spectroscopy. The majority of vibrational fundamentals were observed for both ions and their wavenumbers compare very favourably with results from high-level anharmonic force field calculations performed here at the coupled-cluster singles and doubles level augmented by a perturbative treatment of triple excitations, CCSD(T). As the action scheme employed here probes the Ne-tagged weakly bound variants, Ne–HC$_3$O$^+$ and Ne–HC$_3$S$^+$, corresponding calculations of these systems were also performed. Differences in the structures and molecular force fields between the bare ions and their Ne-tagged complexes are found to be very small.

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1. Introduction
Acylium ions, R–C≡O$^+$, play a vital role as reaction intermediates in preparatory organic synthesis, most notably as electrophiles in coupling reactions such as the Friedel-Crafts acylation (see, e.g. Ref. [1]). These ions and their sulfur analogs, R–C≡S$^+$, have also been invoked in astrochemical reaction networks to account for the production of (carbon-rich) chains via very fast dissociative recombination (DR) with free electrons (e.g. Ref. [2])

$$\text{HC}_3\text{X}^+ + e^- \rightarrow \text{C}_3\text{X} + \text{H}, \quad \text{X} = \text{O}, \text{S}. \quad (1)$$

The astronomical identification of C$_3$O and C$_3$S, both products of reaction (1), nearly 35 years ago [3,4] points to the importance of the parent ions in chemical networks of dark molecular clouds.
The prototypical acylium – formylium ion, HCO\(^+\) – was the first polyatomic ion detected in space, although its identity was originally a mystery when a strong line at 89.2 GHz was observed towards several astronomical objects; for lack of a better name, the line was dubbed \('X-ogen\' [5] (\'extraterrestrial origin\)'). However, it was not until the pure rotational spectrum of this ion was measured by Woods and co-workers a few years later [6] that the carrier of the astronomical line was established with certainty, and in doing so confirmed the bold prediction of Klemperer [7]. Similarly, HCS\(^+\) was first detected in space [8] almost simultaneously with a report of its high-resolution laboratory spectrum [9]. Since then, HCO\(^+\) and HCS\(^+\) have been the subjects of a number of high-resolution spectroscopic investigations [10–17].

While many mass spectrometric studies involving acylium and thioacylium ions have been reported (see, e.g., Refs. [18–24]), gas-phase spectroscopic investigations beyond the simplest members of each family, HCO\(^+\) and HCS\(^+\), are scarce. Thioacylium species appear to have only been studied using mass spectrometry while gas-phase spectroscopy of acylium ions is limited to only a few species. The acetyl cation, CH\(_3\)CO\(^+\), for example, has been studied in a free-jet expansion source by infrared (IR) photodissociation of its weakly bound CH\(_3\)CO\(^+\)–Ar complex [25]. An electronic spectrum of HC\(_3\)O\(^+\) in the gas-phase and trapped in an inert gas matrix has also been obtained [26]. Very recently, IR photodissociation spectra of HC\(_n\)O\(^+\)–CO complexes (n = 5–12) have been reported in the 1600–3500 cm\(^{-1}\) region [27,28].

This paper reports the first spectroscopic observations of the HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\) ions. Experimental measurements were performed at IR wavelengths by making use of sensitive action spectroscopic techniques in combination with modern ion traps. Spectroscopic assignment was based on high-level quantum-chemical calculations performed at the CCSD(T) level of theory [29], in conjunction with the experimental work.

2. Experiment

Experimental characterisation of HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\) in the wavenumber range from 460 to 2500 cm\(^{-1}\) was performed in the cryogenic 22-pole ion trap apparatus FELion connected to the Free Electron Laser for Infrared eXperiments, FELIX [30], located at Radboud University (Nijmegen, The Netherlands). The FELion apparatus has been described in detail recently [31]. Briefly, primary ions are produced using electron impact ionisation of precursor compounds and electron energies of a few tens of eV and source pressures in the 10\(^{-5}\) mbar regime are common. Subsequent reactions in the storage ion source may lead to the formation of secondary ions. A pulse of ions is then extracted from the source into a first quadrupole mass filter to select the ion mass of interest, A\(^+\). These ions are then guided into a 22-pole ion trap [32] where they collide with a bath of rare gas (rg, typically Ne or He) provided as an intense pulse at the beginning of the trapping cycle. Collisions with rg atoms inside the trap cool the ions both kinetically and internally. Provided the temperature is low, of order a few K, weakly bound clusters of ions and the rg will form by three-body collisions. Using a second mass filter stage connected to the exit of the 22-pole ion trap, the ions and their complexes can be mass filtered and detected using a very sensitive Daly type detector after a selected storage time. In the absence of any chemical reactions in the trap, the ion distribution exiting the trap includes the bare ion A\(^+\), with smaller amounts of weakly bound clusters of the ion with one or more rg atoms, A\(^+\)–rg\(_n\) [33,34]. In the infrared predissociation (IRPD) action spectroscopy scheme employed here, the number of singly tagged A\(^+\)–rg cluster ions is constantly monitored while the FELIX (FEL-2) IR radiation traversing the ion trap is tuned in wavenumber. When a vibrational mode of the cluster and the radiation source are coincident in wavenumber, dissociation of the cluster occurs, resulting in depletion in the A\(^+\)–rg counts at the detector. Since the weakly bound rare gases He or Ne generally only slightly perturb the structure of the ion, the IRPD spectrum is highly representative of the nascent ion. Using FELion in combination with FELIX, the IRPD approach has been used successfully in recent years to infer infrared spectra for many fundamental ions [31,35–37].

