

Article

Gas-Phase Infrared Action Spectroscopy of CH_2Cl^+ and CH_3ClH^+ : Likely Protagonists in Chlorine Astrochemistry

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Abstract: Two fundamental halocarbon ions, CH_2Cl^+ and CH_3ClH^+ , were studied in the gas phase using the FELion 22-pole ion trap apparatus and the Free Electron Laser for Infrared eXperiments (FELIX) at Radboud University, Nijmegen (the Netherlands). The vibrational bands of a total of four isotopologs, $\text{CH}_2^{35,37}\text{Cl}^+$ and $\text{CH}_3^{35,37}\text{ClH}^+$, were observed in selected wavenumber regions between 500 and 2900 cm^{-1} and then spectroscopically assigned based on the results of anharmonic force field calculations performed at the CCSD(T) level of theory. As the infrared photodissociation spectroscopy scheme employed probes singly Ne-tagged weakly bound complexes, complementary quantum-chemical calculations of selected species were also performed. The impact of tagging on the vibrational spectra of CH_2Cl^+ and CH_3ClH^+ is found to be virtually negligible for most bands; for $\text{CH}_3\text{ClH}^+\text{-Ne}$, the observations suggest a proton-bound structural arrangement. The experimental band positions as well as the best estimate rotational molecular parameters given in this work provide a solid basis for future spectroscopic studies at high spectral resolutions.

Keywords: chlorine chemistry; astrochemistry; vibrational spectroscopy; ion trap; action spectroscopy



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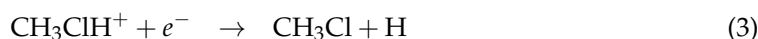
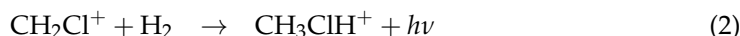
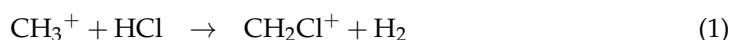


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1. Introduction

Out of the more than 300 inter- and circumstellar molecules detected to date, more than 25% contain heavy elements from the second row of the periodic table. With nearly fifty species, molecules containing silicon and sulfur are particularly abundant (an up-to-date list of astronomically detected molecules with complementary information is maintained at the Cologne Database for Molecular Spectroscopy (CDMS) [1,2] accessible online at <https://cdms.astro.uni-koeln.de/> (accessed on 12 December 2023)).

In contrast, the number of chlorine-bearing molecules is much smaller. Only seven such species have been observed so far: HCl [3]; AlCl, NaCl, and KCl [4]; HCl^+ [5]; H_2Cl^+ [6]; and CH_3Cl [7]. The latter, pentatomic methyl chloride, or CH_3Cl , is the most complex chlorine-bearing species presently known in space and, thus, an interesting target for studies of chlorine astrochemistry. In this context, it is assumed that CH_3Cl may be formed through reactions on grain surfaces but also possibly in the gas phase through ion–molecule reactions, for example, in a scenario suggested by Garrod (cf., Ref. [8]).



Here, in the first step, the chloromethyl ion CH_2Cl^+ is formed from a reaction of the methyl cation CH_3^+ and HCl; in the second, the halonium ion CH_3ClH^+ is produced via

radiative association between CH_2Cl^+ and molecular hydrogen, finally yielding CH_3Cl through dissociate recombination with a free electron.

While the CH_3^+ , HCl , H_2 , and CH_3Cl species are all known to be present in astronomical environments (the non-polar CH_3^+ molecular ion being detected only very recently through observations with the James Webb Space Telescope [9]), our knowledge of the CH_2Cl^+ and CH_3ClH^+ molecular ions also participating in the above chain of reactions is still highly fragmentary. From the viewpoint of laboratory experiments, only little spectroscopic information has been collected previously for the chloromethyl cation. Photoelectron spectroscopy of the CH_2Cl radical has provided a vibrational wavenumber $\nu = 1040(30) \text{ cm}^{-1}$ of the Cl–C-stretching mode of CH_2Cl^+ [10,11]. A somewhat more comprehensive picture of the vibrational spectrum has been obtained through infrared spectroscopy of CH_2Cl^+ trapped in solid Ar matrices [12]. In these studies, four out of the six vibrational fundamentals were observed for the most abundant isotopic species, $\text{CH}_2^{35}\text{Cl}^+$. Using precursors enriched in ^{13}C or deuterium permitted the observation of four vibrational fundamentals of $^{13}\text{CH}_2^{35}\text{Cl}^+$ or five of $\text{CD}_2^{35}\text{Cl}^+$, respectively. Owing to a significant isotopic shift, the C– ^{37}Cl stretching mode could also be observed for all three isotopic species. Direct infrared spectroscopic studies of CH_2Cl^+ in the gas phase have not been reported yet. Hexatomic protonated methyl chloride, CH_3ClH^+ , has been known from mass spectrometry and studies of reaction kinetics [13,14]; however, it has never been spectroscopically studied.

In the present work, the vibrational spectra of the ^{35}Cl and ^{37}Cl isotopic species of CH_2Cl^+ and CH_3ClH^+ were observed in the gas phase, marking the first direct gas-phase infrared study of CH_2Cl^+ and the first ever spectroscopic detection of CH_3ClH^+ . The characterization of both ions was accomplished in an ion trap using a messenger action spectroscopy scheme, i.e., employing infrared photodissociation (IRPD) of their weakly bound complexes with neon, $\text{CH}_2\text{Cl}^+\text{-Ne}$, and $\text{CH}_3\text{ClH}^+\text{-Ne}$. Spectroscopic analysis was supported based on complementary high-level quantum-chemical calculations performed at the CCSD(T) level of theory. A detailed account of the experimental and theoretical work as well as of the analysis will be given in the following.

2. Results and Discussion

2.1. Structures of CH_2Cl^+ , CH_3ClH^+ , and Their Weakly Bound Complexes with Ne

Equilibrium molecular structures of CH_2Cl^+ and CH_3ClH^+ (and their isoelectronic sulfur-bearing counterparts, cf. Section 4) were calculated at the CCSD(T) level of theory using different basis sets. Full sets of internal coordinates are given in Appendices A and B. Best-estimate equilibrium structures were calculated using the cc-pwCVQZ basis set and all electrons in the correlation treatment, providing a level of theory previously shown to be of high accuracy [15]. The fc-CCSD(T)/cc-pV(T + d)Z level was employed for the calculation of harmonic and anharmonic force fields of the bare ions and used for the interpretation of their vibrational spectra. The impact of Ne-tagging on the molecular structures and harmonic force fields was estimated at the fc-CCSD(T)/aug-cc-pV(T + d)Z level of theory. To determine the energetically favorable locations of the Ne atom with respect to the CH_2Cl^+ and CH_3ClH^+ ions, potential energy surfaces (PESs) were calculated using grids of appropriate size and sampling (see also Ref. [16]). Briefly, in these calculations, the fc-CCSD(T)/aug-cc-pV(T + d)Z equilibrium structures of CH_2Cl^+ and CH_3ClH^+ were kept fixed while varying the position of the Ne atom on the grid over an area of a few tens of $\text{\AA}^2$ and at a spacing of 0.25 $\text{\AA}$. At each of the grid points, single-point energy calculations were performed. PESs were calculated for the two mirror planes of CH_2Cl^+ and for the single mirror plane of CH_3ClH^+ . The resulting potential energy maps of CH_2Cl^+ are shown in Figure 1.

