Submillimeter absorption from SH\(^+\), a new widespread interstellar radical, \(^{13}\)CH\(^+\) and HCl\(^*\)

K. M. Menten\(^1\), F. Wyrowski\(^1\), A. Belloche\(^1\), R. Güsten\(^1\), L. Dedes\(^1\), and H. S. P. Müller\(^2\)

\(^1\) Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, 53121 Bonn, Germany
e-mail: [kmenten;wyrowski;belloche;rguesten;lededes]@mpifr-bonn.mpg.de
\(^2\) I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany
e-mail: hspm@ph1.uni-koeln.de

Received 5 March 2010 / Accepted 10 September 2010

ABSTRACT

We have used the Atacama Pathfinder Experiment 12 m telescope (APEX) to carry out an absorption study of submillimeter wavelength rotational ground-state lines of H\(^{15}\)Cl, H\(^{17}\)Cl, \(^{13}\)CH\(^+\), and, for the first time, of the SH\(^+\) radical (sulfonylmidylen or sulfanylium). We detected the quartet of ground-state hyperfine structure lines of SH\(^+\) near 683 GHz with the CHAMP+ array receiver against the strong continuum source Sagittarius B2, which is located close to the center of our Galaxy. In addition to absorption from various kinematic components of Galactic center gas, we also see absorption at the radial velocities belonging to intervening spiral arms. This demonstrates that SH\(^+\) is a ubiquitous component of the diffuse interstellar medium. We do not find clear evidence for other SH\(^+\) lines we searched for, which is partially due to blending with lines from other molecules. In addition to SH\(^+\), we observed absorption from H\(^{16}\)Cl, H\(^{17}\)Cl, and \(^{13}\)CH\(^+\). The observed submillimeter absorption is compared in detail with absorption in 3 mm transitions of H\(^{15}\)CO and \(^{13}\)CH and the CO J = 1–0 and 3–2 transitions.

Key words. astrochemistry – ISM: abundances – ISM: molecules

1. Introduction

1.1. (Sub)millimeter spectroscopy of diffuse interstellar clouds

Starting in the late 1930s, studies of molecular absorption toward diffuse and translucent clouds have traditionally been in the realm of optical and, later, ultraviolet (UV) and infrared (IR) spectroscopy. Over the last 15 years, observations at radio and (sub)mm wavelengths have greatly added to our knowledge of the chemistry of the diffuse interstellar medium (ISM) (see, e.g., the review of Snow & McCall 2006). Measurements toward strong continuum sources are a powerful means to detect spectral lines that have their lower level in (or near) the rotational ground state of a molecule and may be the only way to detect a number of species in low density environments or even at all. In particular, the large rotational constants of light hydrides, resulting in a rotational spectrum starting at submillimeter or far-infrared wavelengths, together with substantial electric dipole moments, make collisional excitation negligible compared to radiative decay. This leaves substantial population only in the lowest energy level, which can be split in the case of fine structure (fs) or hyperfine structure (hfs).

Two particularly fruitful avenues of research have emerged; first, choosing extragalactic sources with strong mm- and cm-wavelength continuum emission as background objects, Liszt and Lucas have studied the abundances of a variety of di-, tri-, and even polyatomic molecules toward up to 20 lines of sight with often surprising results (see, e.g., Liszt & Lucas 2002, and references therein). A second possibility is using as a background the thermal continuum from star-forming regions, (mostly) free-free emission at cm- and longer mm-wavelengths and dust emission at shorter wavelengths. Particularly interesting lines of sights are those toward regions M and N in the Sagittarius B2 Giant Molecular Cloud (GMC), which allow sensitive absorption spectroscopy of the ISM surrounding the Galactic center (GC) near which they are located at a distance of ~8 kpc (Reid et al. 2009) as well as of intervening GMCs. For a long time, absorption between ~120 kms\(^{-1}\) and Sgr B2’s local velocity range (>+s50 kmps\(^{-1}\)) has been observed in the HI 21 cm line (see Garwood & Dickey 1989, and references therein) as well as in (mostly) mm-wavelength lines from quite a number of molecules (see Linke et al. 1981; Nyman 1983; Greaves & Williams 1994, and references therein). Intervening spiral arm absorption toward other bright inner Galaxy (sub)mm continuum sources has been found as well, most prominently toward the central radio/(sub)mm source Sgr A* and W49N (see, e.g., Liszt et al. 1977; Linke et al. 1981; Cox et al. 1988; Greaves & Williams 1994; Plume et al. 2004; Polehampton et al. 2005b).

At submillimeter wavelengths, numerous molecules have been detected in absorption via their ground-state transitions (until recently mostly) toward Sgr B2 (for summaries see Menten 2004; Lis et al. 2009). In particular, the J\(_{10}^{-101}\) transition of ortho-H\(^{15}\)O and \(^{13}\)H\(^{18}\)O was detected with the Submillimeter Wave Astronomy Satellit (Neufeld et al. 2000); this H\(^{13}\)O line, near 557 GHz, is responsible for much of the Earth atmosphere’s shorter-wavelength submillimeter opacity.

In fact, atmospheric absorption by the rotational spectrum of H\(_2\)O (and to a lesser extent of O\(_2\)) makes the ground-state lines of many light hydride species unaccessible from the ground. Using the Long Wavelength Spectrometer (LWS) aboard the...
Infrared Space Observatory (ISO), which covered frequencies >1.5 THz (wavelengths <200 μm), several hydroxyl isotopoloues (Polehampton et al. 2003, 2005a) were detected, as well as CH2 (Polehampton et al. 2005b), and para-H2D* (Cernicharo et al. 2007). From the excellent high altitude site in the Atacama desert, recently OH+ was found with the APEX telescope by Wyrowski et al. (2010a).

Very recently, a new era in submillimeter absorption spectroscopy started with operation of the High Frequency Instrument for the Far Infrared (HIFI, see de Graauw et al. 2010) aboard Herschel (Pilbratt et al. 2010). Utilizing the superb sensitivity of Herschel’s 3.5 m aperture combined with HIFI’s high spectral resolution heterodyne receivers operating in a low thermal background space environment, revolutionized observations of light hydrides. (Mainly) in the framework of the guaranteed time key projects Herschel observations of Emission Line Absorption Spectroscopy with Interspecies and Test Stellar Molecules with Absorption line Studies (PRISMAS, PL: Gerin) observations were made of H2O+, H2O−, H2O, and its isotopologues, H2O+ (C3, CH, and CH+), as well as NH and NH2, while NH+ has so far remained undetected (Ossenkopf et al. 2010; Schilke et al. 2010; Gerin et al. 2010; Wyrowski et al. 2010b; Neufeld et al. 2010a; Lis et al. 2010b; Melnick et al. 2010; Comito et al. 2010; Lis et al. 2010a; Phillips et al. 2010; Neufeld et al. 2010b; Sonnentrucker et al. 2010; Mookerjea et al. 2010; Qin et al. 2010; Falgarone et al. 2010; Persson et al. 2010).

High quality optical/UV observations, needed, e.g., for meaningful abundance determinations, mostly sample relatively nearby clouds since they require optically bright background stars, typically members of OB associations (with HD catalogue numbers) within a few kpc (see, e.g., Gredeel 1997; Stahl et al. 2008, and references therein). In contrast, being much less affected by interstellar extinction, radio/submm and near infrared absorption observations, e.g. of the key H3+ molecular ion (Geballe & Oka 1996), are capable of probing diffuse clouds throughout the Milky Way.

1.2. Interstellar SH+

The ionized hydride SH+ (sulfoniumylidene or sulfanylium) potentially is a probe of comets, photon-dominated regions (PDRs), shocked interstellar gas and diffuse molecular clouds (Horani et al. 1985). Toward the latter, optical absorption measurements have shown for a very long time large abundances of another ionized molecule, methyldiydium, CH+, the first interstellar molecule, detected by Dunham (1937) and identified by Douglas & Herzberg (1941). CH+’s abundance is orders of magnitude higher than predicted by otherwise successful models (see, e.g., van Dishoeck & Black 1986). This has been a long-standing puzzle to astrochemists, who invoked shock wave scenarios to overcome the formation reaction’s endothermicity (Federman 1982).

Millar et al. (1986) and also Pineau des Forêts et al. (1986) have extended chemical models by including sulfur chemistry and predicted efficient SH+ formation to occur in shocked diffuse clouds and that the abundance of SH+ can approach that of CH+ in moderate velocity magnetic shocks, but is negligible for a non-magnetic shock. This, in principle, could make the CH+/SH+ abundance ratio a good shock indicator.

Millar & Hobbs (1988) made sensitive searches of an optical wavelength electronic transition of SH+ from the A1Π−X1Σ0(0,0) band at 3363.49 Å toward the well-studied diffuse cloud in the direction of ζ Oph, which shows significant CH+ absorption.

They were only able to put an upper limit on the SH+ column density of 1 × 1013 cm−2, which is a factor of 3 lower than the measured CH+ column density. Magnani & Salzer (1991) searched for this line and another one at 3366.08 Å toward a sample of 13 stars with known diffuse molecular clouds in front of them and were only able to determine comparable 3σ upper limits on the SH+ column density between 0.4 and 1 × 1013 cm−2 and upper limits on the [SH+/CH+] abundance ratio between 0.12 and 2. An earlier search by Magnani & Salzer (1989) toward a sample of diffuse and high-latitude clouds resulted in a factor of a few coarser limits on the SH+ abundance. High (Galactic) latitude clouds belong to the so-called translucent clouds.