The results presented here were obtained during two independent observing campaigns, carried out at the FELIX laboratory in 2016 (HC\(_3\)O\(^+\)) and 2018 (HC\(_3\)S\(^+\)). Target ions were produced through electron impact ionisation of simple commercially available precursors. HC\(_3\)O\(^+\) was produced via dissociative ionisation of propargyl alcohol (H–C≡C–C\(_2\)H\(_2\)OH, Sigma-Aldrich) and HC\(_3\)S\(^+\) from ionisation and secondary reactions of a mixture of acetylene and CS\(_2\). Following mass selection in the first quadrupole stage, HC\(_3\)O\(^+\) (m/z = 53) or HC\(_3\)S\(^+\) (m/z = 69) were introduced into a cold 3:1 mixture of He:Ne in the ion trap which was maintained at a nominal temperature of about 8 K. Typical mass spectra obtained from acetylene/CS\(_2\)-mixtures are shown in Figure 1 (top, without storing in the ion trap). Per filling cycle of the ion trap, some 1000 Ne–HC\(_3\)O\(^+\) and 5000 Ne-HC\(_3\)S\(^+\) ions were obtained (Figure 1, bottom). Typical experimental conditions were: Trapping times of 2.5–3.5 s, and irradiation (per filling cycle) with 25–35 FELIX macropulses.
Figure 1. Mass spectra obtained from electron impact ionisation of an acetylene/CS$_2$ mixture. Top: Unbiased scan of source content: \( m/z = 76 \) is from the CS$_2^+$ ion, counts of \( m/z = 69 \) from HC$_3$S$^+$ are about 50% that of CS$_2^+$. \( m/z = 51 \) is most probably from a C$_4$H$_3^+$ ion. Bottom: Logarithmic plot of trap content extracted from the cold trap (8 K) after storing mass filtered HC$_3$S$^+$ (\( m/z = 69 \)) for 0.5 s in the presence of neon (some neighbouring masses are observed at low counts due to somewhat course mass selection conditions). In addition to the \( m/z = 69 \) peak at about 50,000 counts, some 5000 counts of the Ne-HC$_3$S$^+$ cluster are detected at \( m/z = 89 \). (10 Hz), typical pulse energies of a few up to a few tens of mJ and a Fourier-limited FWHM bandwidth of 0.5–1%. Action spectroscopy was then performed by tuning the wavenumber of the FELIX light source while monitoring counts of the corresponding Ne-complexes of both ions (Ne–HC$_3$O$^+$, \( m/z = 73 \); Ne–HC$_3$S$^+$, \( m/z = 89 \)). The depletion signal is power normalised prior to averaging over multiple individual scans.

To access the C–H stretching mode \( \nu_1 \) of HC$_3$O$^+$ in the 3 \( \mu \)m region, a table-top pulsed optical parametric oscillator/amplifier (OPO/OPA, Laser Vision) has been used in combination with the cryogenic 22-pole trapping instrument COLTRAP [38] in the Cologne laboratory. The OPO/OPA system is pumped with a pulsed 1064 nm Nd:YAG laser operating at a repetition rate of 10 Hz and maximum pulse energies of up to 600 mJ. This system has been operated in an unseeded mode with a linewidth of about 0.8 cm$^{-1}$ (seeded operation allows a linewidth of well below 0.1 cm$^{-1}$) and pulse energies of up to 20 mJ in the infrared range. The IR laser wavelength is calibrated with a wavemeter (HighFinesse model WS-5).

3. Quantum-chemical calculations

Several computational investigations of HC$_3$O$^+$ [23,39–41] at various levels of theory have been reported previously in the literature, while for structural parameters of HC$_3$S$^+$ only results at the Hartree-Fock level [21,42] are found. In the present work, consistently for all species under study, quantum-chemical calculations have been performed at the coupled-cluster singles and doubles (CCSD) level augmented by a perturbative treatment of triple excitations, CCSD(T) [29], together with correlation consistent (augmented) polarised valence and (augmented) polarised weighted core-valence basis sets, i.e. cc-pVXZ, [43] aug-cc-pVXZ [43–45], cc-pwCVXZ [43,46], and aug-cc-pwCVXZ [43–46] (with \( X = T, Q \)). For basis sets denoted as cc-pV(X+d)Z or aug-cc-pV(X+d)Z an additional tight \( d \) function [47] has been added to the sulfur atom only, while for all other elements cc-pVXZ or aug-cc-pVXZ have been used, respectively. Equilibrium geometries have been calculated using analytic gradient techniques [48], while harmonic frequencies have been computed using analytic second-derivative techniques [49,50]. For anharmonic computations second-order vibrational perturbation theory (VPT2) [51] has been employed and additional numerical differentiation of analytic second derivatives has been applied to obtain the third and fourth derivatives required for the application of VPT2 [50,52]. The frozen core approximation has been indicated throughout by ‘fc’.
Figure 2. Molecular structures of HC$_3$O$^+$ (left) and HC$_3$S$^+$ (right) calculated at the CCSD(T) level of theory using different correlation consistent basis sets. Please note that for the cc-pV(X+d)Z and aug-cc-pV(X+d)Z basis sets the frozen-core (fc) approximation was employed and that one tight $d$-function was added only to the sulfur atom. Bond lengths are given in units of Å.

