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Letter to the Editor

The rotational spectrum of protonated sulfur dioxide, $HOSO^+$

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ABSTRACT

Aims. We report on the millimeter-wave rotational spectrum of protonated sulfur dioxide, $HOSO^+$.
Methods. Ten rotational transitions between 186 and 347 GHz have been measured to high accuracy in a negative glow discharge.
Results. The present measurements improve the accuracy of the previously reported centimeter-wave spectrum by two orders of magnitude, allowing a frequency calculation of the principal transitions to about 4 km s^{-1} in equivalent radial velocity near 650 GHz, or one linewidth in hot cores and corinos.
Conclusions. Owing to the high abundance of sulfur-bearing molecules in many galactic molecular sources, the $HOSO^+$ ion is an excellent candidate for detection, especially in hot cores and corinos in which SO_2 and several positive ions are prominent.

Key words. ISM: molecules – radio lines: ISM – molecular processes – molecular data – line: identification

1. Introduction

Molecules with sulfur account for about 10% of the species identified in the interstellar gas and circumstellar envelopes. Among the most prominent of these is sulfur dioxide (SO_2). Since its detection in Orion and Sgr B2 more than 35 years ago (Snyder et al. 1975), SO_2 has been observed in many astronomical sources including hot cores in giant molecular clouds and low-mass young stellar objects (YSOs; Schilke et al. 2001; Comito et al. 2005; Caux et al. 2011), circumstellar shells of late-type stars (Tenenbaum et al. 2010), cold dense molecular clouds (Turner 1995), and external galaxies (Martín et al. 2003). This simple triatomic molecule is the carrier of a significant fraction of rotational lines in hot sources such as Orion and Sgr B2, which have been observed with ground-based telescopes in the millimeter band or the *Herschel* space observatory in the THz-band (Crockett et al. 2010; Ceccarelli et al. 2010). Despite the high density of spectral lines and wide range of astronomical sources in which it is found, the formation of SO_2 in space and the chemistry of other prominent sulfur bearing molecules in the dense molecular gas such as SO, H_2S, and CS is not well understood (Wakelam et al. 2004, and references therein).

In addition to prominent neutral sulfur-bearing molecules, several positive molecular ions containing sulfur are also observed. Of these, SO^+ is widespread and conspicuous in over 20 galactic sources both warm and cold (Turner 1994), HCS^+ has a similarly wide distribution, and SH^+ was recently shown to be ubiquitous in the diffuse interstellar gas (Menten et al. 2011). Although protonated SO_2 ($HOSO^+$) has not explicitly been considered in most chemical networks, it is an excellent candidate for astronomical detection for several reasons: (1) it does not react with H_2; (2) the proton affinity of SO_2 is high (de Petris et al. 2011); (3) it is formed facilely by the reaction of H_3^+ with SO_2 (Anicich & Huntress 1986); (4) the dipole moment is large ($\mu_a = 1.74$ D; Lattanzi et al. 2010); (5) the parent SO_2 is very abundant in hot regions; (6) and radio observations of SH^+ and SO^+ (Menten et al. 2011; Turner 1994) have established that positive ions of sulfur-bearing molecules are surprisingly abundant with respect to their neutral counterparts and other common sulfur species in many molecular sources.

Here we report the millimeter-wave rotational spectrum of *cis*-$HOSO^+$, the most stable isomeric form of this ion. The present measurements improve the accuracy of the radio spectrum by two orders of magnitude over that obtained from the earlier laboratory measurements of the lowest rotational transitions in the centimeter band (Lattanzi et al. 2010), allowing a deep search for this fundamental positive ion in regions of the interstellar gas where there is an active sulfur chemistry. From the derived spectroscopic constants, the astronomically most interesting lines of $HOSO^+$ up to 700 GHz can be predicted to 4 km s^{-1} or better in equivalent radial velocity.