Translucent clouds, which were recognized as a class by van Dishoeck & Black (1986) have physical properties in between those of diffuse and dense dark clouds. In particular, they have higher visual extinctions, AV < (1–a few mag) than diffuse clouds (<1 mag) and, consequently, a higher ratio of molecular to atomic gas.

Other astrochemical interest in SH+ derives from the fact that, given a possible formation route via doubly ionized sulfur (S2+), it is predicted to be a diagnostic of X-ray dominated regions (XDRs) (Abel et al. 2008). Stüber et al. (2007) report an observation of the SH+ N = 1–0, J = 0–1, F = 0.5–1.5 line near 346 GHz toward the high-mass young stellar object (YSO) AFGL 2591, which is surrounded by an XDR. Since this line is blended with a 34SO2 line, they were only able to quote an upper limit to the SH+ line’s intensity. Again very recently, Herschel/HIFI observations led to the discovery of emission in the 526 GHz 12Π−0 transition of SH+ toward the high-mass protostar W3 IRS 5 (Benz et al. 2010).

In Sect. 2 of this paper we review the laboratory spectroscopy picture for both SH+ and CH+. In Sect. 3 we describe our submillimeter observations. Our results and the analysis procedure used to determine primary parameters of the observed lines are presented in Sect. 4. In Sect. 5 we discuss the derived information in an astrochemical context.

2. Rest frequencies

2.1. Accurate SH+ frequencies

Savage et al. (2004) performed the only measurements of SH+ with microwave accuracy. They obtained rest frequencies for four hfs lines from the X 3Σ− N = 1–0 state, one near 346 and three near 526 GHz. A previous study by Hovde & Saykally (1987) employed laser magnetic resonance to record rotational spectra. Recently, Brown & Müller (2009) used these and further rotovibrational (infrared) data on energy levels of SH+ in and between the ν = 0 and 1 vibrational states of the X3Σ− electronic ground state to perform a single, weighted least-squares fit in order to determine an improved set of molecular parameters for this molecule. They used their results to calculate the rotational spectrum of SH+ in these vibrational levels up to the N = 4–3 transition. The predictions presented in the catalog section1 of the Cologne Database for Molecular Spectroscopy, CDMS, (Müller et al. 2001, 2005) are based on the data from Savage et al. (2004), on weighted averages of the experimental data from Hovde & Saykally (1987) extrapolated to zero field taken from the fit of Brown & Müller (2009) and all available infrared data (up to ν = 4–3). These predictions are essentially

1 http://www.astro.uni-koeln.de/cdms/entries/, see also http://www.astro.uni-koeln.de/cdms/catalog/
Table 1. Spectroscopic data and beam-averaged continuum brightness temperature assumed for the LTE modeling of the absorption lines toward Sgr B2(M).

| Transition | $F' - F''^a$ | Position$^b$ | Frequency (MHz) | $S$ | $E_i$ | $F_{eff}$ | $B_{eff}$ | $T_{cont}^c$ (K) | Reference$^d$ |
|------------|--------------|--------------|----------------|-----|------|---------|---------|----------------|----------------|
| c-C$_3$H$_2$ $2_{2-1_{01}}$ | 2.0–2.0 | 0.0 | 85338.89(14) | 1.50 | 0.00 | 0.95 | 0.78 | 5.9 | JPL, h |
| H$_2$CO$^+$ 1–0 | 2.6–2.0 | 0.0 | 86754.28(46) | 1.0 | 0.0 | 0.95 | 0.78 | 5.9 | CDMS, i |
| CO 1–0 | 2.6–2.0 | 1.15271(2085(5)) | 1.0 | 0.0 | 0.95 | 0.74 | 5.9 | CDMS, j |
| CO 3–2 | 2.6–2.0 | 3.45795(989(5)) | 3.0 | 16.6 | 0.95 | 0.72 | 11.0 | CDMS, k |
| SH$^+$ 1$\alpha$–0$\alpha$ | 0.5–0.5 | 0.0 | 34584.59(128) | 0.2289 | 0.0 | 0.95 | 0.72 | 11.0 | CDMS, – |
| H$^3$Cl 1–0 | 1.5–1.5 | 0.0 | 62496.37(100) | 1.3333 | 0.0 | 0.95 | 0.41 | 33.8 | JPL, l |
| H$^3$Cl 2–1 | 2.5–1.5 | 0.0 | 62497.82(100) | 2.0 | 0.0 | 0.95 | 0.41 | 33.8 | JPL, l |
| H$^3$Cl 3–2 | 0.5–1.5 | 0.0 | 62498.34(100) | 0.6667 | 0.0 | 0.95 | 0.41 | 33.8 | JPL, l |
| SH$^+$ 1$\alpha$–0$\alpha$ | 0.5–0.5 | 0.0 | 683336.08(51) | 0.1890 | 0.0 | 0.95 | 0.41 | 30.0 | CDMS, m |
| SH$^+$ 1$\alpha$–0$\alpha$ | 0.5–0.5 | 0.0 | 683361.98(48) | 0.3778 | 0.0 | 0.95 | 0.41 | 30.0 | CDMS, m |
| SH$^+$ 1$\alpha$–0$\alpha$ | 0.5–1.5 | 0.0 | 683422.31(50) | 0.9441 | 0.0 | 0.95 | 0.41 | 30.0 | CDMS, m |
| SH$^+$ 1$\alpha$–0$\alpha$ | 0.5–1.5 | 0.0 | 683448.20(50) | 0.1887 | 0.0 | 0.95 | 0.41 | 30.0 | CDMS, m |
| $^{13}$CH$^+$ 1–0 | 0.0 | 0.0 | 830216.90(22) | 1.0 | 0.0 | 0.95 | 0.35 | 47.7 | CDMS, n |
| SH$^+$ 2$\alpha$–1$\alpha$ | 0.5–0.5 | 0.0 | 893073.49(96) | 0.1445 | 0.0 | 0.95 | 0.35 | 43.5 | CDMS, – |
| SH$^+$ 0$\alpha$–1$\alpha$ | 1.5–1.5 | 0.0 | 893107.92(105) | 0.1444 | 0.0 | 0.95 | 0.35 | 43.5 | CDMS, – |
| SH$^+$ 0$\alpha$–1$\alpha$ | 1.5–1.5 | 0.0 | 893133.81(94) | 0.7225 | 0.0 | 0.95 | 0.35 | 43.5 | CDMS, – |

Notes. $^a$Hyperfine quantum numbers as far as appropriate. $^b$Equatorial offset (J2000) with respect to Sgr B2(M). (0, 0) corresponds to $(\alpha, \delta)_{2000} = 17^\circ 47^\prime 20^\circ 2,\ 28^\circ 23^\prime 05^\circ$. $^c$Forward efficiency. $^d$Main-beam efficiency. $^e$The beam-averaged continuum brightness temperature was derived from the depth of the saturated absorption lines in the 3 mm wavelength range, and from a direct measurement of the baseline level at higher frequency. $^f$Catalog used for rest frequency and reference for line measurement, see also Sect. 2. $^g$Lower level is ortho ground state; it is 2.35 K above the zero level. $^h$Vršnak et al. (1987). $^i$Schmid-Burgk et al. (2004). $^j$Main-beam efficiency. $^k$Methylidyne, 11CH$_2$, 12CH$_2$, 13CH$_2$, 12CH$_3$, 13CH$_3$, 12CH$_4$, 13CH$_4$, 12CH$_5$, 13CH$_5$. $^l$Our observations of 13CH$_2$ toward the 830.135 GHz line recommended by Pearson & Drouin (2010). $^m$Our observations of 13CH$_2$ toward the 830.135 GHz line recommended by Pearson & Drouin (2010).

Fig. 1. Detail of the energy level diagram of SH$^+$ . The solid arrows mark transitions observed in the course of this work. The thickness of the arrows indicates the relative strengths of the transitions. The hyperfine splitting has been exaggerated slightly for clarity reasons.

identical to those in Brown & Müller (2009), in particular when the uncertainties are taken into account. The dipole moment of 1.285 D in the ground vibrational state has been taken from an ab initio calculation by Senekowitsch et al. (1985). The rest frequencies from the CDMS catalog are given in Table 1. Fig. 1 presents the lower part of the rotational energy level diagram of SH$^+$.

2.2. The J = 1–0 transition of $^{13}$CH$^+$

The X $^1\Sigma^+$ $J = 1–0$ rotational ground-state transition of the main isotopologue of methylidyne, $^{12}$CH$_2$, near 835.2 GHz, cannot be observed from the ground for objects with Galactic radial velocities because of a strong telluric O$_2$ line approximately 1.1 GHz lower (Golubiatnikov & Krupnov 2003; Drouin et al. 2010). Observations of the J = 1–0 line of $^{13}$CH$_2$ at ~5 GHz lower frequency are however possible.

Falgarone et al. (2005) reported its detection toward the bright star-forming region G10.6–0.4 and evaluated from their observation the rest frequency as 830 ± 3 MHz. Two alternative values for the rest frequency, 830 107 ± 1 or 830 193 ± 4 MHz, remained viable due to ambiguities in assigning the observed feature to LSR velocity components possibly associated with this source. These were discarded on the basis of the poor agreement with the prediction of Pearson & Drouin (2006) who had reported a transition frequency for $^{13}$CH$_2$ at ~830 132 MHz. This value was based on a combined analysis of 1.1 GHz lower frequency is however possible.