All calculations have been carried out using the CFOUR program package [53]; for some of the calculations the parallel version of CFOUR [54] has been used.

Figure 3. Potential energy landscapes with respect to the position of the Ne atom in the two Ne-HC$_3$X$^+$ complexes calculated at the fc-CCSD(T)/aug-cc-pV(T+d)Z level of theory. Atom colour code: oxygen (red), sulfur (yellow), carbon (green), hydrogen (black). Contours cover the interval $[0.05, 0.30]$ kcal/mol in steps of 0.05 kcal/mol above the global minimum. In case of HC$_3$O$^+$ one additional contour is located at 0.615 kcal/mol to visualise the shallow minimum of the HC$_3$O$^+$–Ne arrangement. (a) Ne–HC$_3$O$^+$ surface and (b) Ne–HC$_3$S$^+$ surface.

4. Results and discussion

4.1. The structures of HC$_3$O$^+$ and HC$_3$S$^+$ and their weakly bound complexes with Ne

The equilibrium structures of HC$_3$O$^+$ and HC$_3$S$^+$ calculated at the CCSD(T) level of theory using different correlation consistent basis sets are summarised in Figure 2. The calculated bond lengths are slightly elongated for augmented basis sets relative to those calculated using the standard basis sets, while most bond lengths become shorter as the size of the basis set increases. Over the range of basis sets employed here, the structural parameters vary by at most $6 \times 10^{-3}$ Å, with the exception of the C–O and C–S distances, which vary by about $1.5 \times 10^{-2}$ Å.

As a compromise between accuracy and computational demand, the Ne-complexes of HC$_3$O$^+$ and HC$_3$S$^+$ were calculated at the fc-CCSD(T)/aug-cc-pV(T+d)Z level of theory. To determine the most energetically favourable locations of the Ne atom with respect to the HC$_3$O$^+$ and HC$_3$S$^+$ chains, i.e. to identify local minima on the Ne–HC$_3$O$^+$ and Ne–HC$_3$S$^+$ potential energy surfaces, the fc-CCSD(T)/aug-cc-pV(T+d)Z equilibrium structures in Figure 2 were kept fixed and the position of the Ne atom was varied on a $11 \times 7$ Å$^2$ grid using a spacing of 0.25 Å and distances ranging from some 1.5 to 3.5 Å about the HC$_3$O$^+$ and HC$_3$S$^+$ chains. For each of the some 500 grid points for both surfaces single-point energy calculations were performed, the results of which are graphically represented in Figure 3. This approach led to the identification of three minima for each complex: a linear structure Ne–HC$_3$X$^+$ ($X$ = O, S), which is the global minimum for both complexes (e.g. an arrangement similar to that of the Ne–HCO$^+$ cluster [55]), followed by non-linear (T-shaped) variants. A third, shallow minimum exists in which the Ne atom is located adjacent to the O and S atoms in a linear arrangement.

In a second approach, the structural optimizations of all minimum energy configurations were fully relaxed. As indicated in the structural parameters collected in Table 1, the perturbation of Ne on both HC$_3$O$^+$
and HC3S+ is small, with variations on the order of $10^{-3}$ Å. The Ne bond dissociation energies $D_e$ differ by at most 0.6 kcal mol$^{-1}$ in the minimum configurations identified, amounting to 1.0 kcal mol$^{-1}$, 0.9 kcal mol$^{-1}$, and 0.4 kcal mol$^{-1}$ for Ne–HC3O+ and 0.9 kcal mol$^{-1}$, 0.7 kcal mol$^{-1}$, and 0.6 kcal mol$^{-1}$ for Ne–HC3S+. When rough estimates of the zero-point vibrational effects on the Ne bond dissociation energies ($D_0$) are included, the linear Ne–HC3O+ and T-shaped forms are essentially isoe energetic, while the O-bound form is slightly less stable by about 0.4 kcal mol$^{-1}$. For HC3S+, the energy difference between the three structures is negligible.

4.2. The influence of Ne-tagging on the vibrational spectra of HC3O+ and HC3S+

As linear pentaatomic species, HC3O+ and HC3S+ both possess seven fundamental vibrational modes, four stretching ($\sigma$) and three doubly degenerate ($\pi$) bending modes. To further investigate the perturbation caused by a single Ne atom on their vibrational spectra, harmonic vibrational wavenumbers of HC3O+, HC3S+, and their corresponding complexes with Ne were calculated at the fc-CCSD(T)/aug-cc-pV(T+d)Z level of theory. As shown in Table 2, these values differ by a only few cm$^{-1}$. One notable exception is the C–C–H-bending mode $\omega_2$ of the Ne–HC3O+ and Ne–HC3S+ linear isomers. Here, Ne-tagging results in a 25–30 cm$^{-1}$ blueshift of the modes. Nevertheless, no large shifts are expected for any of the vibrational modes in HC3O+ and HC3S+ upon Ne-tagging.