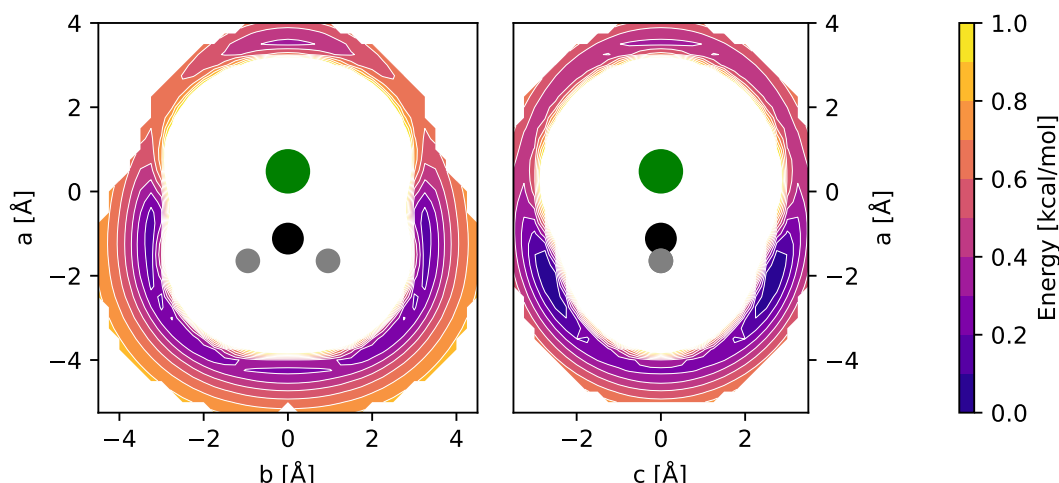


Figure 1. $\text{fc-CCSD(T)}/\text{aug-cc-pV(T} + d\text{)Z}$ potential energy maps of the $\text{CH}_2\text{Cl}^+\text{-Ne}$ weakly bound complex calculated in the two mirror planes of CH_2Cl^+ (see text for details). Atom color code: hydrogen (gray), carbon (black), chlorine (green). Contours show the potential energy of the complex as a function of the Ne atom position relative to the ion and cover the interval $[0.1, 1.0]$ kcal/mol in steps of 0.1 kcal/mol above the global minimum.

Out of the four unique local minima seen, the shallow ones corresponding to linear C-Cl-Ne and Cl-C-Ne cluster variants were not considered further. The global minimum arrangements of each plot, i.e., one H-bound in-plane variant ($\text{CH}_2\text{Cl}^+\text{ Ne-ip}$, Figure 1, left map) and the out-of-plane variant ($\text{CH}_2\text{Cl}^+\text{ Ne-oop}$, right), were finally structurally refined in fully relaxed calculations. The corresponding structures are shown in Figure 2, and the full sets of structural parameters are given in Appendix A. As can be seen, the molecular structure of CH_2Cl^+ hardly changes upon Ne-tagging at either position, and as a consequence, also the harmonic vibrational wavenumbers of CH_2Cl^+ collected in Table 1 show very little dependence on tagging. The Ne-ip and Ne-oop species are calculated to be almost isoenergetic, with the latter configuration being slightly more stable by about 0.1 kcal/mol. Ne bond dissociation energies under the consideration of an estimate of zero-point vibrational effects amount to 0.6 kcal/mol (Ne-ip) and 0.7 kcal/mol (Ne-oop), respectively.

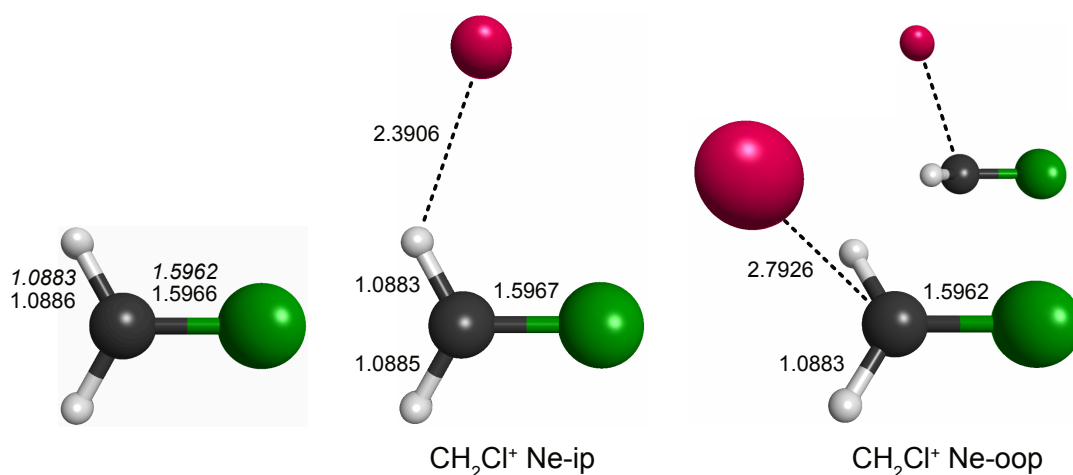


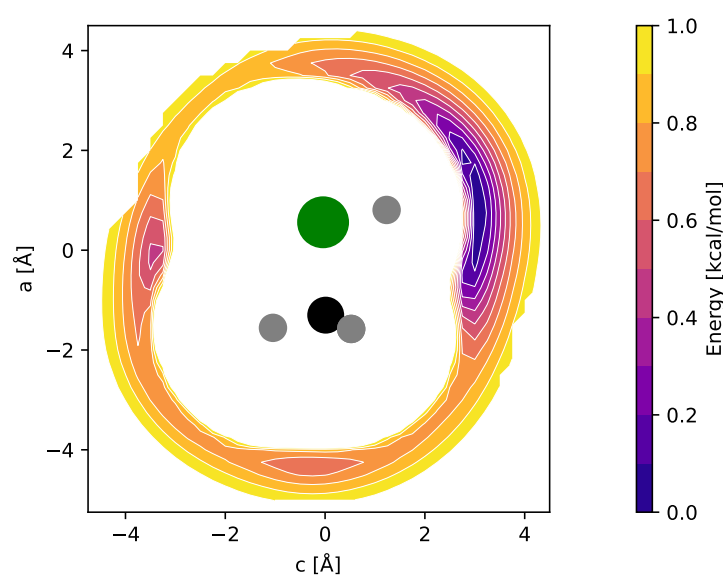
Figure 2. Bond lengths of CH_2Cl^+ and its complexes with neon (in Å; $\text{fc-CCSD(T)}/\text{aug-cc-pV(T} + d\text{)Z}$ values of all three species given in regular font and $\text{fc-CCSD(T)}/\text{cc-pV(T} + d\text{)Z}$ values of the bare species given in italics). Bare CH_2Cl^+ is of C_{2v} symmetry, whereas the symmetry of the Ne-complexes is lowered to C_s . Full sets of structural parameters are given in Appendix A. For further details, see text.

Table 1. Harmonic vibrational wavenumbers of $\text{CH}_2^{35}\text{Cl}^+$ and $\text{CH}_2^{35}\text{Cl}^+-\text{Ne}$ calculated at the CCSD(T)/aug-cc-pV(T + d)Z level of theory (in cm^{-1})¹.