Our observations of $^{13}$CH$_2$, however (see Sect. 3) indicate a rest frequency of around 830.2 GHz if we assume that this cation has an absorption profile similar to SH$^+$, HCl, H$_2$CO, or $c$-C$_3$H$_2$.

Müller (2010) performed an analysis similar to the one published by Pearson & Drouin (2006) in order to evaluate rotational data for isotopologues of CH$^+$ independently. Applying appropriate parameters which describe the breakdown of the Born-Oppenheimer approximation, he obtained a rest frequency for SH$^+$.
13CH⁺ J = 1–0 compatible with the present observations. The reviewer of Müller (2010) pointed out new laboratory measurements of the J = 1–0 transitions of 13CH⁺, 12CH⁺, and 12CD⁺ which were submitted subsequently by Amano (2010). Not only was the value for 13CH⁺ in quite good agreement with the estimate from our observations, but it was also shown that the previously reported value for 13CH⁺ was incorrect by several tens of megahertz. Including the data from Amano (2010) in his analysis, Müller (2010) calculated transition frequencies for several isotopologues of CH⁺ which now should be quite reliable and which are in the CDMS catalog. The 13CH⁺ J = 1–0 value is again given in Table 1.

The dipole moment of H 35Cl for CH⁺ was taken from an ab initio calculation by Cheng et al. (2007); the change in dipole moment upon substitution of 12C with 13C is assumed to be small. A value of 1.7 D was used in the CDMS catalog (Müller et al. 2001, 2005).

2.3. HCl, c-C₃H₂, H +3 CO⁺, and CO

The rest frequencies for the J = 1–0 transitions of both H 35Cl and H 37Cl, which have hfs, were taken from the JPL catalog ² (Pickett et al. 1998). These frequencies were published by De Lucia et al. (1971). The dipole moment of H 35Cl for v = 0, J = 1 has been determined as 1.1086 (3) D by de Leluw & Dymanus (1973); the dipole moment of H 37Cl is expected to be only marginally different. See Table 1 for the frequencies of HCl and the other species considered.

The estimated accuracy for each of the three hyperfine components is 100 kHz, sufficient for the present analysis. It should be mentioned in this context that improved rest frequencies have been published by Klaus et al. (1998) and Cazzoli & Puzzarini (2004) employing Lamb-dip spectroscopy.

The c-C₃H₂ frequency data were also taken from the JPL catalog. The 212−101 transition was measured by Vrtilek et al. (1987); the reported uncertainty is smaller than the value used in the JPL catalog.

The H +3 CO⁺ and CO rest frequencies were taken from the CDMS catalog (Müller et al. 2001, 2005). The rest frequency of the J = 1–0 transition of H +3 CO⁺ is from an astronomical observation by Schmid-Burgk et al. (2004); values for both CO transitions result from Lamb-dip measurements by Winnewisser et al. (1997).

3. Observations and data reduction

3.1. Overview

We have used the Atacama Pathfinder Experiment (APEX) 12 m telescope for observations of several sources in a number of submillimeter wavelength transitions of SH⁺ whose accurate frequencies have recently been determined (see Sect. 2); these include the quartet of ground-state hfs lines near 683 GHz. Our observations, described in Sect. 3.2, led to the detection of these lines in absorption against Sgr B2(M) and (N). In addition to absorption from gas associated with the GC, we also find absorption at the radial velocities belonging to intervening spiral arms, which demonstrates that this species is widespread in the Galactic ISM.

For diverse reasons, our results for other SH⁺ lines were not as clear as those obtained for the 683 GHz line, namely the N = 1–0, J = 0–1 lines near 346 GHz, which are completely blended with the CO J = 3–2 line and our observations of the N = 2–1, J = 1–1 lines were inconclusive. We made, however, an unambiguous detection of absorption in the J = 1–0 transition of the 13CH⁺ radical near 830 GHz, again from gas in the Sgr B2 region and from spiral arm clouds. Absorption in that line has previously been reported by Falgarone et al. (2005) toward G10.6+0.4, leading to an estimate of its rest frequency that is discussed in Sect. 2.2.

Finally, we took a wide bandwidth spectrum that covers the J = 1–0 transitions of both the H 35Cl and H 37Cl isotopologues of hydrochloric acid. The former had been observed by Zmuidzinas et al. (1995) toward a position midway between Sgr B2(M) and (N). Since their spectrum only covered the LSR velocity range between −10 and +140 km s⁻¹ it does not contain information for the spiral arm feature velocities. While we confirm the Sgr B2 velocity absorption, no clear absorption is found toward the latter in our more sensitive and wider bandwidth spectra. In Sect. 4.1.4, our upper limits for these diffuse lines of sight are compared with the tentative ultraviolet detection of HCl absorption toward ζ Oph by Federman et al. (1995).

3.2. APEX observations and data reduction

Our SH⁺ observations were made on 2008 September 19 and 25 under good to very good weather conditions with the 12-m Atacama Pathfinder Experiment telescope, APEX³ (Güsten et al. 2006). The precipitable water vapor (PWV) content was between 0.3 and 0.7 mm throughout the observations.

The 683 and 893 GHz lines were measured in the lower sideband (LSB) with the MPIfR-built CHAMP+ receiver array (Kasemann et al. 2006). CHAMP+ consists of two modules of 7 pixels each with one central pixel and the others forming a hexagon around it. The one module covers the 350 µm atmospheric window and the other the 450 µm window. Calibration was obtained using the chopper wheel technique, considering the different atmospheric opacities in the signal and image sidebands of the employed double sideband receivers. The image sideband was rejected to the 10 dB level. During the observations the single sideband system temperatures at 683 GHz were between 1700 and 2600 K. To ensure flat spectral baselines, the wobbling secondary was chopped with a frequency of 1.5 Hz and a throw of 240° about the cross elevation axis. The wobbler was operated in symmetric mode, which means that the on source and off positions are interchanged between subsequent subscans, which cancels any asymmetries in the optical paths. Such observations deliver a reliable estimate of the continuum level. We found, however, that the quality of the baseline deteriorated with increasing continuum flux density.

The radiation was analyzed with a new incarnation of the MPIfR Fast Fourier Transform spectrometer (FFTS) (Klein et al. 2006), which provided two 1.5 GHz wide modules set to 1024 frequency channels each. The resultant channel spacing was 1.46 MHz, corresponding to 0.49 and 0.70 km s⁻¹ at the highest and lowest frequency we observed (893 and 625 GHz, respectively). The FFTS modules were operated in series with an overlap of 300 MHz to provide a total coverage of 2.4 GHz bandwidth. To check the telescope pointing, drift scans were made across the continuum of Sgr B2(N). Pointing corrections were

³ This publication is based on data acquired with the Atacama Pathfinder Experiment (APEX), APEX is a collaboration between the Max-Planck-Institut für Radioastronomie, the European Southern Observatory, and the Onsala Space Observatory.
4. Results and data analysis

During our three observing campaigns, we have gathered data that allow unambiguous identification of the SH$^+$ and $^{13}$CH$^+$ molecules toward Sgr B2. In addition, we have made observations of the $J = 1−0$ ground-state transition of both the H$^{35}$Cl and H$^{37}$Cl isotopologues of hydrogen chloride.

In absorption spectroscopy, the column density in a transition’s lower energy level, $N_l$, can be calculated from its observed optical depth, $\tau$, and line width $\Delta v$ if its excitation temperature, $T_{ex}$, is known:

$$N_l = \frac{h}{8\pi^2S\mu^2} \left[1 - e^{-\Delta v/\tau_{rot}}\right]^{-1} \tau \Delta v,$$

where $A_D$ is the Einstein A coefficient; $h$ and $k$ are the Planck and Boltzmann constants, respectively, and $\tau = E_a - E_l$ the transition’s rest frequency; $E_a$ and $E_l$ are its upper and lower energy levels, respectively.

The total column density, $N_{tot}$, is given by

$$N_{tot} = \frac{N_l}{g_l} e^{E_l/kT_{rot}} Q(T_{rot}),$$

where $Q$ is the partition function for the rotation temperature, $T_{rot}$.

In the case of a line with a single absorption component, the optical depth and line width are usually determined by a Gaussian fit to the line profile and $\tau$ is calculated from the line to continuum intensity ratio:

$$\tau = -\ln(1-T_{L}/T_{C})$$

where $T_{L}$ and $T_{C}$ are the observed line and continuum brightness temperature, respectively.

Things are generally not so simple for the immensely line-rich Sgr B2 sources, for which practically the whole (sub)mm range contains a large number of lines from different species in each chosen frequency interval, many of them blended. To make things even more complex, many of the simpler species show multiple absorption components originating from various spiral arms along the line of sight that are blended with each other and with spectral components from lines of other species at GC velocities. Lines showing hfs, such as SH$^+$ are yet more difficult to analyze. To deal with this, we employ, as described by Belloche et al. (2008), the XCLASS package created and developed by Peter Schilke. XCLASS is an extension of the CLASS spectral line data reduction program that is part of the GILDAS software package developed by the Institute for Radio Astronomy at Millimeter Wavelengths (IRAM). Using XCLASS one may fit all lines in a spectrum simultaneously as described in Sect. 4.1.