4.3. Experimental spectra of Ne–HC3O+ and Ne–HC3S+

The IR results for HC3O+ and HC3S+ are summarised in the following section. It should again be emphasised that the present IRPD scheme traces the weakly bound complexes with Ne rather than the bare ions themselves, but, as demonstrated in the previous section, the perturbation of the Ne atom on the vibrational fundamentals of the ions is predicted very small, i.e. a few cm$^{-1}$ at most. The anharmonic vibrational force fields guiding spectroscopic assignment and analysis were calculated at the fc-CCSD(T)/cc-pVTZ (HC3O+) and fc-CCSD(T)/cc-pV(T+d)Z (HC3S+) levels. In an attempt to further improve the vibrational wavenumbers calculated for HC3O+, scaling factors derived from a comparison of the corresponding experimental and calculated values of isoelectronic HC3N were employed (Table 3). These empirical corrections, however, were found to be very small ($\leq 9$ cm$^{-1}$) and do not affect any spectroscopic assignment. They are given here nonetheless for the sake of completeness.

4.3.1. FELIX and OPO spectra of Ne–HC3O+

The FELIX IRPD spectra of Ne–HC3O+ are shown in Figure 4. For comparison, a simulation of the vibrational

### Table 1. Variation of bond distances of HC3O+ and HC3S+ with respect to Ne tagging as well as Ne bond dissociation energies $D_e$.

| Species    | R(CH) | R(CC) | R(CC) | R(CO/S) | $D_e$ | $D_0$ |
|------------|-------|-------|-------|---------|-------|-------|
| HC3O+      | 1.0757 | 1.2197 | 1.3462 | 1.1295  | 1.0   | 0.7   |
| Ne–HC3O+   | 1.0763 | 1.2195 | 1.3459 | 1.1297  | 1.0   | 0.7   |
| Ne–HC3O+ (nonlin.) | 1.0756 | 1.2195 | 1.3463 | 1.1294  | 0.9   | 0.7   |
| HC3O+−Ne (lin.) | 1.0757 | 1.2197 | 1.3463 | 1.1295  | 0.4   | 0.3   |
| HC3O+−Ne (nonlin.) | 1.0757 | 1.2197 | 1.3463 | 1.1295  | 0.4   | 0.3   |
| HC3S+      | 1.0732 | 1.2241 | 1.3427 | 1.5123  | –     | –     |
| Ne–HC3S+   | 1.0735 | 1.2243 | 1.3423 | 1.5125  | 0.9   | 0.6   |
| Ne–HC3S+ (nonlin.) | 1.0731 | 1.2240 | 1.3427 | 1.5122  | 0.7   | 0.6   |
| HC3S+−Ne   | 1.0732 | 1.2241 | 1.3429 | 1.5124  | 0.6   | 0.5   |

$D_e$ denotes the electronic contribution at the equilibrium geometry, while $D_0$ denotes $D_e$ augmented by a harmonic estimate of the zero-point vibrational contribution. All results have been obtained at the fc-CCSD(T)/aug-cc-pV(T+d)Z level of theory. Bond lengths given in units of Å, Ne bond dissociation energies in kcal mol$^{-1}$.

### Table 2. Harmonic frequencies (in cm$^{-1}$) of HC3O+, HC3S+, and the corresponding complexes with Ne evaluated at the fc-CCSD(T)/aug-cc-pV(T+d)Z level of theory.

| Mode | HC3O+ | Ne–HC3O+ | HC3O+−Ne | HC3S+ | Ne–HC3S+ | HC3S+−Ne |
|------|-------|----------|----------|-------|----------|----------|
| $\omega_1$ | 3351  | 3347  | 3352  | 3351  | 3370  | 3371  |
| $\omega_2$ | 2346  | 2345  | 2347  | 2346  | 2132  | 2134  |
| $\omega_3$ | 2094  | 2093  | 2095  | 2094  | 1634  | 1634  |
| $\omega_4$ | 916   | 918   | 916   | 916   | 730   | 731   |
| $\omega_5$ | 775   | 806   | 774/774| 774   | 733   | 758   |
| $\omega_6$ | 546   | 547   | 546/546| 547   | 472   | 473   |
| $\omega_7$ | 162   | 168   | 163/161| 162   | 176   | 183   |
| $\omega_8$ | 75    | 61    | 48    | –     | 67    | 48    |
| $\omega_9$ | 32    | 31    | 10    | –     | 29    | 22    |

$\omega_i$ Mode index borrowed from untagged HC3O+ and HC3S+ for the sake of comparability.

$\omega_i$ Double degenerate bending mode in linear species.

$\omega_i$ Degeneracy is lifted in the non-linear forms.

$\omega_i$ Extra low-frequency vibrational modes introduced in the Ne–HC3O+ and Ne–HC3S+ complexes, arbitrary mode index.
Table 3. Fundamental vibrational wavenumbers of HC$_3$N and HC$_3$O$^+$ (in cm$^{-1}$) and IR band intensities of HC$_3$O$^+$ (km/mol).