2. Experiment and analysis

The rotational spectrum of protonated SO_2 ($HOSO^+$) was first observed at centimeter wavelengths in a supersonic molecular beam with a Fourier transform microwave (FTM) spectrometer used to detect many new reactive radicals and ions of astrophysical interest (Lattanzi et al. 2010, and references therein). The $HOSO^+$ ion was produced in a small nozzle by a low-current DC discharge through SO_2 heavily diluted in H_2. Following the detection of the four lowest *a*-type transitions, two *b*-type cross-ladder ($K_a = 1 \rightarrow 0$) transitions in the centimeter band were observed in double resonance, thereby confirming the spectroscopic identification and yielding a precise determination of all three rotational constants.

Millimeter-wave rotational lines of the ground state (*cis*) isomer of $HOSO^+$ were observed in a negative glow discharge cell (7.6 cm diameter, 1.4 m long) similar in design to that originally described by De Lucia et al. (1983). The experimental

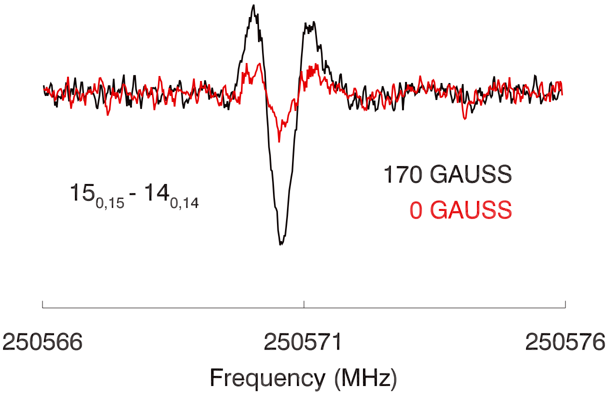

Fig. 1. The $J = 15_{0,15}-14_{0,14}$ rotational transition of *cis*-$HOSO^+$, illustrating the effect of an applied magnetic field on the line intensity in the negative glow discharge. Owing to the modulation and detection scheme employed, the instrumental lineshape is approximately the second derivative of a Lorentzian. Each spectrum is the result of 12 min of integration.

conditions were optimized by first observing the known positive ions HCO^+, SO^+, and HCS^+ whose rotational lines all exhibited enhancements in intensity of 50 or more upon application of a strong axial magnetic field of 170–200 G. The most intense lines of $HOSO^+$ (e.g., Fig. 1) were observed in a DC discharge (3 mA) through a flowing mixture of Ar, SO_2, and H_2 with the discharge cell cooled to 245 K. The total pressure with the discharge running (3.5 mTorr) was maintained by a small diffusion pump (800 l/s pumping speed). Cooling of the discharge cell was accomplished by flowing liquid nitrogen through copper tubing in thermal contact with the solenoid, with the space between the glass cell and the aluminum solenoid form filled with aluminum wool.

The search for $HOSO^+$ in the millimeter band was guided by the rotational constants that have been derived from the centimeter-wave data and theoretical centrifugal distortion constants (Lattanzi et al. 2010). Owing to the bent heavy atom backbone of this ion (Fig. 2), the A rotational constant is fairly small (44 GHz) and $B - C$ is large (1.8 GHz). As a result, the departure from harmonicity of a-type transitions in the $K_a = 0$ ladder is large (e.g., 555 MHz at 298.7 GHz). Thus, when the first suspected millimeter-wave rotational line of $HOSO^+$ was observed, the identification could not be confirmed by simply observing other harmonically related lines. Instead, our search relied on frequencies calculated with the experimental and theoretical spectroscopic constants. Recent work on rigid molecules with two or three heavy atoms established that the fourth-order distortion constant D_J calculated at a high level of theory is usually accurate to about 3% or better (McCarthy et al. 2011; Spezzano et al. 2011). We found that subsequent lines of $HOSO^+$ could be predicted to within about 5 MHz near 300 GHz, because the contribution from D_J to transitions in the $K_a = 0$ ladder is small. The departure from harmonicity can be calculated to fairly high accuracy from previous data.