Mode	Bare Ion	Ne-ip	Ne-oop
ω_1 CH sym stretching	3102 (a_1 , 18)	3106 (a' , 17)	3105 (a' , 16)
ω_2 CH ₂ scissoring	1478 (a_1 , 0.3)	1476 (a' , 1)	1478 (a' , 0.2)
ω_3 Cl–C stretching	1059 (a_1 , 80)	1059 (a' , 78)	1058 (a' , 82)
ω_4 oop bending	1137 (b_1 , 22)	1138 (a'' , 21)	1136 (a' , 20)
ω_5 CH asym stretching	3239 (b_2 , 51)	3243 (a' , 59)	3243 (a'' , 50)
ω_6 CH ₂ wagging	1047 (b_2 , 0.02)	1048 (a' , 0.3)	1047 (a'' , 0.003)
ω_7 ^{2,3}	...	93 (a' , 21)	131 (a'' , 1)
ω_8 ^{2,4}	...	70 (a'' , 0.2)	89 (a' , 22)
ω_9 ^{2,5}	...	25 (a' , 1)	34 (a' , 4)

¹ Mode symmetries and infrared band intensities (km/mol) are given in parentheses. Mode indices of the Ne-tagged variants are borrowed from bare CH_2Cl^+ for the sake of comparability. ² Extra-low-frequency vibrational modes introduced through Ne-tag, arbitrary mode index. ³ H–Ne stretching (Ne-ip species) and CH₂ twisting (Ne-oop species). ⁴ C–H–Ne stretching oop bending (Ne-ip species) and C–Ne stretching (Ne-oop species). ⁵ C–H–Ne ip bending (Ne-ip species) and Cl–C–Ne bending (Ne-oop species).

For CH_3ClH^+ , by analogy with other rare gas-tagged protonated species, one would expect the Ne atom to be bound to the proton in a near-linear Cl–H...Ne fashion (e.g., Refs. [17–19]). Indeed, from the potential energy map obtained for the molecular mirror plane (Figure 3), this arrangement is identified as a deep, putatively global minimum. Another minimum is identified on the opposite side of the molecule and a third shallow one where Ne is arranged in a near-linear Cl–C–Ne fashion. Fully relaxed structures of the first two configurations (“p-bound” and “CH₃/Cl-bound”) are shown in Figure 4. According to those calculations, the p-bound variant is more stable by 0.4 kcal/mol. The third minimum as well as potential arrangements where the Ne atom would be located outside of the symmetry plane of CH_3ClH^+ have not been studied further. The results of harmonic force field calculations to study the influence of Ne-tagging are presented in Table 2. As can be seen, the influence of tagging is virtually negligible for the majority, but not all, of the vibrational fundamentals (see further discussion in Section 2.3). Under the consideration of zero-point vibrational effects, the Ne bond dissociation energies are 1.0 kcal/mol and 0.7 kcal/mol for the p-bound and CH₃/Cl-bound species, respectively.

**Figure 3.** fc-CCSD(T)/aug-cc-pV(T + d)Z potential energy map of the $\text{CH}_3\text{ClH}^+-\text{Ne}$ weakly bound complex calculated in the mirror plane of CH_3ClH^+ (see text for details). Atom color code: hydrogen (gray), carbon (black), chlorine (green). Contours show the potential energy of the complex as a function

of the Ne atom position relative to the ion and cover the interval [0.1, 1.0] kcal/mol in steps of 0.1 kcal/mol above the global minimum.

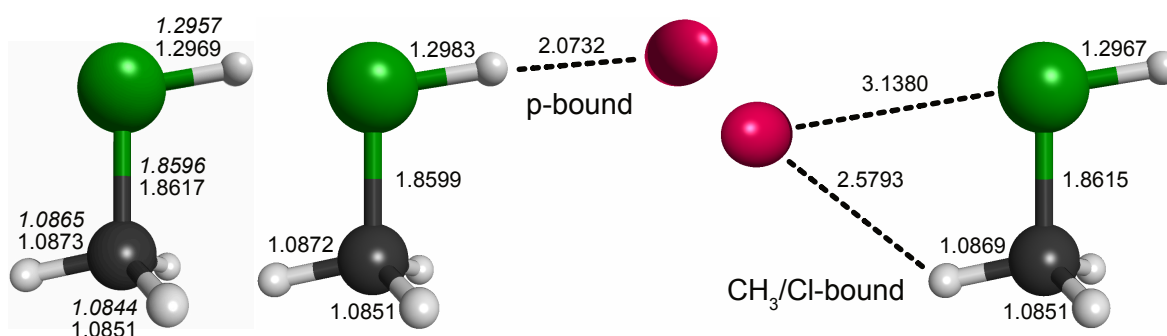


Figure 4. Bond lengths of CH_3ClH^+ and the p-bound and CH_3 -bound complexes with neon (in Å; fc-CCSD(T)/aug-cc-pV(T + d)Z values of all three species given in regular font and fc-CCSD(T)/cc-pV(T + d)Z values of the bare species given in italics). All species exhibit C_s symmetry. Full sets of structural parameters are given in Appendix A. For further details, see text.

Table 2. Harmonic vibrational wavenumbers of $\text{CH}_3^{35}\text{ClH}^+$ and two $\text{CH}_3^{35}\text{ClH}^+ - \text{Ne}$ variants calculated at the CCSD(T)/aug-cc-pV(T + d)Z level of theory (in cm^{-1})¹.

Mode	Bare Ion	p-bound	CH_3/Cl -bound
ω_1 C–H asym stretching	3220 (<i>a'</i> , 18)	3220 (<i>a'</i> , 17)	3224 (<i>a'</i> , 20)
ω_2 C–H sym stretching	3087 (<i>a'</i> , 5)	3087 (<i>a'</i> , 5)	3089 (<i>a'</i> , 5)
ω_3 Cl–H stretching	2823 (<i>a'</i> , 176)	2811 (<i>a'</i> , 307)	2824 (<i>a'</i> , 174)
ω_4 CH_3 asym bending	1472 (<i>a'</i> , 14)	1472 (<i>a'</i> , 14)	1471 (<i>a'</i> , 13)
ω_5 CH_3 umbrella	1386 (<i>a'</i> , 11)	1386 (<i>a'</i> , 11)	1385 (<i>a'</i> , 10)
ω_6 CH_3 ip rocking	1118 (<i>a'</i> , 3)	1120 (<i>a'</i> , 3)	1118 (<i>a'</i> , 3)
ω_7 C–Cl–H bending	771 (<i>a'</i> , 13)	784 (<i>a'</i> , 11)	773 (<i>a'</i> , 14)
ω_8 Cl–C stretching	565 (<i>a'</i> , 51)	570 (<i>a'</i> , 50)	566 (<i>a'</i> , 50)
ω_9 C–H asym stretching	3238 (<i>a''</i> , 15)	3237 (<i>a''</i> , 15)	3238 (<i>a''</i> , 15)
ω_{10} CH_3 asym bending	1468 (<i>a''</i> , 14)	1469 (<i>a''</i> , 14)	1470 (<i>a''</i> , 12)
ω_{11} CH_3 oop rocking	1040 (<i>a''</i> , 0.5)	1040 (<i>a''</i> , 0.5)	1040 (<i>a''</i> , 0.4)
ω_{12} torsion	202 (<i>a''</i> , 39)	244 (<i>a''</i> , 43)	211 (<i>a''</i> , 42)
$\omega_{13}^{2,3}$	...	90 (<i>a'</i> , 7)	69 (<i>a'</i> , 8)
$\omega_{14}^{2,4}$	...	72 (<i>a''</i> , 7)	46 (<i>a'</i> , 0.4)
$\omega_{15}^{2,5}$	...	20 (<i>a'</i> , 7)	40 (<i>a''</i> , 10)

¹ Mode symmetries and infrared band intensities (km/mol) are given in parentheses. ² Extra-low-frequency vibrational modes introduced through Ne-tag, arbitrary mode index. ³ H–Ne stretching. ⁴ Ne–H–Cl oop bending (p-bound species) and Ne–H–Cl ip bending (CH_3/Cl -bound species). ⁵ Ne–H–Cl ip bending (p-bound species) and Ne–H–Cl oop bending (CH_3/Cl -bound species).