| Mode                  | Harm$^a$ | Anharm$^a$ | Exp$^b$ | Harm$^c$ | Anharm$^c$ | BE$^c$ | Exp$^d$ | Int$^e$ |
|-----------------------|----------|------------|---------|----------|------------|--------|---------|---------|
| $\nu_1(\sigma)$ C–H stretch | 3459     | 3325       | 3327    | 3362     | 3229       | 3231   | 3232    | 96      |
| $\nu_2(\sigma)$ C ≡ N/O stretch | 2312     | 2271       | 2274    | 2353     | 2313       | 2316   | 2313    | 782     |
| $\nu_3(\sigma)$ C ≡ C stretch | 2104     | 2069       | 2079    | 2097     | 2064       | 2074   | ...     | 104     |
| $\nu_4(\sigma)$ C–C stretch | 875      | 853        | 862     | 918      | 901        | 911    | 906     | 7       |
| $\nu_5(\pi)$ C–C–H bending | 498      | 486        | 498.8   | 552      | 547        | 558    | 558     | 54      |
| $\nu_6(\pi)$ C–C–O bending | 663      | 650        | 662.2   | 773      | 758        | 773    | 764     | 54      |
| $\nu_7(\pi)$ C–C–C bending | 227      | 217        | 222.4   | 181      | 166        | 169    | ...     | 6       |

$^a$fc-CCSD(T)/cc-pVTZ.
$^b$Experimental vibrational wavenumbers from Ref. [56].
$^c$Best estimate (BE) value: Anharmonic vibrational wavenumber of HC$_3$O$^+$ scaled by the ratio of Exp/Anharmonic wavenumbers of HC$_3$N.
$^d$This study, see Figure 4.
$^e$IR intensities obtained via VPT2.

Figure 4. The vibrational spectrum of Ne–HC$_3$O$^+$ as observed employing IRPD with FELIX between 500 and 2500 cm$^{-1}$ and an optical parametric oscillator around 3200 cm$^{-1}$ in the Cologne laboratory (top, black). Each peak in the experimental spectrum corresponds to a power-normalised relative depletion of the Ne–HC$_3$O$^+$ counts upon excitation of a vibrational transition. For comparison, the vibrational fundamentals from a VPT2 calculation of the bare ion performed at the fc-CCSD(T)/cc-pVTZ level of theory are shown as red sticks. For better visibility of the fundamentals in the stick simulation, the intensity of the $\nu_2$ mode has been multiplied by 1/4. At the predicted location of the $\nu_1$ mode, the experimental spectrum shows a doublet separated by about 17 cm$^{-1}$, see text.

fundamentals based on results of an anharmonic VPT2 calculation of bare HC$_3$O$^+$ at the fc-CCSD(T)/cc-pVTZ level is also presented. Wavenumbers of the experimental vibrational bands and those predicted theoretically are compared in Table 3. Experimentally, two regions were covered with FELIX: 530 to 1000 cm$^{-1}$ and 2060 to 2500 cm$^{-1}$. Four prominent features, all of which are in almost quantitative agreement with the calculated vibrational fundamentals of HC$_3$O$^+$, were observed in these two regions. The features are assigned as the $\nu_2$ fundamental (C–O stretch) at 2313 cm$^{-1}$ (best estimate value at 2316 cm$^{-1}$), $\nu_4$ (C–C stretch) at 906 cm$^{-1}$ (best estimate value 911 cm$^{-1}$), $\nu_5$ (C–C–H bending) at 764 cm$^{-1}$ (best estimate 773 cm$^{-1}$), and $\nu_6$ (C–C–O bending) at 555 cm$^{-1}$ (best estimate at 558 cm$^{-1}$). Unfortunately, the $\nu_3$ mode (C≡C stretch) predicted at 2074 cm$^{-1}$, was not detected. Presumably this band lies just outside the region accessible with FELIX during our observing run. As shown in Section 4.3.2, the corresponding mode of Ne–HC$_3$S$^+$ is rather prominent.

The $\nu_1$ mode around 3200 cm$^{-1}$ was detected in the Cologne laboratory using a commercial pulsed OPO system. Based on the empirically-scaled predictions from Table 3, our best estimate was 3231 cm$^{-1}$ for this mode, and indeed it was found very close by, at 3232 cm$^{-1}$. Scanning further up in energy revealed a second band of similar intensity at 3249 cm$^{-1}$. The origin of this second band is not entirely clear, since only one band is expected for the bare ion. Also, a combination of the $\nu_2$ and $\nu_4$ modes seems unlikely, which would be expected
a few tens of cm\(^{-1}\) below \(v_1\). The presence of a second Ne-tag-isomer cannot be confirmed conclusively (nor can it be ruled out with certainty) as the calculated \(v_1\) vibrational wavenumbers for any of the three Ne-HC\(_3\)O\(^+\) complexes (Table 2) differ significantly less than the observed splitting. Also, one might wonder why no ‘band-doubling’ is observed in case of the prominent \(v_5\) band at 764 cm\(^{-1}\) for which the theoretical estimates predict a more significant band separation between the linear and the T-shaped forms (Table 2). Combination modes involving the Ne atom also need to be considered further. Such vibrational ‘tag-satellites’ have been observed previously [37,57,58], albeit at much less intensity. Assuming that the complex being probed is the linear Ne-HC\(_3\)O\(^+\) form (global minimum), the Ne–H–C bending mode would be the energetically lowest vibrational fundamental. While anharmonic force field calculations of weakly-bound molecules employing VPT2 are intrinsically difficult, trial calculations performed here at the fc-CCSD(T)/aug-cc-pVTZ level predict this mode has a vibrational frequency of roughly 10 cm\(^{-1}\) in qualitative agreement with the band splitting observed. However, in summary, from the present sets of experimental and theoretical data, the spectroscopic peculiarity of \(v_1\) band-doubling cannot be resolved beyond speculation. Future measurements at high spectral resolution should help to resolve this issue and others in the IR spectrum of Ne–HC\(_3\)O\(^+\). For example, an analysis of the underlying rotational structure for the \(v_1\) mode would likely clarify the carrier of these spectroscopic features. Rotational resolution of the rather broad \(v_2\) mode observed with FELIX would also be key to understanding possible causes for its width, such as lifetime broadening or the more speculative explanation that it arises from tag-satellites from the Ne tag.