Five lines between 186 and 347 GHz in the $K_a = 0$ ladder of the *cis* isomer of $HOSO^+$ were observed in our negative glow discharge, each exhibiting a small enhancement in intensity when an axial magnetic field was applied (Table 1). The observed enhancement of between a factor of 3–5 with a field strength of ~170 G was sufficient to allow us to discriminate between ions and neutral species produced in the discharge (Fig. 1). Although the magnitude of the magnetic field enhancement was about 10 times smaller than that of other molecular ions observed with this spectrometer (i.e., HCO^+, $HOCO^+$, and HCS^+), the effect of the magnetic field was the same for all millimeter-wave lines assigned to $HOSO^+$ and was repeatable. The identification of lines of $HOSO^+$ observed here in the millimeter band was supported by the detection of four lines in the $K_a = 1$ ladder that were close in frequency to the prediction.

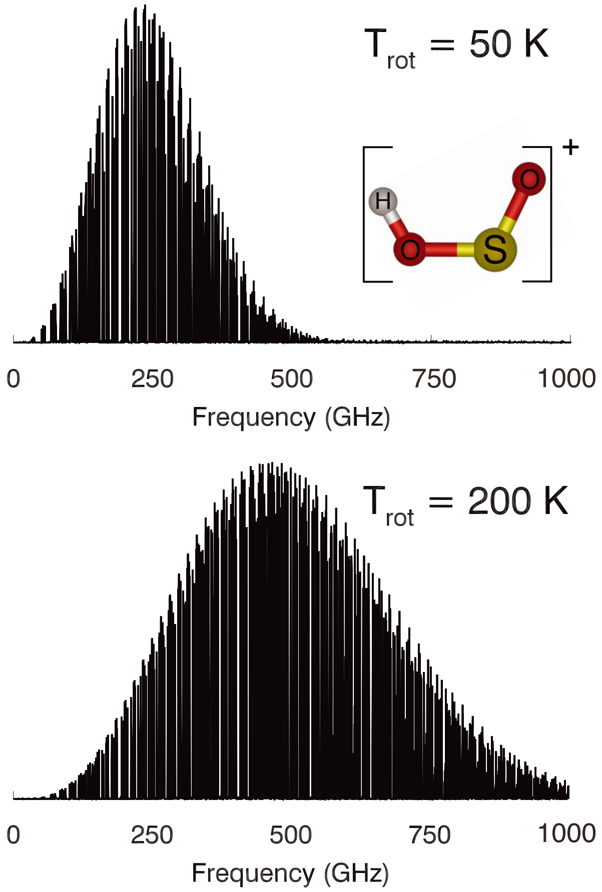

Fig. 2. Relative intensities of the a-type spectrum of *cis*-$HOSO^+$ at 50 K (*top*) and 200 K (*bottom*). The intensities were calculated on the assumption that the populations of all rotational levels are described by a single temperature, and only the ground vibrational state is populated. Shown in the insert (*top*) is the molecular structure from Lattanzi et al. (2010).

The rotational spectrum of *cis*-$HOSO^+$ was analyzed with the Watson S-reduced Hamiltonian with three rotational and two centrifugal distortion constants (D_J and D_K), and the remaining three fourth-order distortion constants constrained to the theoretical values. With seven spectroscopic constants (Table 2), the ten-millimeter-wave and seven-centimeter-wave lines were reproduced with an rms uncertainty (19 kHz) that is well within the measurement uncertainties.

3. Discussion

The high observed abundance of the SH^+ ion with respect to that of CS, SO, SO_2, and H_2S (0.5 to >55; Menten et al. 2011), and the similarly high ratio of SO^+ to that of SO and SO_2 (~1; Turner 1994) establish that positive ions of sulfur-bearing molecules are conspicuous in the interstellar gas. On the assumption that $HOSO^+$ is formed in space by the reaction of SO_2 with H_3^+, the best sources for detecting this ion are those with the highest abundance of SO_2, such as hot cores in high-mass star-forming regions and low-mass YSOs.

Table 1. Measured rotational transitions of *cis*-HOSO$^+$.