For each species, XCLASS assumes that the level populations are described by a single excitation temperature, which we refer to as the rotation temperature, $T_{rot}$. Different species can have different rotation temperatures. Here we divide between two cases: First, the critical densities of all the lines in the frequency range of interest are lower than the density in the modeled emission region. Then we are dealing with local thermodynamic equilibrium (LTE), which applies, e.g., for the extremely line rich hot cores associated with Sgr B2(M) and (N). In particular in the latter, the complex molecules NH$_2$CH$_2$CN, C$_2$H$_5$OCHO, and C$_2$H$_7$CN along with the $^{13}$C isotopologues of vinyl cyanide have recently been identified using XCLASS with model temperatures of ≈100–150 K (Belloche et al. 2008, 2009; Müller et al. 2008). In the second, very low density case, which applies for the absorption lines discussed in this paper, $T_{rot}$ equals the temperature of the cosmic microwave background radiation, $T_{CMB}$, i.e. 2.728 K. While this might be a good assumption for clouds far from the strong Sgr B2 continuum sources, e.g., in the spiral arms, assuming $T_{rot} = T_{CMB}$ will underestimate column densities for molecules in the vicinity of Sgr B2(M) and (N).

4.1. Modeling of the absorption lines toward Sgr B2(M)

4.1.1. The model for the spiral arm and galactic center LSR velocity features

The SH$^+(1−0)$ spectra obtained with the CHAMP+ array consist of the superposition of a number of absorption components associated with the dense core Sgr B2(M) and several molecular clouds distributed along the line of sight with different systemic velocities (see, e.g., Greaves & Williams 1994).

The association of the absorption components’ LSR velocities with Galactic spiral arms or kinematic features associated with the GC located along the line of sight is presented in Table 2. It is essentially based on the velocity interpretation of H$_2$CO and CS absorption by Whiteoak & Gardner (1979) and Greaves & Williams (1994), respectively, as well as the analyses of Sofue (2006) and Vallée (2008). Although in the GC direction absorption close to $V_{LSR} = 0$ could in principle come from any location on the line of sight, we favor a physical association with the GC since Gardner & Whiteoak (1981) found low values of the $^{12}$C/$^{13}$C ratio (20–30) for this velocity range, consistent with a Galactic center origin.

The blending of these absorption components is further complicated by the hyperfine structure of the SH$^+$ transition. To allow meaningful fitting, we used information derived from the absorption spectra of other molecules obtained as part of a complete line survey done with the IRAM 30 m telescope in the

$^4$ http://www.astro.uni-koeln.de/projects/schilke/

$^5$ http://www.irmf.fr/IRAMFR/GILDAS/
Table 2. Velocity ranges and $^{12}\text{C}^{13}\text{C}$ isotopic ratios of the Galactic absorption components along the line of sight of Sgr B2(M).

| Velocity range (1) | $^{12}\text{C}^{13}\text{C}$ (2) | Location (3)            |
|-------------------|---------------------------------|-------------------------|
| ~62               | 20                              | Galactic Center, Sgr B2 |
| 39–25             | 40                              | Scutum/Crux arm         |
| 22–12             | 60                              | Sagittarius arm         |
| 8 – 9             | 20                              | Galactic Center         |
| ~13 – 50          | 40                              | 3 kpc expanding ring    |
| < – 53            | 20                              | Galactic Center         |

3 mm atmospheric window toward both hot cores Sgr B2(M) and Sgr B2(N) (see Belloche et al. 2008, 2009).

The line survey was analysed with the XCLASS software (see Sect. 4) . Each molecule identified in the survey was modeled with the following free parameters: source size, temperature, column density, linewidth, and velocity offset with respect to the systemic velocity of the source, 62 km s$^{-1}$ for Sgr B2(M). When several components were needed to reproduce the observed spectrum of a molecule, we fitted a set of parameters for each component. The combination of the predicted spectra of all identified molecules was done assuming that the emission adds up linearly (for more details, see Belloche et al. 2008).

To model the absorption lines observed toward Sgr B2(M), we assumed a beam-averaged continuum brightness temperature $T_{\text{cont}}$ of 5.9 K in the 3 mm window, as derived from the saturated absorption spectra of HCN and CN (see Table 1). The modeling of the absorption components was done in the $T_{\text{tot}} = T_{\text{CMB}}$ approximation with a flag indicating that the absorption spectrum has to be computed against a background emission consisting of both the continuum emission and the contribution of the other molecules seen in emission, i.e. for each absorption component with the equation

$$T_v = (J_v(T_{\text{ex}}) - J_v(T_{\text{cont}})) \left(1 - e^{-\tau_v}\right) + T_{\text{em}}^\text{cont} e^{-\tau_v},$$

with $T_{\text{ex}}$, the excitation temperature, $T_{\text{cont}}$ the background brightness temperature, $T_{\text{em}}^\text{cont}$ the emission line spectrum, and $\tau_v$ the opacity of the line at frequency $v$, for a beam filling factor of 1.

Table 2 also lists the $^{12}\text{C}^{13}\text{C}$ isotopic ratios we assumed. The $^{12}\text{C}^{13}\text{C}$ isotopic ratio of the Galactic Center components was fixed to 20 (Müller et al. 2008). This value is compatible with the Galactic gradient derived by Milam et al. (2005, Eq. (5)). Their equation was additionally employed to fix the ratio to 40 for the Scutum and Norma arm components, and 60 for the Sagittarius arm components, with the galactocentric distances of Vallée (2008). The $^{16}\text{O}^{18}\text{O}$ isotopic ratio was taken from Wilson & Rood (1994): 250 for the GC components, 327 for the Scutum and Norma arm components, and 560 for the Sagittarius arm components.

We present, in Fig. 2d and e, the results of our modeling for $^{c}$C$_2$H$_2$(2$_{12}$–1$_{01}$) and H$^{13}$CO$^+$ (1–0), respectively. The model for H$^{13}$CO$^+$ (1–0) was obtained by fitting HCO$^+$, H$^{12}$CO$^+$, and HC$^{18}$O$^+$ simultaneously. The fit to the observed H$^{13}$CO$^+$ (1–0) spectrum consists of four components in emission (one for the main emission peak and three to reproduce the wings), one absorption component to mimic the self-absorption in Sgr B2(M)\(^6\) and 34 absorption components associated with the diffuse clouds along the line of sight, with linewidths varying between 3 and 8 km s$^{-1}$ and an excitation temperature arbitrarily fixed to 2.7 K. The parameters of the fit to H$^{13}$CO$^+$ are listed in Table 4. The model predicts too strong absorption for the H$^{13}$CO$^+$ (1–0) components with $v < -50$ km s$^{-1}$, while the corresponding HCO$^+$ (1–0) components are well fitted (not shown here). The disagreement must result either from an underestimate of the $^{12}\text{C}^{13}\text{C}$ isotopic ratio or from contamination by emission lines that are not yet included in our complete model. It could in principle also.

---

\(^6\) Where noted, for the components associated with Sgr B2 (around +62 km s$^{-1}$), a $T_{\text{rot}} > T_{\text{CMB}}$ was assumed.

\(^7\) Although the fits to the self-absorption features in Fig. 2d and e look relatively good, we emphasize that a uniform $T_{\text{rot}} = T_{\text{CMB}}$ model is not complex enough to provide reliable physical parameters to describe the self-absorption. The parameters listed for the self-absorption components in the following tables should therefore be viewed with caution.
result from larger excitation temperatures for HCO$^+$. All components have a rotation temperature of 2.7 K except components \( n_1 = 1 \) of c-C\(_3\)H\(_2\) with 15.0 and 3.0 K, respectively, and component \( n_1 = 2 \) of H\(^{13}\)CO$^+$ which has 3.1 K. The emission components of the H\(^{13}\)CO$^+$ model are the same as in Table 4 and are not listed here. (a) Component number. (b) LSR velocity, the same for all four molecules except for 1 component of 13CH$^+$ (2: 68.7 km s\(^{-1}\)), 2 components of c-C\(_3\)H\(_2\) (1: 6.01 km s\(^{-1}\); 2: 6.05 km s\(^{-1}\)), and 1 component of H\(^{13}\)CO$^+$ (2: 64.5 km s\(^{-1}\)). (c) Linewidth (FWHM), the same for all four molecules except for 2 components of c-C\(_3\)H\(_2\) (1:15.0 km s\(^{-1}\); 2:11.0 km s\(^{-1}\)) and for 1 component of H\(^{13}\)CO$^+$ (2: 12.0 km s\(^{-1}\)). (d) Assumed $^{13}$C/$^{12}$C isotopic ratio for HCO$^+$ and CH$^+$. (e) Column density. (f) Column density ratio SH$^+$/13CH$^+$. (g) Column density ratio SH$^+$/c-C\(_3\)H\(_2\). (h) Column density ratio SH$^+$/HCO$^+$.

The fit to c-C\(_3\)H\(_2\) was done with velocity and linewidth parameters slightly different from HCO$^+$, although we tried to stay as close as possible to the components identified in HCO$^+$. The parameters of the fit to c-C\(_3\)H\(_2\) are listed in Table 3. The model consists of one component in emission (we did not attempt to model the possible wing emission in this case), one absorption component to mimic the self-absorption, and 30 absorption components associated with the diffuse clouds, with an excitation temperature of 2.7 K and linewidths varying between 3 and 6 km s\(^{-1}\).