4.3.2. Ne–HC\(_3\)S\(^+\) observed with FELIX

The FELIX spectra of Ne–HC\(_3\)S\(^+\) are shown in Figure 5 along with a simulation of the vibrational fundamentals based on results from an anharmonic VPT2 calculation of the bare ion done at the fc-CCSD(T)/cc-pV(T+d)Z level. As the vibrational spectrum of isoelectronic HC\(_3\)P has not yet been studied experimentally, no empirical Table 4. Fundamental vibrational wavenumbers of HC\(_3\)S\(^+\) (in cm\(^{-1}\)) and IR band intensities (km/mol).

| Mode                  | Harm\(^a\) | Anharm\(^a\) | Exp\(^b\) | Int\(^c\) |
|-----------------------|------------|--------------|-----------|-----------|
| \(v_1(\sigma)\) C–H stretch | 3381       | 3247         | ...       | 111       |
| \(v_2(\sigma)\) C \equiv C stretch | 2137       | 2093         | 2097      | 730       |
| \(v_3(\sigma)\) C–S stretch | 1636       | 1613         | 1624      | 168       |
| \(v_4(\sigma)\) C–C stretch | 729        | 719          | 731       | 0.1       |
| \(v_5(\pi)\) C–C–H bending | 738        | 715          | 731       | 50        |
| \(v_6(\pi)\) C–C–S bending | 485        | 466          | 481       | 1         |
| \(v_7(\pi)\) C–C–C bending | 185        | 175          | ...       | 18        |

\(^a\)fc-CCSD(T)/cc-pV(T+d)Z.

\(^b\)This study, see Figure 5.

\(^c\)IR intensities obtained via VPT2.

Figure 5. The vibrational spectrum of Ne–HC\(_3\)S\(^+\) as observed with FELIX between 460 and 2500 cm\(^{-1}\) (top, black). Each peak in the experimental spectrum corresponds to a power-normalised relative depletion of the Ne–HC\(_3\)S\(^+\) counts upon excitation of a vibrational transition. For comparison, the vibrational fundamentals from a VPT2 calculation of the bare ion performed at the fc-CCSD(T)/cc-pV(T+d)Z level of theory are shown as red sticks. For better visibility of the fundamentals in the simulation, the intensity of the \(v_2\) band has been multiplied by 1/4. The calculated intensity of the \(v_6\) mode was multiplied by a factor of 20 to be visible in the stick spectrum. The weakest feature in the experimental spectrum at 1446 cm\(^{-1}\) is not from a vibrational fundamental but most likely from an overtone, the \(2v_5\) mode, see text.
scaling was possible. Experimentally, three regions were covered with FELIX: 460–540 cm\(^{-1}\), 600–1800 cm\(^{-1}\), as well as 2010–2490 cm\(^{-1}\). In total, four prominent features are observed; the frequencies of each agree very well with vibrational fundamentals calculated for HC\(_3\)S\(^+\): \(v_2\) observed at 2097 cm\(^{-1}\) (calculated at 2093 cm\(^{-1}\); see Table 4), \(v_3\) at 1624 cm\(^{-1}\) (calculated at 1613 cm\(^{-1}\)), \(v_4\) and \(v_5\) most likely overlapped to one feature observed at 731 cm\(^{-1}\) (calculated at 719 and 715 cm\(^{-1}\), respectively), and finally the \(v_6\) mode at 481 cm\(^{-1}\) (calculated at 466 cm\(^{-1}\)). The C–H stretching (\(v_1\)) and C–C–C (\(v_7\)) bending modes calculated at 3247 cm\(^{-1}\) and 175 cm\(^{-1}\) lie outside our our measurement range, and were not observed experimentally here. The weakest feature in the Ne–HC\(_3\)S\(^+\) spectrum is observed at 1446 cm\(^{-1}\). This feature is not from a vibrational fundamental, however, it is located close to two times the wavenumber of the \(v_4/v_5\) fundamental feature observed at 731 cm\(^{-1}\) and hence very likely corresponds to an overtone/combination mode. While the intensities observed in action spectra are not strictly related to spectroscopic band intensities, they are often found to be in qualitative agreement. From this viewpoint, it can be assumed that both the 731 cm\(^{-1}\) and 1446 cm\(^{-1}\) features are dominated by the contribution from the \(v_5\) mode whose IR intensity in the bare ion is calculated to be 500 times higher than that of \(v_4\) (Table 4).

### 5. Conclusions and prospects

The present study marks the first spectroscopic detection of two molecular ions of potential astronomical relevance, HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\). The detections were made possible by using very sensitive IR action spectroscopic methods in combination with ion traps, an approach that can likely be adapted to study similar and even (much) more complex species at high spectral resolution. Owing to mass selection prior to spectroscopic interrogation in the ion trap, the resulting spectra are free from contamination and can be readily assigned using high-level quantum-chemical calculations of the bare ion since coupling of the Ne tag to the ion is very weak.