2.2. IRPD Spectrum of $\text{CH}_2^{35}\text{Cl}^+ - \text{Ne}$

The $m/z = 69$ filtered IRPD spectrum from 900 to 1600 cm^{-1} is shown in Figure 5 (top red trace). From Table 3, it can be seen that four fundamental modes of the $\text{CH}_2^{35}\text{Cl}^+$ species are calculated in this wavenumber range: the ν_6 mode at 1038 cm^{-1} , ν_3 at 1046 cm^{-1} , ν_4 at 1134 cm^{-1} , and ν_2 at 1451 cm^{-1} , only two of which have sizable calculated infrared intensities: ν_3 (Cl–C stretching) and ν_4 (out-of-plane (oop) bending). While infrared intensities are not strictly related to the intensities in the action spectroscopy scheme employed here, usually good qualitative agreement is observed. Clearly, ν_3 and ν_4 are detected at 1048 cm^{-1} and 1129 cm^{-1} , respectively, which is in very good agreement with the anharmonic CCSD(T)/cc-pV(T + d)Z values (1046 and 1134 cm^{-1} , as shown in Table 3) and also show proper intensity behavior. Both ν_3 and ν_4 show weak satellite band progressions with approximate spacings of 20 cm^{-1} to their blue sides (see inset in Figure 5), which is thought to originate from combination modes with the participation of the Ne-tag (most likely involving the ω_9 fundamental (Table 1); see,

e.g., Refs. [20,21]). The CH_2 scissoring mode ν_2 is calculated to be very weak and would be located in a region affected by somewhat higher noise and some baseline instabilities. The CH_2 wagging mode ν_6 is calculated to have almost no infrared intensity and is either too weak to be detected or overlapped with the much stronger ν_3 band. Apart from that, no other clear spectroscopic feature is observed. As concluded from harmonic $\text{fc-CCSD(T)}/\text{aug-cc-pV(T+d)Z}$ calculations of bare CH_2Cl^+ and its singly tagged Ne-clusters (Table 1), tagging is expected to have a negligible influence on the IRPD spectrum of this ion.

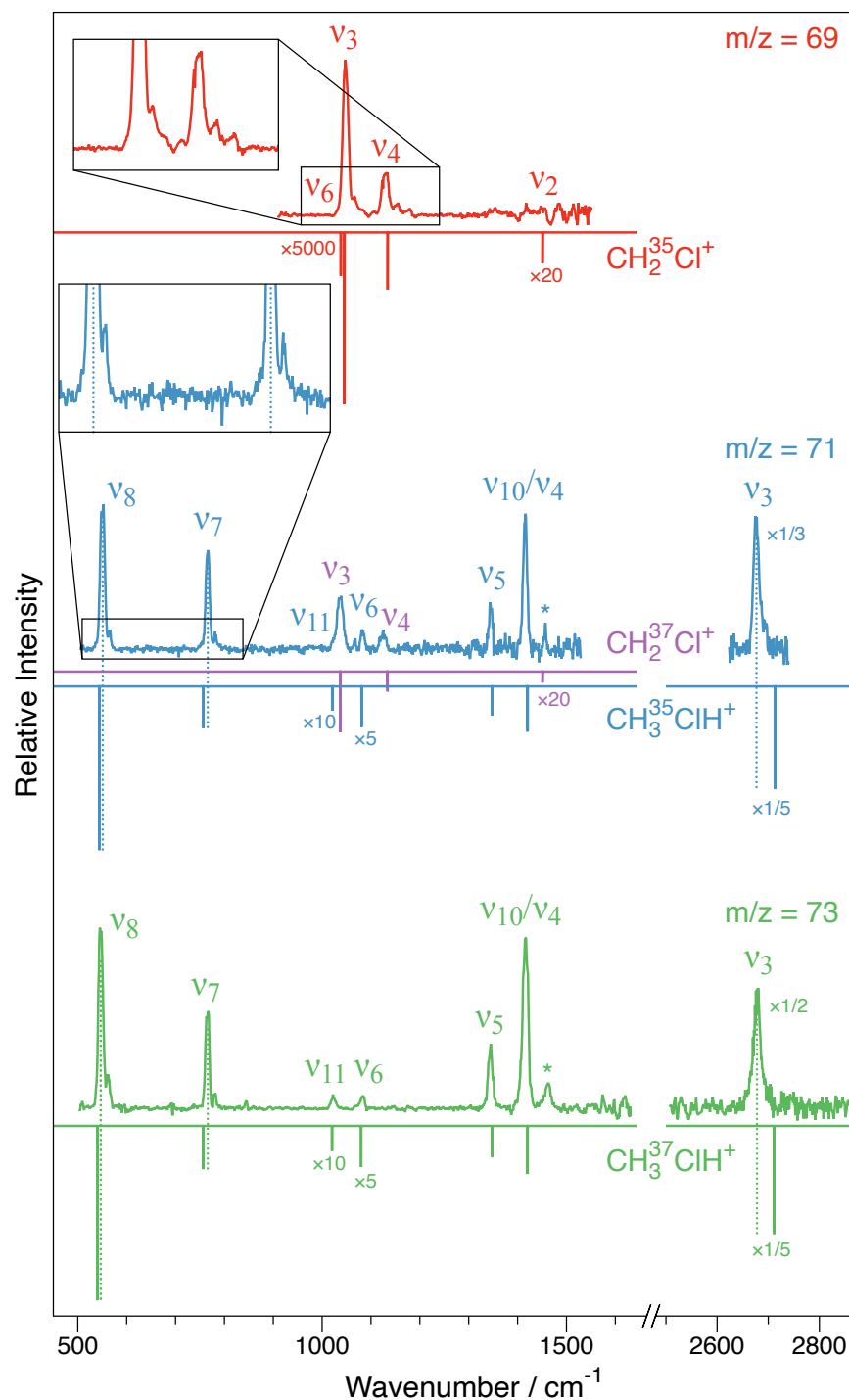


Figure 5. $\text{CH}_2\text{Cl}^+-\text{Ne}$ and $\text{CH}_3\text{ClH}^+-\text{Ne}$ infrared photodissociation (IRPD) spectra as obtained here. The traces indicate $m/z = 69$ corresponding to the $\text{CH}_2^{35}\text{Cl}^+-\text{Ne}$ species (top spectrum in red),