### 4.1.2. Modeling the SH$^+$ absorption

Since we considered c-C\(_3\)H\(_2\) a priori to be a better diffuse gas tracer than H\(^{13}\)CO$^+$ (but see Sect. 5) and because of the added uncertainty of assigning a $^{13}$C/13C ratio to each absorption component, we decided to model the SH$^+$ absorption spectrum based on the parameters derived for c-C\(_3\)H\(_2\), i.e. we used the same number of absorption components with the same velocities and line widths, except for the component physically associated with Sgr B2(M) itself. Again, we fixed the excitation temperature of each component to 2.7 K. Since the observations were done in wobbler mode, we trusted the baseline level and derived the level of continuum emission directly from the observed spectra shown in Fig. 5. To compute the synthetic spectra, we assumed that the physical parameters of the absorbing components are uniform across the CHAMP+ field of view and therefore we used the same set of parameters for all pixels. The resulting synthetic spectra are overlaid on the observed spectra in Fig. 5. The agreement is quite good in general, which gives us some more confidence in the way we estimated the continuum level. However, significant deviations are seen for pixels 1, 3, and 4. As mentioned in Sect. 3, the baseline quality of the CHAMP+ array drops with increasing level of continuum emission and
Fig. 3. a)–d) Column density profiles computed by adding the Gaussian velocity absorption components listed in Table 3. The components with upper limit were not included. e)–g) Abundance profiles relative to H$_2$. The H$_2$ column density was computed from the HCO$^+$ column density assuming an HCO$^+$ abundance of $5 \times 10^{-9}$. h)–j) Abundance profiles relative to H$_2$. k) The H$_1$ column density was computed from comparing an H$_1$ absorption with an H$_1$ emission profile (see text).

line contamination from the hot molecular core associated with Sgr B2(M). Pixel 4 is the most affected, and we believe that the poor quality of the fit is mainly due to this problem. As far as the northern pixels 1 and 3 are concerned, the main absorption component is much stronger than the one predicted by our simple model. This may be due to spatial variations of the SH$^+$ column density across the Sgr B2 molecular cloud since the cloud is far from being uniform (in particular, the hot, dense core Sgr B2(N) is located $\sim$50$''$ to the north of Sgr B2(M)). If the variations from pixel to pixel can be trusted, then we can estimate the variations of the SH$^+$ column densities in the spiral arm diffuse clouds over the footprint of CHAMP$^+$ by modeling each pixel separately. This exercise yields column density variations typically on the order of a factor 2, but in some cases up to a factor 5. However, given the low signal-to-noise ratio, the unknown baseline quality, and the line blending, these numbers are very uncertain and it is unlikely that they really reflect the spatial variations of the SH$^+$ column density.

The parameters used to fit the SH$^+$ 1$_1$–0$_1$ absorption spectrum are listed in Table 3 and the fit to the spectrum obtained with pixel 2 is plotted again in Fig. 2b for a direct comparison with HCl, $^{13}$CH$^+$, c-C$_3$H$_2$, and H$^{13}$CO$^+$. Although the decision to fix the linewidths and velocities to those derived from c-C$_3$H$_2$ helps a lot to constrain the SH$^+$ model, the hyperfine structure of SH$^+$ and the limited signal-to-noise ratio of the observed spectra do not allow to find a unique solution. Using the somewhat different set of velocity and linewidth parameters derived from HCO$^+$, we were able to find a synthetic spectrum for SH$^+$ as good as the SH$^+$ model derived from c-C$_3$H$_2$ (the parameters of this alternative model are listed in Table 4). Therefore, the SH$^+$ model described in Table 3 should be considered as a possible model rather than the best-fit model. Nevertheless, if we assume that c-C$_3$H$_2$ and SH$^+$ trace the same diffuse clouds, then it makes sense to compare the column densities listed in Table 3. Column 10 lists the column density ratio SH$^+$/c-C$_3$H$_2$. It varies by nearly two orders of magnitude, from <0.6 to $\sim$33. As a caveat, we remind that the SH$^+$ model assumes no contamination from emission lines of other molecules. If there are contaminating emission lines, then the column densities derived for the SH$^+$ components contaminated by these emission lines are lower limits.

Unfortunately, the SH$^+$ 1$_0$–0$_1$ line at 345.9 GHz is heavily blended with the spiral arm components of the CO 3–2 line seen in absorption (see Fig. 6a). The $T_{\text{rot}} = T_{\text{CMB}}$ model derived for the 1$_1$–0$_1$ line predicts 1$_0$–0$_1$ spiral arm components in absorption that are relatively consistent with the observed spectrum dominated by the CO 3–2 features, except around 62 km s$^{-1}$, the systemic velocity of Sgr B2(M). At 893 GHz, there is no clear evidence for the SH$^+$ 2$_1$–1$_1$ line (see Fig. 7). Our $T_{\text{rot}} = T_{\text{CMB}}$ model predicts no significant absorption for this higher energy transition (see red spectrum in Fig. 7). On the other hand, this transition could partly contribute to the broad feature detected in emission between 58 and 125 km s$^{-1}$ (although the higher velocity half of that feature is uncertain due to the limited baseline quality). An additional model component in emission is indeed permitted by the 893 GHz spectrum and can even solve the disagreement at 62 km s$^{-1}$ between the synthetic and observed spectra of the 1$_0$–0$_1$ transition. If this emission component has a size smaller than $\sim$20$''$, then the $T_{\text{rot}} = T_{\text{CMB}}$ synthetic spectrum of the ($-20.4''$,+1.4'') CHAMP+ pixel at 683 GHz (shown in Fig. 2) will be unaffected and still provide a good fit to the observations. However, the fit to the spectrum of the central pixel at 683 GHz (see Fig. 5) will be worse, and a more elaborate radiative transfer modeling would be needed to find a consistent fit for this potential emission component.
we showed in Fig. 2e, but it can be used to roughly estimate the listed in Table 5. Only the main absorption component is clearly detected for both isotopologues. For all other velocity components but one, we used a column density of $2^{11}$.

### 4.1.4. Modeling the HCl absorption only from the Sgr B2 region

The HCl and $^{35}$Cl transitions detected in absorption toward Sgr B2(M) were also modeled in the $T_{\text{rot}} = T_{\text{CMB}}$ approximation (see Fig. 8). We used the SH$^+$ model as a reference, keeping the velocity offsets and linewidths unchanged. The resulting fit, shown in red in this figure, is in good agreement with the observed spectrum, although it could certainly be somewhat better if the line widths were taken as free parameters for the fitting.

The column densities resulting from this fit are listed in Table 3, as well as the SH$^+$/$^{35}$Cl$+$ and the SH$^+$/$^{37}$Cl$+$ column density ratio. The latter varies significantly from component to component, from 0.07 to 1.2, if we exclude components 31 and 32 in Table 3 at whose velocity the signal-to-noise ratio in the SH$^+$ spectrum is very low and which are not detected in the $^{13}$CH$^+$ absorption at all.

The $^{13}$CH$^+$ 1–0 spectrum shows an absorption feature at $+172.6$ km s$^{-1}$. Although absorption in CO is detected at this velocity in our 3 mm line survey in the CO 1–0 and $^{13}$CO 1–0 lines (see Fig. 6), this component is neither detected in H$^{13}$CO$^+$ 1–0, c-C$_3$H$_2$ 2–1, nor in SH$^+$ 1–0 (see Fig. 2). Features at this velocity are usually attributed to the Expanding Molecular Ring (EMR, e.g., Morris & Serabyn 1996) but $+172.6$ km s$^{-1}$ would refer to the far side of the ring, hence no absorption is expected and it is possibly more likely that this feature is an as yet unidentified (U) absorption line.

We also list in Table 3 the parameters of an alternative H$^{13}$CO$^+$ $T_{\text{rot}} = T_{\text{CMB}}$ model fitted with the same velocity components as c-C$_3$H$_2$ (i.e. same linewidths and LSR velocities). This model is less good than the one that we described above and that we showed in Fig. 2e, but it can be used to roughly estimate the SH$^+$/HCO$^+$ column density ratio (Col. 12 of Table 3). This ratio varies by about one order of magnitude, from 0.07 to 2.38.

### 4.1.3. The $^{13}$CH$^+$ absorption

The $^{13}$CH$^+$ 1–0 transition detected in absorption toward Sgr B2(M) was also modeled in the $T_{\text{rot}} = T_{\text{CMB}}$ approximation (see Fig. 2c). We used the SH$^+$ model as a reference, keeping the velocity offsets and linewidths unchanged. The resulting fit, shown in red in this figure, is in good agreement with the observed spectrum, although it could certainly be somewhat better if the line widths were taken as free parameters for the fitting.

The column densities resulting from this fit are listed in Table 3, as well as the SH$^+$/$^{13}$CH$^+$ and the SH$^+$/$^{37}$CH$^+$ column density ratio. The latter varies significantly from component to component, from 0.07 to 1.2, if we exclude components 31 and 32 in Table 3 at whose velocity the signal-to-noise ratio in the SH$^+$ spectrum is very low and which are not detected in the $^{13}$CH$^+$ absorption at all.

The $^{13}$CH$^+$ 1–0 spectrum shows an absorption feature at $+172.6$ km s$^{-1}$. Although absorption in CO is detected at this velocity in our 3 mm line survey in the CO 1–0 and $^{13}$CO 1–0 lines (see Fig. 6), this component is neither detected in H$^{13}$CO$^+$ 1–0, c-C$_3$H$_2$ 2–1, nor in SH$^+$ 1–0 (see Fig. 2). Features at this velocity are usually attributed to the Expanding Molecular Ring (EMR, e.g., Morris & Serabyn 1996) but $+172.6$ km s$^{-1}$ would refer to the far side of the ring, hence no absorption is expected and it is possibly more likely that this feature is an as yet unidentified (U) absorption line.