While the molecular carriers of the vibrational features studied here, HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\), have been established beyond any reasonable doubt, the present measurements lack the rotational information that is required for more detailed spectroscopic analysis or to undertake a radio astronomical search. Nevertheless, the present work provides a firm foundation for subsequent analysis in this and other wavelength regions. For example, now that the positions of several vibrational bands of HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\) are known, the use of narrow-linewidth continuous-wave IR sources such as quantum cascade lasers or optical parametric oscillators may permit the observation of selected bands at very high spectral resolution. Recent examples of such studies in the Cologne laboratory include CH\(^+\) and CD\(_2\)H\(^+\) using laser induced reaction (LIR) or laser induced inhibition of complex growth (LIICG) schemes [59,60], which provide spectroscopic information on the bare ions. Analogous higher-resolution studies of the Ne-ion complexes described here would allow to determine their precise geometrical structure and resolve the issue surrounding the assignment of the peculiar second band observed in the vicinity of the \(v_1\) band of HC\(_3\)O\(^+\).

In addition to studies in the infrared, rotational spectra may be observed directly using the method of rotational state-specific attachment of rare gas atoms (ROSA) to cations at very low temperatures [61], a method that has been used recently with excellent success to obtain the pure rotational spectra of fundamental ions (see, e.g. [62–64]). The rotational spectra of two species isoelectronic with HC\(_3\)O\(^+\) and HC\(_3\)S\(^+\) – HC\(_3\)N and HC\(_3\)P – have been studied at high resolution (see Refs. [65,66], and references therein), and therefore can be used to calibrate the computational results of the two ions obtained here (Table 5). For HC\(_3\)N, the ground state rotational constant \(B_0\) obtained by combining Be computed at the CCSD(T)/cc-pwCVQZ level and \(\Delta B_0\) determined via a fc-CCSD(T)/cc-pVTZ VPT2 computation is 4542.7 MHz and hence deviates by only 0.14%

### Table 5. Rotational parameters of HC\(_3\)N, HC\(_3\)O\(^+\), HC\(_3\)P and HC\(_3\)S\(^+\) (in MHz).

| Parameter | HC\(_3\)N | HC\(_3\)O\(^+\) | HC\(_3\)P | HC\(_3\)S\(^+\) |
|-----------|-----------|---------------|-----------|---------------|
| \(B_0\)   | 4544.861  | 4533.556      | 2656.610  | 2734.566      |
| \(\Delta B_0\) | 2.205   | 0.609         | 1.655     | 1.466         |
| \(B_0\)   | 4542.656  | 4544.165      | 2654.935  | 2733.100      |
| \(D \times 10^3\) | 0.505   | 0.437         | 0.169     | 0.163         |

\(^{a}\) This study; \(B_0\) calculated at the CCSD(T)/cc-pwCVQZ level and \(\Delta B_0\) and \(D\) from the fc-CCSD(T)/cc-pVTZ and fc-CCSD(T)/cc-pwCVQZ force fields, respectively.

\(^{b}\) Ref. [65].

\(^{c}\) Scaled by the ratio \(X_{\text{exp}}/X_{\text{calc}}\) of the corresponding parameter of the isoelectronic neutral species.

\(^{d}\) Ref. [66].
from the experimental value of 4549.059 MHz. Using the ratio $B_{\text{exp}}/B_{\text{calc}}$ of HC$_3$N for scaling $B_0 = 4454.2$ MHz of HC$_3$O$^+$ calculated at the same levels of theory yields a best estimate value of 4460.4 MHz (for Michael C. McCarthy and Oskar Asvany). For HC$_3$P, this treatment yields $B_{0, \text{calc}} = 2655.0$ MHz and $B_{0, \text{exp}} = 2656.393$ MHz (0.05%). Applying the ratio $B_{\text{exp}}/B_{\text{calc}}$ (HC$_3$P) to the calculated $B_0 = 2733.1$ MHz constant of HC$_3$S$^+$, a best estimate value of $B_0 = 2734.5$ MHz is obtained. The uncertainties of these best estimates may well be within 1 MHz, more than adequate for experimental searches by microwave techniques. Both ions are calculated to be very polar, with (center-of-mass frame) dipole moments $\mu_e$ of 3.26 D for HC$_3$O$^+$ and 1.73 D for HC$_3$S$^+$ computed at the CCSD(T)/aug-cc-pwCVQZ level of theory.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Sven Thorwirth http://orcid.org/0000-0001-8200-6710
Michael E. Harding http://orcid.org/0000-0002-3633-493X
Oskar Asvany http://orcid.org/0000-0003-2995-0803
Sandra Brinken http://orcid.org/0000-0001-7175-4828
Kin Long Kelvin Lee http://orcid.org/0000-0002-1903-9242
Thomas Salomon http://orcid.org/0000-0003-4068-7444
Michael C. McCarthy http://orcid.org/0000-0001-9142-0008
Stephan Schlemmer http://orcid.org/0000-0002-1421-7281

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Appendix

Internal coordinates for the Ne-complexes of HC$_3$O$^+$ (calculated at the fc-CCSD(T)/aug-cc-pVTZ level) and HC$_3$S$^+$ (fc-CCSD(T)/aug-cc-pVTZ) from fully relaxed structural calculations. Bond lengths are given in Å, angles in degrees.