$m/z = 71$ (isobaric mixture of $\text{CH}_2^{37}\text{Cl}^+-\text{Ne}$ and $\text{CH}_3^{35}\text{ClH}^+-\text{Ne}$, blue center trace) and $m/z = 73$ ($\text{CH}_3^{37}\text{ClH}^+-\text{Ne}$, green bottom trace). For comparison, the vibrational fundamentals from VPT2 calculations (fc-CCSD(T)/cc-pV(T + d)Z) of the bare ions are shown as inverted sticks. For clarity, the intensities of selected calculated and experimental bands have been multiplied by the factors indicated. For the $\text{CH}_3\text{ClH}^+-\text{Ne}$ species, dashed sticks indicate blueshifts of the ν_8 and ν_7 bands and a redshift of the ν_3 band, which is indicative of Ne being bound to the proton in a near-linear $\text{Cl-H}\cdots\text{Ne}$ fashion. The bands labeled with an asterisk are not vibrational fundamentals. Insets highlight blueshifted satellites, presumably due to combination modes involving the Ne tag. For further details, see text.

Table 3. Harmonic and anharmonic fc-CCSD(T)/cc-pV(T + d)Z vibrational wavenumbers (in cm^{-1}) and infrared band intensities (int, km/mol), experimental wavenumbers (exp, cm^{-1}), full width at half maximum of observed bands (FWHM, cm^{-1}), and difference between observed and calculated anharmonic wavenumbers δ (cm^{-1}) of CH_2Cl^+ .

Mode	$\text{CH}_2^{35}\text{Cl}^+$					
	Harm	Anharm	Int	Exp ¹	FWHM	δ
$\nu_1(a_1)$ CH sym stretching	3105.2	2993.3	14	nc	...	...
$\nu_2(a_1)$ CH ₂ scissoring	1491.1	1451.1	0.7	...	...	...
$\nu_3(a_1)$ Cl–C stretching	1061.8	1045.6	81	1048	13	2
$\nu_4(b_1)$ oop bending	1151.9	1134.1	27	1129	17	−5
$\nu_5(b_2)$ CH asym stretching	3243.9	3101.1	47	nc	...	...
$\nu_6(b_2)$ CH ₂ wagging	1054.8	1038.2	<0.01	...	...	...

Mode	$\text{CH}_2^{37}\text{Cl}^+$					
	Harm	Anharm	Int	Exp ¹	FWHM	δ
$\nu_1(a_1)$ CH sym stretching	3105.2	2993.3	14	nc	...	...
$\nu_2(a_1)$ CH ₂ scissoring	1491.0	1451.0	0.7	...	...	...
$\nu_3(a_1)$ Cl–C stretching	1053.6	1037.6	82	1037	15	−1
$\nu_4(b_1)$ oop bending	1151.8	1134.0	27	1125	13	−9
$\nu_5(b_2)$ CH asym stretching	3243.9	3101.1	47	nc	...	...
$\nu_6(b_2)$ CH ₂ wagging	1054.2	1037.6	<0.01	...	...	...

¹ Wavenumber errors amount to 0.5% of the band position; nc: not covered.

2.3. IRPD Spectra of $\text{CH}_2^{37}\text{Cl}^+-\text{Ne}$ and $\text{CH}_3^{35}\text{ClH}^+-\text{Ne}$

Because $\text{CH}_2^{37}\text{Cl}^+-\text{Ne}$ and $\text{CH}_3^{35}\text{ClH}^+-\text{Ne}$ are isobaric species ($m/z = 71$), both ions were present in the ion trap, and hence, the corresponding spectrum comprises the spectra of both ions superimposed. The center trace in Figure 5 shows the final spectrum obtained in the wavenumber regions from 500 to 1530 cm^{-1} and from 2625 to 2740 cm^{-1} . The two regions feature no less than seven vibrational bands, all but one of which can be assigned in a straightforward fashion based on the CCSD(T)/cc-pV(T + d)Z force field calculations. The two vibrational bands located at 1037 cm^{-1} and 1125 cm^{-1} are assigned as the strong ν_3 and ν_4 vibrational fundamentals of $\text{CH}_2^{37}\text{Cl}^+$ (cf. Table 3). By comparison with the results from the CCSD(T)/cc-pV(T + d)Z force field calculations collected in Table 4, five bands are assigned as to originate from $\text{CH}_3^{35}\text{ClH}^+$, marking the first spectroscopic detection of this molecular ion. CH_3ClH^+ has a total of $3N - 6 = 12$ vibrational fundamentals, four of which are lying outside of the spectral regions covered here, namely, the three C–H stretching modes ν_1 (calculated at 3085 cm^{-1}), ν_2 (2979 cm^{-1}), and ν_9 (3101 cm^{-1}), as well as the low-energy torsional mode ν_{12} (177 cm^{-1}). Most other fundamentals are clearly identified, i.e., the Cl–C stretching mode ν_8 at 551 cm^{-1} , the C–Cl–H bending mode ν_7 at 766 cm^{-1} , the CH_3 in-plane rocking mode ν_6 at 1083 cm^{-1} , and the CH_3 umbrella mode ν_5 at 1345 cm^{-1} . According to the calculations, the strong feature at 1420 cm^{-1} is from an overlap of the energetically nearly degenerate CH_3 asymmetric bending modes $\nu_4(a')$ and $\nu_{10}(a'')$. The vibrational band with the largest calculated infrared intensity (Table 4) and indeed the strongest feature in the spectrum covered here is the Cl–H stretching mode ν_3 detected at 2677 cm^{-1} . The weak out-of-plane rocking mode ν_{11} is overlapping with the much

stronger ν_3 band of $\text{CH}_2^{37}\text{Cl}^+$. Overall, the agreement between the IRPD spectrum and the anharmonic CCSD(T)/cc-pV(T + d)Z force field calculation is excellent. The harmonic force field calculations of the bare ions and the singly tagged variants in Table 2 suggest that the influences of Ne should be subtle for most bands but noticeable for some. For the bands covered here, significant shifts might be expected for the ν_3 (redshift), ν_7 (blueshift), and, possibly, ν_8 bands (blueshift) if Ne was connected to the site of protonation. Indeed, the experimental findings are qualitatively consistent with this geometrical arrangement, as the largest differences δ between experimental and calculated wavenumbers of all bands observed are found for these three modes that also agree with the predicted sign of the shift. Lastly, as seen from the inset in Figure 5 (blue center trace), similarly to the ν_3 and ν_4 bands in CH_2Cl^+ , the ν_8 and ν_7 bands (possibly also ν_3) show weak satellite bands about 15 cm^{-1} blueshifted from the fundamentals, presumably combination modes involving low-energy fundamentals introduced through Ne-tagging (most likely the ω_{15} mode, as shown in Table 2).

Table 4. Harmonic and anharmonic fc-CCSD(T)/cc-pV(T + d)Z vibrational wavenumbers (in cm^{-1}) and infrared band intensities (int, km/mol), experimental wavenumbers (exp, cm^{-1}), full width at half maximum of observed bands (FWHM, cm^{-1}), and difference between observed and calculated wavenumbers δ (cm^{-1}) of CH_3ClH^+ .