$J'_{K'_a,K'_c} - J_{K_a,K_c}$	Frequency (MHz)	(O−C^a) (kHz)
$1_{0,1}-0_{0,0}$	17 969.837^b	−4
$2_{1,2}-1_{1,1}$	34 110.247^b	−2
$2_{0,2}-1_{0,1}$	35 868.210^b	8
$1_{1,0}-1_{0,1}$	36 112.603^b	12
$2_{1,1}-1_{1,0}$	37 769.444^b	−3
$1_{1,1}-0_{0,0}$	52 252.779^b	5
$3_{0,3}-2_{0,2}$	53 624.380^b	34
$11_{0,11}-10_{0,10}$	186 685.031	−41
$14_{1,14}-13_{1,13}$	233 697.778	5
$14_{0,14}-13_{0,13}$	234 564.185	−14
$15_{0,15}-14_{0,14}$	250 570.579	5
$16_{1,16}-15_{1,15}$	266 143.651	−32
$15_{1,14}-14_{1,13}$	269 518.985	16
$17_{0,17}-16_{0,16}$	282 657.801	−24
$18_{0,18}-17_{0,17}$	298 729.954	23
$21_{1,21}-20_{1,20}$	346 931.570	−3
$21_{0,21}-20_{0,20}$	347 010.817	23

Notes. [a] Frequencies calculated with spectroscopic constants in Table 2. [b] Centimeter-wave measurements from Lattanzi et al. (2010).

Table 2. Spectroscopic constants of *cis*-HOSO$^+$ (in MHz).

Constant	This work^a	Centimeter-wave^b	Theoretical^b
A	44 183.605(41)	44 183.527(35)	44 358.4
B	9899.77223(67)	9899.77130(77)	9897.1
C	8070.09973(58)	8070.09978(75)	8074.3
$10^3 D_J$	7.5849(12)	[7.52]	7.52
$10^3 D_{JK}$	[−86.6]	[−86.6]	−86.6
D_K	1.078(14)	[1.00]	1.00
$10^3 d_1$	[−2.29]	[−2.29]	−2.29
$10^3 d_2$	[−0.13]	[−0.13]	−0.13

Notes. [a] Uncertainties (1σ) are in units of the last significant digit. Quantities in brackets were constrained to the theoretical values in the least-squares fit to the measurements in Table 1. [b] Lattanzi et al. (2010).

Many rotational transitions of HOSO$^+$ of comparable predicted intensity are accessible throughout the millimeter- and THz-bands, facilitating a deep search with ground-based and space-borne telescopes. Figure 2 shows a simulated spectrum of HOSO$^+$ calculated for a rotational temperature ($T_{\rm rot}$) of 200 K appropriate for a typical hot core region, on the assumption that all rotational levels are described by a single temperature. The dominant features are strong R-branch ($\Delta J = 1$) transitions separated by 16 GHz, with transitions in the $K_a = 1$ and $K_a = 2$ ladders nearly as intense as those in the $K_a = 0$ ladder owing to the fairly small value of the A rotational constant. As this plot illustrates, the THz band is the most favorable spectral region for a radioastronomical search in sources with $T_{\rm rot}$ near 200 K. Also shown in Fig. 2 is the spectrum calculated for a warm region with $T_{\rm rot} = 50$ K, such as that between the hot corino in IRAS 16293-2442 and the cool (~10 K) surrounding dust envelope (Caux et al. 2011). At this intermediate temperature, the peak line-intensity shifts to the millimeter-band, which is readily accessible with ground based telescopes.

The spectroscopic constants of HOSO$^+$ (Table 2) allow an accurate prediction of transitions up to the 600−700 GHz region (Band 9 of ALMA). The sixth-order distortion constant H_J was not determined in the measurements here, but on the assumption that it is similar to that of SO_2 ($H_J = 1.1 \times 10^{-8}$ MHz; Müller, & Brünken 2005), we estimate that the uncertainty in the calculated frequencies near 650 GHz owing to neglect of H_J (~4 km s^{-1}) is comparable to the linewidths in hot cores and corinos.