A.1 Ne–HC$_3$O$^+$, fc-CCSD(T)/aug-cc-pVTZ

A.1.1 Ne–HC$_3$O$^+$, linear form

\[
\begin{align*}
\text{C} & \quad 1 \quad r_1 \\
& \times 2 \quad rd \quad 1 \quad a_90 \\
\text{C} & \quad 2 \quad r_2 \quad 3 \quad a_90 \quad 1 \quad d_{180} \\
& \times 4 \quad rd \quad 2 \quad a_90 \quad 3 \quad d_0 \\
\text{C} & \quad 4 \quad r_4 \quad 5 \quad a_90 \quad 2 \quad d_{180} \\
& \times 6 \quad rd \quad 4 \quad a_90 \quad 5 \quad d_0 \\
\text{H} & \quad 6 \quad r_6 \quad 7 \quad a_90 \quad 4 \quad d_{180} \\
& \times 8 \quad rd \quad 6 \quad a_90 \quad 7 \quad d_0 \\
\text{NE} & \quad 8 \quad r_8 \quad 9 \quad a_90 \quad 6 \quad d_{180} \\
r_1 & = 1.129675503855228 \\
rd & = 1.0000000409314806 \\
a_90 & = 90.00000000000000 \\
r_2 & = 1.345852682859310 \\
d_{180} & = 180.00000000000000000000 \\
d_0 & = 0.00000000000000000000 \\
r_3 & = 1.219943167034099 \\
r_4 & = 1.076271649098733 \\
r_5 & = 2.191966102105850
\end{align*}
\]
A.1.2 \( \text{HC}_3\text{O}^+\text{-Ne, non-linear (T-) form} \)

\[
\begin{align*}
\text{H} & \\
C & 1 \ r1 \\
X & 2 \ \text{rd} \ 1 \ a90 \\
C & 2 \ \text{rd} \ 2 \ a90 \ 3 \ d0 \\
C & 4 \ \text{rd} \ 4 \ a90 \ 5 \ d0 \\
X & 6 \ \text{rd} \ 6 \ a90 \ 7 \ d0 \\
\text{NE} & 8 \ \text{rd} \ 9 \ a90 \ 6 \ \text{d180} \\
\text{r1} & = 1.075618393685392 \\
\text{rd} & = 1.0000002251233508 \\
a90 & = 90.000000000000000 \\
r2 & = 1.219547134225782 \\
a1 & = 89.987605394672087 \\
d180 & = 180.000000000000000 \\
d0 & = 0.000000000000000 \\
r3 & = 1.34636497375038 \\
a2 & = 90.223210508956072 \\
r4 & = 1.129411452271238 \\
a3 & = 90.218170030502677 \\
r5 & = 3.167121007415886 \\
a4 & = 69.294364994274972 \\
\end{align*}
\]

A.1.3 \( \text{HC}_3\text{O}^+\text{-Ne, linear form} \)

\[
\begin{align*}
\text{O} & \\
C & 1 \ r1 \\
X & 2 \ \text{rd} \ 1 \ a90 \\
C & 2 \ \text{rd} \ 2 \ a90 \ 3 \ d0 \\
C & 4 \ \text{rd} \ 4 \ a90 \ 5 \ d0 \\
H & 6 \ \text{rd} \ 6 \ a90 \ 7 \ d0 \\
\text{NE} & 1 \ \text{rd} \ 9 \ a90 \ 2 \ \text{d180} \\
\text{r1} & = 1.129522777467840 \\
\text{rd} & = 1.000000613972272 \\
a90 & = 90.000000000000000 \\
r2 & = 1.346337295083560 \\
d180 & = 180.000000000000000 \\
d0 & = 0.000000000000000 \\
r3 & = 1.219669287299509 \\
a2 & = 90.223210508956072 \\
r4 & = 1.129411452271238 \\
a3 & = 90.218170030502677 \\
r5 & = 3.167121007415886 \\
a4 & = 69.294364994274972 \\
\end{align*}
\]

A.2 \( \text{Ne-\text{HC}_3\text{S}^+}, \text{fc-CCSD(T)/aug-cc-pV(T+d)Z} \)

A.2.1 \( \text{Ne-\text{HC}_3\text{S}^+}, \text{linear form} \)

\[
\begin{align*}
\text{S} & \\
C & 1 \ r1 \\
X & 2 \ \text{rd} \ 1 \ a90 \\
C & 2 \ \text{rd} \ 2 \ a90 \ 3 \ d0 \\
C & 4 \ \text{rd} \ 4 \ a90 \ 5 \ d0 \\
H & 6 \ \text{rd} \ 6 \ a90 \ 7 \ d0 \\
\text{NE} & 1 \ \text{rd} \ 9 \ a90 \ 2 \ \text{d180} \\
\text{r1} & = 1.508396620643273 \\
\text{rd} & = 1.000000000000000 \\
a90 & = 90.000000000000000 \\
r2 & = 1.342701023969591 \\
d180 & = 180.000000000000000 \\
d0 & = 0.000000000000000 \\
r3 & = 1.224200791251630 \\
r4 & = 1.073475625100924 \\
r5 & = 2.24187954940575 \\
\end{align*}
\]