Mode	$\text{CH}_3^{35}\text{ClH}^+$					
	Harm	Anharm	Int	Exp ¹	FWHM	δ
$\nu_1(a')$ C–H asym stretching	3225.4	3084.9	16	nc	...	...
$\nu_2(a')$ C–H sym stretching	3091.6	2978.8	5	nc	...	...
$\nu_3(a')$ Cl–H stretching	2829.5	2713.5	173	2677	15	−37
$\nu_4(a')$ CH_3 asym bending	1465.1	1420.6	15	1415	10	−6
$\nu_5(a')$ CH_3 umbrella	1378.2	1348.1	10	1345	8	−3
$\nu_6(a')$ CH_3 ip rocking	1113.6	1080.8	3	1083	9	2
$\nu_7(a')$ C–Cl–H bending	768.4	757.1	14	766	9	9
$\nu_8(a')$ Cl–C stretching	569.8	544.1	55	551	11	7
$\nu_9(a'')$ C–H asym stretching	3242.9	3100.6	14	nc	...	...
$\nu_{10}(a'')$ CH_3 asym bending	1462.5	1419.6	15	1415	10	−5
$\nu_{11}(a'')$ CH_3 oop rocking	1033.2	1020.6	1	blended	...	...
$\nu_{12}(a'')$ torsion	205.5	177.4	45	nc	...	...

Mode	$\text{CH}_3^{37}\text{ClH}^+$					
	Harm	Anharm	Int	Exp ¹	FWHM	δ
$\nu_1(a')$ C–H asym stretching	3225.4	3084.9	16	nc	...	...
$\nu_2(a')$ C–H sym stretching	3091.6	2978.8	5	nc	...	...
$\nu_3(a')$ Cl–H stretching	2827.3	2711.5	173	2678	20	−34
$\nu_4(a')$ CH_3 asym bending	1465.1	1420.5	15	1416	13	−5
$\nu_5(a')$ CH_3 umbrella	1377.9	1347.9	10	1344	11	−4
$\nu_6(a')$ CH_3 ip rocking	1112.7	1079.9	3	1082	11	2
$\nu_7(a')$ C–Cl–H bending	768.1	756.8	14	765	9	8
$\nu_8(a')$ Cl–C stretching	565.3	539.9	56	547	11	7
$\nu_9(a'')$ C–H asym stretching	3242.9	3100.6	14	nc	...	...
$\nu_{10}(a'')$ CH_3 asym bending	1462.5	1419.6	15	1416	13	−4
$\nu_{11}(a'')$ CH_3 oop rocking	1032.8	1020.2	1	1023	12	3
$\nu_{12}(a'')$ torsion	205.4	177.3	45	nc	...	...

¹ Wavenumber errors amount to 0.5% of the band position; nc: not covered.

2.4. IRPD Spectrum of $\text{CH}_3^{37}\text{ClH}^+ - \text{Ne}$

The IRPD spectrum of the $m/z = 73$ species covering the 500 to 1630 cm^{-1} and 2505 to 2880 cm^{-1} regions is shown in Figure 5 (green bottom trace). Clearly, the strong vibrational band quintett comprising the ν_8 , ν_7 , ν_5 , ν_{10}/ν_4 , and ν_3 bands nicely matches the pattern observed also for the $\text{CH}_3^{35}\text{ClH}^+ - \text{Ne}$ isotopic species at $m/z = 71$. Likewise, the ν_8 and ν_7 bands of $\text{CH}_3^{37}\text{ClH}^+ - \text{Ne}$ show weaker yet clearly discernible shoulders to their blue sides. IRPD scans of the strong ν_8 band reveal that depletion is nearly 100%, suggesting that the

$m/z = 73$ spectrum should provide a clean view of the $\text{CH}_3^{37}\text{ClH}^+-\text{Ne}$ species and not be affected by isobaric contamination. As a consequence, in addition to the weak CH_3 ip rocking mode ν_6 band at 1082 cm^{-1} , now also the very weak CH_3 out-of-plane rocking mode ν_{11} can be identified at 1023 cm^{-1} . In addition to these vibrational fundamentals, the spectrum shows a spectroscopic feature at 1461 cm^{-1} that is also seen as a somewhat less prominent signal in the $m/z = 71$ spectrum (see bands marked with asterisks in Figure 5). From the anharmonic force field calculations, this feature is not compatible with a binary but, possibly, a ternary combination mode comprising the three energetically lowest fundamental modes, $\nu_7 + \nu_8 + \nu_{12}$. However, from the present investigation, a definitive assignment is not feasible.

3. Materials and Methods

3.1. Quantum-Chemical Calculations

Theoretical molecular structures of both CH_2Cl^+ (C_{2v}) and CH_3ClH^+ (C_s) have previously been provided on several occasions (e.g., Refs. [12,22–25]). In the present study, complementary quantum-chemical calculations of CH_2Cl^+ and CH_3ClH^+ (as well as their isostructural and isoelectronic sulfur analogs, H_2CS and CH_3SH) were performed at the coupled cluster single and double (CCSD) level augmented by a perturbative treatment of triple excitations (CCSD(T)) [26], together with correlation-consistent (augmented) polarized valence and (augmented) polarized weighted core–valence basis sets, i.e., cc-pVXZ [27], aug-cc-pVXZ [27–29], and cc-pwCVXZ [27,30] (with $X = \text{T, Q}$). For basis sets denoted as cc-pV($X + d$)Z or aug-cc-pV($X + d$)Z, an additional tight d function [31] was added to the chlorine (and sulfur) atom only, while for all other elements, cc-pV(X)Z or aug-cc-pV(X)Z was used, respectively. Equilibrium geometries were calculated using analytic gradient techniques [32], while harmonic frequencies were computed using analytic second-derivative techniques [33,34]. For anharmonic computations, second-order vibrational perturbation theory (VPT2) [35] was employed, and an additional numerical differentiation of analytic second derivatives was applied to obtain the third and fourth derivatives required for the application of VPT2 [34,36]. The frozen core approximation is indicated throughout with “fc”, and “ae” indicates that all electrons were used in the correlation treatment. All calculations were carried out using the CFOUR program package [37,38].

3.2. Experiment

Experimental infrared action spectroscopic characterization of CH_2Cl^+ and CH_3ClH^+ was performed in selected wavenumber ranges from 500 to 2900 cm^{-1} using a cryogenic 22-pole ion trap apparatus FELion connected to the Free Electron Laser for Infrared experiments (FELIX) [39], located at Radboud University (Nijmegen, the Netherlands). The FELion apparatus and its central part, the 22-pole ion trap, have been described elsewhere in detail [40,41], and the experimental conditions applied were similar to those used in other recent studies of molecular ions [16,17,42–44]. $\text{CH}_2^{35,37}\text{Cl}^+$ ($m/z = 49, 51$) and $\text{CH}_3^{35,37}\text{ClH}^+$ ($m/z = 51, 53$) were produced in an ion source under the same experimental conditions from commercially available methyl chloride, CH_3Cl , using electron impact ionization at an electron energy of about 30 eV . Because of the high natural abundance of ^{37}Cl (24.24%), the corresponding heavy isotopologs $\text{CH}_2^{37}\text{Cl}^+$ and $\text{CH}_3^{37}\text{ClH}^+$ were easily accessible. It should be stressed that $\text{CH}_2^{37}\text{Cl}^+$ and $\text{CH}_3^{35}\text{ClH}^+$ are isobaric species ($m/z = 51$); hence, the corresponding spectra were expected to appear superimposed in the same scan.