We also list in Table 3 the parameters of an alternative H$^{13}$CO$^+$ $T_{\text{rot}} = T_{\text{CMB}}$ model fitted with the same velocity components as c-C$_3$H$_2$ (i.e. same linewidths and LSR velocities). This model is less good than the one that we described above and that we showed in Fig. 2e, but it can be used to roughly estimate the SH$^+$/HCO$^+$ column density ratio (Col. 12 of Table 3). This ratio varies by about one order of magnitude, from 0.07 to 2.38.

#### 4.1.4. Modeling the HCl absorption only from the Sgr B2 region

The HCl and $^{37}$Cl transitions detected in absorption toward Sgr B2(M) were also modeled in the $T_{\text{rot}} = T_{\text{CMB}}$ approximation (see Fig. 8). We used the SH$^+$ model as a reference, keeping the velocity offsets and linewidths unchanged, except for the main absorption component associated with Sgr B2(M) itself. The resulting fit is shown in red in Fig. 8 and the fit parameters are listed in Table 5. Only the main absorption component is clearly detected for both isotopologues. For all other velocity components but one, we used a column density of $2.8 \times 10^{12}$ cm$^{-2}$, represented by the red line in Fig. 8, to get a rough estimate of the column density upper limits. Only one additional velocity component ($n_\text{c} = 6; -17$ km s$^{-1}$) marginally shows absorption in the main isotopologue HCl at 2.8 times this value. Due to the compact hyperfine structure, the line width of the main absorption component (8 km s$^{-1}$) is somewhat uncertain, but our modeling suggests that it is significantly smaller than for the other species. Finally, for Sgr B2(M) we derive an isotopic [H$^{35}$Cl/H$^{37}$Cl] ratio of $\sim 4$, consistent with the terrestrial value.

#### 4.2. Summary of modeling

To visualize the results of our modeling presented in Tables 3 and 4, we show, in Fig. 3, the column densities and abundances that we derived for the species considered as functions of LSR velocity. Figure 4 presents the CH$^+$ to SH$^+$ abundance ratio vs. LSR velocity.

### 5. Discussion

#### 5.1. Column densities and abundances

##### 5.1.1. Caveats

We would like to preclude our discussion of the SH$^+$, $^{13}$CH$^+$, and HCl abundances in the spiral arm clouds with some cautionary notes. First, the assignment of velocity features to Galactocentric distance is by no means clear-cut. For example, Sofue (2006), from a careful analysis of the longitude-velocity diagram of the GC region, assigns certain velocity features to peculiar components of the complex Galactic center velocity field, namely the GC molecular ring and the GC expanding ring, both within a Galactocentric radius, $R$, of 600 pc of the GC. In addition to several spiral arms, he invokes expanding rings at $R = 3$ and 4 kpc. Some of Sofue’s conclusions are at variance from the LSR velocity-location assignment we present in Sect. 4.1. Second, SH$^+$ and $^{13}$CH$^+$ may in principle be associated with predominantly atomic or molecular diffuse clouds. For meaningful abundance calculations, it is thus necessary to have values for both the atomic hydrogen column density, $N$(HI), and the molecular hydrogen column density, $N$(H$_2$). Actually, the clouds from which we see absorption may have complex structure, e.g., a Giant Molecular Cloud region and a diffuse atomic envelope (see Sect. 5.2) and/or we may be dealing with more than one cloud along each line of sight. Certainly, the HI spin temperatures are in the range of values found for diffuse clouds and significantly higher than the canonical GMC temperatures values of 20–30 K.

Two final, more technical caveats relate to the way we derive column densities. For the 3 mm Sgr B2(M) spectra for H$^{13}$CO$^+$ and c-C$_3$H$_2$ we have constructed full XCLASS models considering all the absorption from these molecules plus emission from them and all other molecules. In contrast, for the submillimeter spectra, we have not done this. While even the 3 mm spectra may be contaminated by emission features inadequately treated by the model, for the submm absorption spectra this is a much greater source of uncertainty for line assignments and intensity predictions, making, strictly speaking all the column densities we determine lower limits. We do at present not feel confident to construct a comprehensive model for the submm spectra. Similarly, if, as discussed in Sect. 4, excitation by the ambient radiation field is non-negligible, then $T_{\text{rot}} > T_{\text{CMB}}$, which would make our column densities underestimates.

Finally, our XCLASS-based method makes it difficult to derive statistical errors and, thus, upper limits rigorously in a $\chi^2$ sense. Rather, upper limits are determined by assuming a column density, calculating a model spectrum and then “eye-balling” whether it is consistent with the data.
5.1.2. Atomic and molecular hydrogen column densities

The column density of atomic hydrogen, $N(\text{HI})$, can be calculated from measurements of the 21 cm HI line’s optical depth, $\tau(\text{HI})$, at the intervening clouds’ velocities (e.g., Garwood & Dickey 1989) and a determination of their spin temperatures, $T_s$, as described by Lazareff (1975). The method invokes a combination of interferometric observations to, first, directly determine the optical depths of the absorption components and, second, single dish observations to measure the (optically thick) line’s brightness temperature. As described in a forthcoming paper, we have performed the necessary single dish observations with the Effelsberg 100 m telescope and obtained an optical depth spectrum ($\tau(\text{HI})$ vs. $V_{\text{lsr}}$) measured toward Sgr B2(M) with the NRAO Very Large Array from Lang (pers. comm.). We note our values for $N(\text{HI})$ are generally lower than those derived by Vastel et al. (2002). This is partially due to their assumption of $T_s = 150$ K for all velocity components.

A determination of $N(\text{H}_2)$ is more difficult, as selection of a “universal” trace molecule for molecular hydrogen is not straightforward. For meaningful modeling, such a molecule’s lines would be required to be subthermally excited, meaning that their relative level populations be determined by $T_{\text{CMB}}$. This means, for example that, due to their small dipole moments and resulting low critical densities, isotopologues of CO are not suited. A possible choice for an H$_2$ tracer, which we adopt here, might be HCO$^+$. Lucas & Liszt (1996) from their study of this molecule’s 89 GHz $J = 1-0$ ground-state transition, conclude its abundance (relative to H$_2$) to be “$\sim$3–6 $\times 10^{-9}$ across a very broad range of extinction”, meaning between hydrogen column densities $\sim$0.1 and $4 \times 10^{20}$ cm$^{-2}$. These authors base this finding, first, on the very tight correlation between the HCO$^+$ and the OH column densities and, second, on the fact that OH has the same abundance ($10^{-7}$) in diffuse as in dense dark clouds. While their own absorption data only sample hydrogen column densities within the range quoted above, they find that the correlation holds at $>10$ times higher values than its upper boundary. Here we adopt $5 \times 10^{-9}$ for the HCO$^+$/H$_2$ abundance ratio. This value is of the same magnitude as that listed by van Dishoeck et al. (1993) for (high column density) regions of low and high mass star formation.

Since HCO$^+$ absorption toward Sgr B2 is optically thick even for the non-Sgr B2 region velocity features, we use, as described in Sect. 4.1, H$_{13}$CO$^+$ spectra and obtain the main-isotope’s column density by scaling with the appropriate $^{12}$C/$^{13}$C ratios given in Col. 4 of Table 3.

Our estimates for $N(\text{HI})$ and $N(\text{H}_2)$ for the absorption components are listed in Table 6. For simplicity’s sake and motivated by our optical depth fitting of the HI data and also to allow comparison with other studies, we have grouped the velocity components into seven intervals. The HI and H$_2$ column densities and HI spin temperatures were derived as described above from HI and H$_{13}$CO$^+$ data fixed to values compatible with the values given in the table. The column densities of SH$^+$ and CH$^+$, presented in Table 7, were obtained by summing over the individual velocity components in Table 3 and multiplying the CH$^+$ column densities by the $^{12}$C/$^{13}$C ratios given for each component in that table.

5.2. The origin of the $^{13}$CH$^+$ and SH$^+$ absorption

Since it is a priori not clear whether the observed SH$^+$, CH$^+$ and HCl molecules are only associated with either atomic or
Table 4. Parameters of the best-fit LTE model of HІІCO+ and the LTE model of SH+ fitted with the same velocity components as HІІCO+.