We find no evidence for HOSO$^+$ in published spectral line surveys in Orion where the column density of SO_2 is high (5×10^{16} cm^{-2}; Schilke et al. 2001; Comito et al. 2005), or in Sgr B2 where the abundance of SO_2 is at least 20 times higher ($\geq 1 \times 10^{18}$ cm^{-2}; Nummelin et al. 2000). On the assumption that the ion is present in the same region as SO_2, the column density of HOSO$^+$ in Orion ($\leq 3 \times 10^{15}$ cm^{-2}) implies that the upper limit of the HOSO$^+$/SO_2 ratio ($\leq 6\%$) is comparable to the observed $^{34}SO_2/SO_2$ ratio in this source. Interferometric observations of the hot corino in IRAS 16293-2422 with the SMA confirm that the abundances of sulfur-bearing molecules in this source are high as well (2.9×10^{16} cm^{-2}; Chandler et al. 2005). Chandler et al. covered a range of about 3 GHz near 305 GHz, which unfortunately does not encompass a strong transition of HOSO$^+$, so we are unable to determine whether there is any evidence for this ion in the corino. The HOSO$^+$ ion might be detectable in IRAS 16293-2422 in a dedicated search with the SMA if the abundance of HOSO$^+$ is comparable to that of $^{34}SO_2$, which is observed with a signal-to-noise of 2−3. The combination of high sensitivity and high spatial resolution should greatly advance the study of corinos and the search for this protonated species when ALMA comes online.

The rotational spectrum of the *trans* isomer of protonated sulfur dioxide, calculated to lie only 2.4 kcal/mol or ~1200 K higher in energy, has also been measured in the centimeter-band (Lattanzi et al. 2010). If this isomer is produced in our negative glow discharge in comparable abundance to that of the *cis* isomer, its millimeter-wave rotational lines should also be observable because of its higher dipole moment ($\mu_a = 3.16$ D versus 1.74 D for *cis*-HOSO$^+$). Measurements of both the *cis* and *trans* isomers in a molecular beam with our FTM spectrometer imply that this might be the case. By analogy with the *cis* isomer reported here, a laboratory search for the millimeter-wave transitions of *trans*-HOSO$^+$ should be undertaken now that the rotational constants have been derived from the rotational data, and the leading centrifugal distortion constants were calculated at the same level of theory as that of the *cis* isomer (Lattanzi et al. 2010). It is anticipated that an extended search in frequency will not be required for the identification of the millimeter-wave lines of *trans*-HOSO$^+$.

Other small sulfur-bearing molecules of astrophysical interest whose rotational spectra have not been measured in the millimeter and THz band include the HOSO radical and the HSO$^+$ ion. The HOSO radical is an excellent candidate for detection in space. In some recent calculations (Garrido et al. 2011; Ballester et al. 2010), full dimensional quasi-classical trajectory studies of OH+SO reaction were undertaken. They find that (1) the reaction is exothermic, with an enthalpy of formation of −29.4 kcal/mol; (2) there is no barrier in the entrance channel to form the HOSO intermediate; (3) HOSO represents the global minimum on the potential energy surface, lying 71.8 kcal/mol below the OH + SO limit; and (4) HOSO is the only product that is formed in the energy range studied. Recently rotational lines of the radical have been observed in the centimeter-band and the leading distortion constants have been determined by high-level quantum chemical calculations (Lattanzi et al. 2011).

Protonated SO (HSO$^+$) is an especially attractive candidate for detection: it is predicted to have a closed-shell $^1A'$ electronic ground state (Li et al. 2006); the dipole moment is high (equilibrium values calculated at the CCSD(T)/cc-pwCVQZ level of theory are $\mu_a = 2.9$ D and $\mu_b = 1.1$ D; this work); and it has a rich spectrum in the millimeter and THz bands. With only two heavy atoms the lowest rotational transition of HSO^+ lies outside the range of our FTM spectrometer, but the same experimental techniques used here for *cis*-$HOSO^+$ can be applied to the laboratory search for this ion in the millimeter-band. The column density of HSO^+ is predicted to be high in the envelopes around massive YSOs ($\sim10^{15}$ cm^{-2}; Stäuber et al. 2005), owing to the considerable predicted enhancement in the envelope by X-rays. Therefore, the HSO^+ ion might be an important tracer of X-rays in these objects when its rotational spectrum has been measured in the laboratory.

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