After extracting the ion cloud from the source and selection in the first quadrupole mass analyzer, the m/z of choice was introduced into the 22-pole ion trap, where it was cooled via a cold pulse of a 3:1 mixture of He:Ne kept at a nominal temperature of 8 K and at a high number density, leading to efficient tagging with Ne atoms. Per filling cycle of the ion trap, typically, several thousand cation–Ne complexes ($\text{CH}_2^{35,37}\text{Cl}^+-\text{Ne}$ at $m/z = 69/71$ or $\text{CH}_3^{35,37}\text{ClH}^+-\text{Ne}$ at $m/z = 71, 73$) can be formed via three-body collisions (Figure A1 in Appendix C). After a selected storage time of typically 1.6 or 2.6 s , the trap content was

extracted from the trap, mass-filtered in a second quadrupole mass analyzer, and counted using a very sensitive Daly-type detector.

In the infrared photodissociation (IRPD) action spectroscopy scheme employed herein, the number of singly tagged $\text{CH}_2\text{Cl}^+\text{-Ne}$ cluster ions (similar for $\text{CH}_3\text{ClH}^+\text{-Ne}$) was monitored while the FELIX (FEL-2) IR radiation traversing the ion trap was tuned in wavenumber. FELIX was operated in a pulsed mode (10 Hz), with typical pulse energies of a few up to a few tens of mJ (measured at the exit of the ion trap) and a Fourier-limited full width at half maximum (FWHM) bandwidth on the order of 0.7%. 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 ion–Ne counts. Finally, several power-normalized spectra were co-added to obtain the final spectrum. Details on the normalization procedure have been given in Ref. [41].

Since the weakly bound, rare gas Ne generally only slightly perturbs the structure of the ion, an IRPD spectrum is highly representative of that of the bare ion (e.g., Refs. [16,17,21,44]). Band parameters such as positions and FWHM were obtained by fitting (multi-component) Gaussian profiles to the experimental spectra. Typical wavenumber uncertainties of 0.5% are mainly dependent on calibration uncertainties due to the grating spectrum analyzer.

4. Conclusions

The present study reports on the first infrared gas-phase study of CH_2Cl^+ and the first spectroscopic detection and characterization of CH_3ClH^+ , two fundamental chlorine-bearing ions possibly linked to the astrochemical gas-phase production of methyl chloride, CH_3Cl . Now that the IR spectra of CH_2Cl^+ and CH_3ClH^+ have been detected at low spectral resolution, corresponding studies at high resolution are imperative, in particular, to permit radio astronomical searches. Following the very recent technical developments in action spectroscopy of molecular ions, high-resolution infrared spectroscopy of both species may be performed using leak-out spectroscopy [45], a new method that does not require any rare gas tagging and has already been shown, on several occasions, to yield spectra of superb signal-to-noise ratios [46–49]. The method may even be combined with millimeter-wave radiation in a double-resonance fashion to derive accurate information about the pure rotational spectrum [46,47,50], a prerequisite for radio astronomy. Using the high-level CCSD(T) structural and force field calculations performed here, very good predictions of the ground state rotational and centrifugal distortion constants can be derived. These estimates may even be further improved using a simple scaling procedure, if experimental data of isostructural/isoelectronic species are available (see, e.g., Refs. [16,50,51]). As the Cl^+ ion is isoelectronic with neutral atomic S, thioformaldehyde, H_2CS , and methyl mercaptan, CH_3SH , may potentially be used as calibrators, the pure rotational spectra of which are very well known from previous microwave and millimeter-wave studies (see, e.g., Refs. [52,53] for recent reports). Calculated and experimental rotational constants of H_2CS and CH_3SH (structural parameters are given in Appendix B) as well as calculated constants of CH_2Cl^+ and CH_3ClH^+ are collected in Table 5. For the sulfur species, the agreement between the calculated and experimental ground state rotational constants is already very good. Consequently, the scaling factors, i.e., the ratios $A_{0,\text{exp}}/A_{0,\text{calc}}$, $B_{0,\text{exp}}/B_{0,\text{calc}}$, and $C_{0,\text{exp}}/C_{0,\text{calc}}$ are almost but not quite unity. Multiplying those factors with the calculated ground state rotational constants of CH_2Cl^+ and CH_3ClH^+ finally yields the scaled best-estimate rotational constants in the last column of Table 5. Both species are very polar with center-of-mass frame equilibrium dipole moment components $\mu_a = 3.02$ D of CH_2Cl^+ as well as $\mu_a = 1.22$ D and $\mu_b = 1.42$ D of CH_3ClH^+ .

From a chemical viewpoint, extending the spectroscopy of CH_2X^+ and CH_3XH^+ to halogens other than chlorine also seems appealing. The situation for $\text{X}=\text{Br}$, for example, appears similar to the one with $\text{X}=\text{Cl}$ prior to the present study. To date, spectroscopic studies of CH_2Br^+ have been restricted to infrared matrix isolation [12,54]. Protonated methyl bromide, CH_3BrH^+ , seems not to have been spectroscopically studied to date.

Table 5. Rotational parameters of H₂CS, CH₂³⁵Cl⁺, CH₃SH, and CH₃³⁵ClH⁺ (in MHz) ¹.

Parameter	H ₂ CS		CH ₂ ³⁵ Cl ⁺	
	Calc.	Exp. [52]	Calc.	Scaled
<i>A_e</i>	295,043.772	...	278,232.178	...
<i>B_e</i>	17,770.906	...	17,929.887	...
<i>C_e</i>	16,761.346	...	16,844.397	...
ΔA_0	1928.402	...	2249.656	...
ΔB_0	76.366	...	91.765	...
ΔC_0	109.739	...	125.604	...
<i>A₀</i>	293,115.370	291,613.339	275,982.522	274,568.285
<i>B₀</i>	17,694.540	17,698.994	17,838.122	17,842.613
<i>C₀</i>	16,651.607	16,652.498	16,718.793	16,719.687

Parameter	CH ₃ SH		CH ₃ ³⁵ ClH ⁺	
	Calc.	Exp. [53] ²	Calc.	Scaled
<i>A_e</i>	103,863.953	...	103,144.040	...
<i>B_e</i>	13,029.847	...	12,472.858	...
<i>C_e</i>	12,493.723	...	12,016.948	...
ΔA_0	1054.186	...	1069.132	...
ΔB_0	131.546	...	207.375	...
ΔC_0	117.267	...	184.225	...
<i>A₀</i>	102,809.767	102,767.147	102,074.907	102,032.592
<i>B₀</i>	12,898.301	12,951.372	12,265.483	12,315.950
<i>C₀</i>	12,376.457	12,388.033	11,832.724	11,843.792

¹ Equilibrium rotational constants and zero-point vibrational contributions calculated at the ae-CCSD(T)/cc-pwCVQZ and fc-CCSD(T)/cc-pV(T + *d*)/Z levels of theory, respectively. ² For the sake of comparability, the rotational constants from Ref. [53] given in the rho-axis system were converted to the principal axis system. Differences are virtually negligible.