| n° | V⊙a | ΔVc | N° | t°/c | N° | R12f |
|----|-----|-----|----|------|----|------|
| (km s⁻¹) | (km s⁻¹) | (cm⁻³) | | | (cm⁻³) | |
| 1  | 62.0 | 12.0 | 3.75 × 10¹⁴ | 20 | – | – |
| 2  | 80.0 | 20.0 | 5.00 × 10¹³ | 20 | – | – |
| 3  | 104.0 | 20.0 | 4.00 × 10¹² | 20 | – | – |
| 4  | 51.0 | 12.0 | 4.00 × 10¹³ | 20 | – | – |
| 5  | 64.5 | 12.0 | 1.36 × 10¹⁴ | 20 | 1.97 × 10¹⁴ | 0.07 |
| 6  | 35.0 | 7.0 | 4.82 × 10¹¹ | 40 | <2.82 × 10¹² | <0.14 |
| 7  | 30.0 | 5.0 | 7.83 × 10¹¹ | 40 | <2.82 × 10¹² | <0.09 |
| 8  | 25.5 | 3.0 | 3.01 × 10¹¹ | 40 | <2.82 × 10¹² | <0.23 |
| 9  | 22.0 | 5.0 | 2.53 × 10¹² | 60 | 8.45 × 10¹² | 0.05 |
| 10 | 17.0 | 5.0 | 2.05 × 10¹² | 60 | 2.25 × 10¹³ | 1.08 |
| 11 | 12.0 | 6.0 | 1.81 × 10¹² | 60 | 2.92 × 10¹³ | 0.25 |
| 12 | 7.6 | 4.5 | 1.20 × 10¹² | 20 | 2.54 × 10¹³ | 0.03 |
| 13 | 1.1 | 6.2 | 4.15 × 10¹² | 20 | 1.69 × 10¹³ | 0.20 |
| 14 | –5.5 | 7.0 | 6.02 × 10¹¹ | 20 | 1.97 × 10¹³ | 1.61 |
| 15 | –13.5 | 5.0 | 3.01 × 10¹¹ | 40 | 1.55 × 10¹³ | 1.26 |
| 16 | –19.5 | 5.0 | 6.62 × 10¹¹ | 40 | 8.45 × 10¹² | 0.31 |
| 17 | –26.3 | 5.0 | 7.22 × 10¹¹ | 40 | 8.45 × 10¹² | 0.29 |
| 18 | –31.0 | 5.0 | 2.17 × 10¹¹ | 40 | 8.45 × 10¹² | 0.96 |
| 19 | –36.5 | 4.0 | 1.20 × 10¹¹ | 40 | 8.45 × 10¹² | 1.72 |
| 20 | –41.0 | 3.0 | 1.57 × 10¹² | 40 | 7.04 × 10¹² | 0.11 |
| 21 | –45.7 | 3.0 | 6.02 × 10¹¹ | 40 | 4.23 × 10¹² | 0.17 |
| 22 | –49.5 | 3.0 | 3.01 × 10¹¹ | 40 | 4.23 × 10¹² | 0.34 |
| 23 | –54.0 | 4.0 | 1.99 × 10¹¹ | 20 | 9.30 × 10¹² | 1.59 |
| 24 | –59.3 | 4.0 | 5.72 × 10¹¹ | 20 | <2.82 × 10¹² | <0.24 |
| 25 | –66.0 | 5.0 | 4.21 × 10¹¹ | 20 | <2.82 × 10¹² | <0.33 |
| 26 | –72.0 | 5.0 | 4.21 × 10¹¹ | 20 | 9.86 × 10¹² | 1.15 |
| 27 | –76.3 | 4.0 | 2.71 × 10¹¹ | 20 | 8.45 × 10¹² | 0.98 |
| 28 | –80.1 | 4.0 | 2.71 × 10¹¹ | 20 | 7.04 × 10¹² | 1.27 |
| 29 | –84.3 | 5.0 | 5.12 × 10¹¹ | 20 | 1.27 × 10¹³ | 1.21 |
| 30 | –88.5 | 3.5 | 4.21 × 10¹¹ | 20 | <2.82 × 10¹² | <0.33 |
| 31 | –92.6 | 3.5 | 5.42 × 10¹¹ | 20 | 9.26 × 10¹² | 0.76 |
| 32 | –97.2 | 4.0 | 6.62 × 10¹¹ | 20 | 1.41 × 10¹³ | 1.04 |
| 33 | –102.2 | 5.0 | 1.57 × 10¹² | 20 | 1.69 × 10¹³ | 0.53 |
| 34 | –108.0 | 4.0 | 3.61 × 10¹¹ | 20 | 1.13 × 10¹³ | 1.53 |
| 35 | –112.0 | 4.0 | 4.82 × 10¹¹ | 20 | 8.45 × 10¹² | 0.86 |
| 36 | –116.0 | 4.0 | 3.61 × 10¹¹ | 20 | 1.41 × 10¹³ | 1.91 |
| 37 | –120.0 | 4.0 | 1.20 × 10¹¹ | 20 | 5.63 × 10¹² | 2.29 |
| 38 | –123.7 | 4.0 | 1.20 × 10¹¹ | 20 | 5.63 × 10¹² | 2.29 |
| 39 | –130.4 | 8.0 | 1.99 × 10¹¹ | 20 | 7.04 × 10¹² | 1.74 |

Notes. All components have a rotation temperature of 2.7 K except components n° = 1 to 4 of HІІCO+ which have 20.0 K and n° = 5 of HІІCO+ which has 3.1 K. (a) Component number. (b) LSR velocity, the same for both molecules except for one component of SH+ (5: 64.0 km s⁻¹). (c) Linewidth (FWHM), the same for both molecules except for one component of SH+ (5: 19.0 km s⁻¹). (d) Column density. (e) Assumed isotopic ratio HІІCO/HІІCO+. (f) Column density ratio SH+/HCO++.
Fig. 6. a) Spectrum obtained toward Sgr B2(M) at the frequency of the SH$^+$ $1_{0}$−$0_{1}$ line with the APEX telescope in main beam brightness temperature. The red curve is the synthetic spectrum described in Sect. 4.1, the horizontal dotted line shows the continuum level, and the vertical dotted line marks the systemic velocity of the source (62 km s$^{-1}$). The strong absorption lines are spiral arm components of CO 3–2. The lower axis gives the LSR velocity for SH$^+$, while the upper axis refers to CO, with the same labeling as in panel b). b) CO(1–0) spectrum obtained toward Sgr B2 as part of our line survey with the IRAM 30 m telescope. The horizontal dotted line indicates the zero level (after baseline removal because the observations were performed in position-switching mode with a far OFF position, which yields a very uncertain baseline level). In both panels, the dashed line marks the systemic velocity of the source in CO 3–2 and the dot-dashed line indicates the CO velocity $+172.6$ km s$^{-1}$ at which an extra absorption component appears in the $^{13}$CH$^+$ spectrum (see discussion in Sect. 4.1.3.).

Table 5. Parameters of the best-fit LTE model of HCl and H$^{37}$Cl.

| Molecule  | $n_{i}$ (1) | $V_{\text{LSR}}$ (2) | $\Delta V$ (3) | $N_{i}$ (4) |
|-----------|------------|---------------------|----------------|-------------|
| HCl       | 2          | 65.0                | 8.0            | $1.99 \times 10^{14}$ |
| H$^{37}$Cl| 2          | 65.0                | 5.0            | $7.60 \times 10^{12}$ |

Notes. (a) Same component numbering as in Table 3. (b) LSR velocity. (c) Linewidth. (d) Column density.

Fig. 7. Spectrum obtained toward Sgr B2(M) at the frequency of SH$^+$ $2_{1}$−$1_{1}$ with the APEX telescope in main beam brightness temperature. The red curve is the synthetic spectrum described in Sect. 4.1, i.e., showing no detectable emission, the horizontal dotted line shows the continuum level, and the vertical dotted line marks the systemic velocity of the source (62 km s$^{-1}$). The absorption line appearing at $\sim-105$ km s$^{-1}$ is the $J_{K, K_e} = 1_{11}$–$0_{10}$ ground-state line of HDO at 893.6387 MHz (Comito et al. 2003).

Fig. 8. Spectrum obtained toward Sgr B2(M) around 625 GHz with the APEX telescope in main beam brightness temperature. The red curve is the synthetic spectrum described in Sect. 4.1, the horizontal dotted line shows the continuum level, and the left and right vertical dotted lines mark the systemic velocity of the source (62 km s$^{-1}$) for HCl and H$^{37}$Cl, respectively. The strong emission close to the HCl line is likely due to a SO$_2$ line at 626.0873 MHz.

Notes. (a) Same component numbering as in Table 3. (b) LSR velocity. (c) Linewidth. (d) Column density.

(Abel et al. 2008). However, both dense P and XDRs have small volume filling factors, making them unlikely absorbers. These findings point to an (at least) two component picture for most of the absorption components, i.e., a diffuse envelope traced by HI, CH$^+$ and SH$^+$ absorption plus a denser core region, a view that is also invoked by Vastel et al. (2002) to explain the absorption they observed with ISO in the C$^+$ and O$^0$ fine structure transitions.

In Fig. 9 we plot CH$^+$ column density vs. hydrogen column density, $N$(HI) as defined above, for the seven velocity ranges in Table 6 (coded A–G). For each CH$^+$ column density entry two data points are plotted, both taken from the table. The left one (open squares) assumes that the CH$^+$ is only associated with atomic hydrogen, whereas the right one (filled squares) assumes it is only associated with molecular hydrogen or, essentially, all the hydrogen since $N$(H$_2$) = $N$(HI) for all velocities. We also plot (as circles) data for the two classic diffuse clouds against $\zeta$ Oph and $\zeta$ Per. For these, $N$(H$_2$) $\approx$ $N$(HI) $\approx 5 \times 10^{20}$ cm$^{-2}$. In addition, we present data for the translucent cloud toward HD 210121 where, again, two points assuming that the CH$^+$ is only associated with atomic (left) or molecular gas (right) are plotted. All values for the latter three sources, $N$(H$_2$), $N$(HI), and $N$(CH$^+$), are taken from de Vries & van Dishoeck (1988). The circles represent the absorption data Gredel (1997) determined toward a sample of southern OB associations. For these lines of sight, which have higher extinctions, between 0.36 and 4.2 mag, (mostly) corresponding to translucent clouds, we cannot discriminate between atomic and molecular hydrogen columns as Gredel lists $N$(CH$^+$) vs. $A_V$, which contains contributions from both. To convert his $A_V$ values to hydrogen column densities we use the results of the classic study of Bohlin et al. (1978), who found for low values of visual extinction (0.02 < $A_V$ < 0.6) a linear relation between $A_V$ and hydrogen column density, which as first argued by Dickman (1978), also holds for significantly higher $A_V$ values. It is consistent with a relation derived from
Table 6. H1 and H2 column densities of the absorption components.