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Appendix A. Molecular Structures of CH_2Cl^+ and CH_3ClH^+ and Their Weakly Bound Clusters with Neon

Appendix A.1. CH_2Cl^+

CL

C 1 r1

H 2 r2 1 a1

H 2 r2 1 a1 3 d180

	cc-pV(T+d)Z	/	aug-cc-pV(T+d)Z	/	cc-pwCVQZ
r1	= 1.59619	/	1.59662	/	1.58812
r2	= 1.08829	/	1.08860	/	1.08620
a1	= 119.09851	/	119.03255	/	119.07897
d180	= 180.00000	/	180.00000	/	180.00000

Appendix A.2. CH_2Cl^+ Ne-ip

CL

C 1 r1

H 2 r2 1 a1

H 2 r3 1 a2 3 d180

NE 4 r4 2 a3 3 d180

	aug-cc-pV(T+d)Z
r1	= 1.59672
r2	= 1.08853
a1	= 119.01368
r3	= 1.08827
a2	= 118.82770
d180	= 180.00000
r4	= 2.39056
a3	= 133.32909

Appendix A.3. CH_2Cl^+ Ne-oop

CL

C 1 r1

NE 2 rNE 1 aNE

H 2 r2 3 a1 1 d1

H 2 r2 3 a1 1 md1

	aug-cc-pV(T+d)Z
r1	= 1.59691
rNE	= 2.79264
aNE	= 108.25118
r2	= 1.08829
a1	= 81.35078
d1	= 117.85276
md1	= -117.85276

Appendix A.4. CH_3ClH^+

H

C 1 r1

CL 2 r2 1 a1

H 3 r3 2 a2 1 d180

H 2 r4 3 a3 1 d1

H 2 r4 3 a3 1 md1

	cc-pV(T+d)Z	/	aug-cc-pV(T+d)Z	/	cc-pwCVQZ
r1	=	1.08652	/	1.08729	/ 1.08435
r2	=	1.85970	/	1.86174	/ 1.84696
a1	=	101.97978	/	101.91486	/ 102.10778
r3	=	1.29569	/	1.29687	/ 1.29436
a2	=	99.43628	/	99.36597	/ 99.64973
d180	=	180.00000	/	180.00000	/ 180.00000
r4	=	1.08443	/	1.08514	/ 1.08215
a3	=	105.70626	/	105.53383	/ 105.84821
d1	=	118.70156	/	118.73149	/ 118.68039
md1	=	-118.70156	/	-118.73149	/ -118.68039

Appendix A.5. $\text{CH}_3\text{ClH}^+ - \text{Ne}$, *p*-bound

H
C 1 r1
CL 2 r2 1 a1
H 3 r3 2 a2 1 d180
H 2 r4 3 a3 1 d1
H 2 r4 3 a3 1 md1
X 4 rd 3 a90 2 d180
NE 4 r5 7 a4 3 d180

r1	=	1.08720
r2	=	1.85987
a1	=	102.05144
r3	=	1.29827
a2	=	99.19249
d180	=	180.00000
r4	=	1.08515
a3	=	105.57033
d1	=	118.75594
md1	=	-118.75594
rd	=	1.00000
a90	=	90.00000
r5	=	2.07322
a4	=	94.38835

Appendix A.6. $\text{CH}_3\text{ClH}^+ - \text{Ne}$, CH_3/Cl -bound

H
C 1 r1
CL 2 r2 1 a1
H 3 r3 2 a2 1 d180
H 2 r4 3 a3 1 d1
H 2 r4 3 a3 1 md1
X 1 rd 2 a90 3 d0
NE 1 r5 7 a4 2 d180

r1	=	1.08692
r2	=	1.86155
a1	=	101.81875
r3	=	1.29674
a2	=	99.27846

```

d180 =      180.00000
r4   =      1.08514
a3   =     105.52239
d1   =     118.75328
md1  =    -118.75328
rd   =      1.00000
a90  =     90.00000
d0   =      0.00000
r5   =      2.57934
a4   =     40.24330

```

Appendix B. Molecular Structures of H₂CS and CH₃SH

Appendix B.1. H₂CS

```

S
C 1 r1
H 2 r2 1 a1
H 2 r2 1 a1 3 d180

cc-pV(T+d)Z / cc-pwCVQZ
r1   =      1.61826 /   1.60890
r2   =      1.08766 /   1.08531
a1   =     121.92777 / 121.85524
d180 =     180.00000 / 180.00000

```

Appendix B.2. CH₃SH

```

H
C 1 r1
S 2 r2 1 a1
H 3 r3 2 a2 1 d180
H 2 r4 3 a3 1 d1
H 2 r4 3 a3 1 md1

cc-pV(T+d)Z / cc-pwCVQZ
r1   =      1.08915 /   1.08669
r2   =      1.82085 /   1.81020
a1   =     106.24841 / 106.25194
r3   =      1.33803 /   1.33502
a2   =      96.64050 /   96.88414
d180 =     180.00000 / 180.00000
r4   =      1.08804 /   1.08554
a3   =     111.27155 / 111.25848
d1   =     118.26139 / 118.25357
md1  =    -118.26139 / -118.25357

```

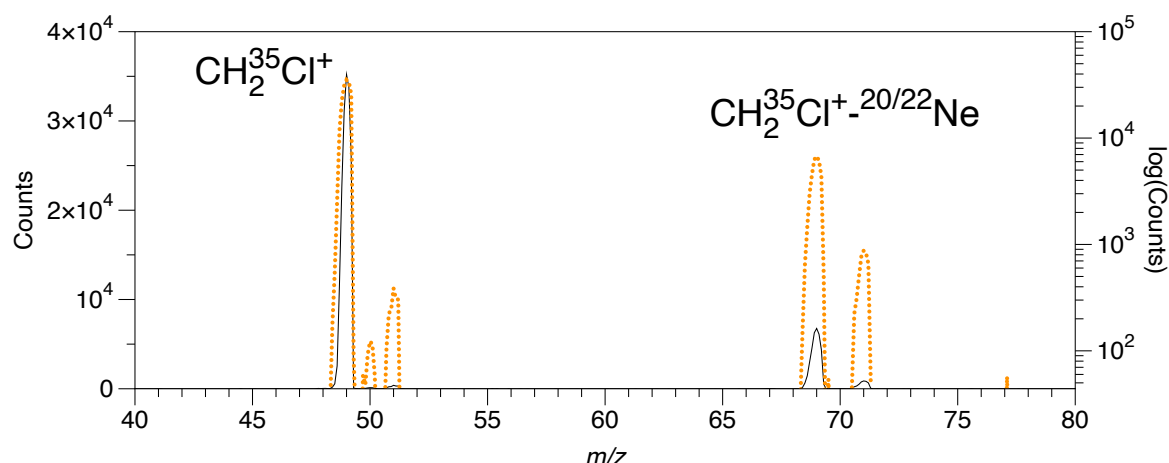

Appendix C. Mass Spectrum of CH_2Cl^+ and $\text{CH}_2\text{Cl}^+-^{20/22}\text{Ne}$ as Extracted from the Ion Trap

Figure A1. Trap content extracted after initial mass selection for $m/z = 49$, trapping and cooling in the 8 K He/Ne-bath of the 22-pole ion trap featuring some 35,000 CH_2Cl^+ ions and almost 7000 weakly bound clusters with ^{20}Ne available for IRPD. Black trace and left ordinate: linear plot of counts; orange dotted trace and right ordinate: logarithmic plot of counts

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