| Label | Velocity range\(^{a}\) (km s\(^{-1}\)) | \(N_{\text{H1}}/T_b^{b}\) (cm\(^{-2}\) K\(^{-1}\)) | \(T_c^{c}\) (K) | \(N_{\text{H1}}^{d}\) (cm\(^{-2}\)) | \(N_{\text{H2}}^{e}\) (cm\(^{-2}\)) | Abs. comp./f |
|-------|-----------------|----------------|----------------|----------------|----------------|----------------|
| A     | 95.3–38.6       | 9.0(1.8) \times 10^{10} | 43(5)          | 3.9(0.9) \times 10^{21} | 5.4 \times 10^{23} | [2]           |
| B     | 23.2–12.9       | 1.5(0.5) \times 10^{10} | 65(10)         | 1.0(0.4) \times 10^{21} | 5.5 \times 10^{23} | [5, 6]        |
| C     | −12.9–33.5      | 8.5(2.0) \times 10^{10} | 93(10)         | 7.9(2.0) \times 10^{20} | 1.4 \times 10^{22} | [12, 13, 14, 15] |
| D     | −56.1–51.5      | 1.6(0.4) \times 10^{10} | 20(3)          | 3.1(0.9) \times 10^{20} | 2.0 \times 10^{22} | [17, 18, 19] |
| E     | −54.1–64.4      | 3.0(0.9) \times 10^{10} | 55(6)          | 1.7(0.6) \times 10^{20} | 2.6 \times 10^{21} | [16]          |
| F     | −69.6–85.0      | 2.6(0.7) \times 10^{10} | 80(8)          | 2.1(0.6) \times 10^{20} | 7.1 \times 10^{21} | [22, 23, 24, 25] |
| G     | −90.2–123.7     | 2.8(0.7) \times 10^{10} | 43(7)          | 1.2(0.4) \times 10^{20} | 1.6 \times 10^{22} | [27, 28, 29, 30, 31, 32] |

Notes. The numbers in parentheses are the uncertainties. \((^{a})\) Velocity range over which the H1 column density is computed. \((^{b})\) Ratio of H1 column density to spin temperature, obtained from the VLA data. \((^{c})\) H1 spin temperature derived from the Effelsberg data. \((^{d})\) H1 column density. \((^{e})\) H2 column density derived from the H\(^{13}\)C\(^{+}\) column densities assuming the isotopic ratios listed in Col. 4 of Table 3 and an HCO\(^{+}\) abundance of 5 \times 10\(^{-9}\) relative to H2. \((^{f})\) List of the absorption components used to compute the H2 column densities, with the same numbering as in Col. 1 of Table 3.

5.2.1. Comparison with individual diffuse clouds

While we advocate above a diffuse cloud origin of the CH\(^{+}\) absorption, we note that, apart from one velocity range (B, 12.9–23.2 km s\(^{-1}\)), our CH\(^{+}\) column densities are much higher than found in diffuse clouds and mostly higher than in the translucent cloud sample. However, the velocity ranges over which the values were determined, are mostly much larger than the line widths found in diffuse or translucent clouds (and even GMCs). For this reason, we plot in the lower panel of Fig. 9 the average column densities that a cloud with “typical” line width \(\Delta V_{\text{typ}}\) would have. This means we have divided for each of the velocity intervals A–G, both, CH\(^{+}\) and hydrogen column densities by the ratio of the width of the velocity interval and \(\Delta V_{\text{typ}}\). We chose \(\Delta V_{\text{typ}}\) to be 4.3 km s\(^{-1}\) FWHM, which is the mean of the sample of diffuse lines of sight for which Crane et al. (1995) present high spectral resolution CH\(^{+}\) data. This value is consistent with that discussed by Gredel (1997) for his translucent cloud sample. The thus calculated values correspond to a “typical” cloud with averaged properties.

Inspecting the CH\(^{+}\) column densities for these typical clouds we find values very similar to those found in diffuse and translucent clouds. We note that the ratio of molecular to atomic hydrogen column densities is in most cases higher than that found in translucent and much higher than in diffuse molecular clouds. The reason for this is almost certainly sight line superposition of the CH\(^{+}\)-containing diffuse/translucent and denser molecular clouds, as discussed above.

5.3. Comparison – SH\(^{+}\) and other S-bearing species and the CH\(^{+}\)/SH\(^{+}\) ratio

The values we derive for the SH\(^{+}\) column density, \(N(\text{SH}\(^{+}\))\), for the non-Sgr B2 region velocity ranges go up to 7 \times 10\(^{13}\) cm\(^{-2}\) (see Table 7). Considering again the differences in line widths, these values are comparable with the upper limits found for optical SH\(^{+}\) absorption from diffuse and translucent clouds (i.e. 1 \times 10\(^{13}\) cm\(^{-2}\); see Sect. 1.2).

8 The Doppler parameter, \(b\), listed by this and numerous other optical absorption studies and FWHM line width are related via \(\Delta V_{1/2} = 2 \sqrt{\ln 2} \times b \approx 1.665 \times b\).
Table 7. Column densities of the absorption components and abundances relative to H.

| Component | N(H) | X(H) | N(HCl) | X(HCl) |
|-----------|------|------|--------|--------|
| CH$^+$    |      |      |        |        |
| SO        |      |      |        |        |
| H$_2$S     |      |      |        |        |
| Notes.     |      |      |        |        |

With respect to chemical models (Millar et al. 1986; Pineau des Forêts et al. 1986), it is also worth noting that, as can be seen from Table 7, the SH$^+$/CH$^+$ ratio, [SH$^+$/CH$^+$], which is 0.56 for Sgr B2(M) only varies between 0.11 and 0.26 for all but one of the non-Sgr B2 absorption features. These values are consistent with the upper limits on this ratio (0.12–2) for diffuse and translucent lines of sight (see Sect. 1.2). The component with the higher ratio, $\approx 0.9$, is in the $–90.2$ to $–123.7$ km s$^{-1}$ range, which corresponds to peculiar velocity gas associated with the GC. Interestingly, this velocity range has also by far the highest SiO column density measured for the various velocity components by Greaves et al. (1996). These two findings may have a common (shock-wave) origin as an increased SiO abundance is commonly ascribed to shock chemistry (Schilke et al. 1997).

5.4. Limits on HCl absorption in the diffuse material

The HCl column density, N(HCl), we derive for the gas associated with Sgr B2(M) (see Table 5) is in good agreement, i.e. 16% higher, with the value derived by Zmuidzinas et al. (1995).

For the velocity components corresponding to the diffuse lines of sight we derive an upper limit on the HCl column density, N(HCl), of $8.4 \times 10^{12}$ cm$^{-2}$ (see Table 5 and Fig. 8 in Sect. 4.1.4). Since N(H) ranges from 0.5–2.4 $\times 10^{12}$ cm$^{-2}$ we calculate an HCl to hydrogen nuclei abundance ratio [HCl/H] of 0.6–3 $\times 10^{-10}$. Our upper limit is much coarser than the (2.7 $\pm$ 1.0) $\times 10^{11}$ cm$^{-2}$ Federman et al. (1995) determine for N(HCl) from an UV absorption line toward ζ Oph.

6. Conclusions

We have reported submillimeter wavelength absorption from rotational ground-state transitions of $^{13}$CH$^+$, H$^{13}$Cl, H$^{17}$Cl, and, for the first time, of the SH$^+$ molecule toward the strong Galactic center continuum source Sgr B2(M). From $^{13}$CH$^+$ and SH$^+$ we detect absorption at the systemic LSR velocity of Sgr B2(M) and in addition over a wide range of lower velocities belonging to intervening material. For the intervening clouds we have derived molecular hydrogen column densities from optically thin H$^{13}$CO emission and atomic column densities from HI 21 cm line data. For all the clouds we find that the former is larger than the latter by factors between 15 and 130. If we “scale” the observed velocity ranges of the individual clouds to the line widths of single diffuse and translucent molecular clouds in the Solar neighborhood, we find similar $^{13}$CH$^+$ column densities in both types of clouds. Most likely the reason for this is that the observed $^{13}$CH$^+$ is indeed mostly associated with atomic material surrounding molecular material. The [SH$^+$/CH$^+$] ratio is consistent with upper limits from optical data. Our upper limits on the [SH$^+$/H$_2$S] ratio we find values $>2$, except for the $–33.2$ to $–50.1$ km s$^{-1}$ velocity range, for which we find the low ratio of 0.3. We note that the velocity of this absorption places it in the Norma spiral arm. From Table 6 we see that this range has the highest H$_2$ column density and the highest H$_2$/HI ratio of all the (non-Sgr B2 region) absorption components and resembles most closely a GMC or GMC core. This reinforces SH$^+$’s nature as a tracer of more diffuse gas whose abundance drops in denser environments.

As discussed by Tieftrunk et al. (1994), SH$^+$ and H$_2$S are chemically related, as H$_2$S$^+$, from which the latter forms via dissociative recombination is formed by the reaction

$$\text{SH}^+ + \text{H}_2 \rightarrow \text{H}_3\text{S}^+ + \text{h}^+$$
