

## Laboratory detection of protonated SO<sub>2</sub> in two isomeric forms

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By means of Fabry–Pérot Fourier transform microwave spectroscopy, the rotational spectrum of protonated sulfur dioxide in two distinct isomeric forms, a *cis*- and a *trans*-geometry, is reported. The search for both isomers was based on theoretical structures obtained at the CCSD(T)/cc-pwCVQZ level of theory corrected for zero-point vibrational effects. At a similarly high level of theory, the *cis*-isomer is calculated to be the global minimum on the potential energy surface, but the *trans*-isomer is predicted to lie only a few kcal/mol higher in energy. A total of seven lines, including *a*- and *b*-type transitions, has been observed for both isomers, and precise rotational constants have been derived. Because sulfur dioxide, SO<sub>2</sub>, is a widespread and very abundant astronomical species, and because it possesses a large proton affinity, HOSO<sup>+</sup> is an excellent candidate for radioastronomical detection. © 2010 American Institute of Physics. [doi:10.1063/1.3491510]

### I. INTRODUCTION

Sulfur dioxide is one of the most important triatomic molecules containing a second-row atom because of the role it plays as a molecular coolant in star-forming regions, as a pollutant in the Earth's atmosphere, and as a precursor in the industrial production of sulfuric acid. Since its detection in 1975 (Ref. 1) in the Orion molecular cloud and Sagittarius (Sgr) B2, SO<sub>2</sub> has now been observed in more than 15 astronomical sources including planetary atmospheres,<sup>2</sup> cold molecular clouds,<sup>3</sup> circumstellar shells of evolved stars,<sup>4</sup> and in other galaxies.<sup>5</sup> SO<sub>2</sub> is frequently observed in hot cores of high mass star-forming regions<sup>6</sup> with a high fractional abundance relative to molecular hydrogen, of the order of 10<sup>-5</sup>–10<sup>-6</sup>. In their Sgr B2 line survey at 330–350 GHz, Sutton *et al.*<sup>7</sup> found SO<sub>2</sub> to dominate the submillimeter spectrum to a much greater extent than it does in the millimeter wave band. This effect becomes more pronounced at higher frequencies, as demonstrated by Schilke *et al.*<sup>8</sup> and Comito *et al.*<sup>9</sup> in their line surveys toward Orion KL between 607 and 903 GHz. There the integrated line intensities of sulfur dioxide and methanol are far larger than those of any other species.

The molecular properties of SO<sub>2</sub> have been the subject of extensive theoretical and experimental studies. In recent work, its rotational spectrum<sup>10</sup> has been studied up to 2 THz, and more than 150 transitions from the ground vibrational state and the first bending mode  $\nu_2$  were identified. The rotational spectrum of sulfur dioxide has also attracted interest as a secondary frequency standard in the millimeter and submillimeter wave regions, as described in several papers.<sup>11</sup>

Despite the widespread interest in SO<sub>2</sub>, there is surprisingly little information on its protonated derivatives, even

though SO<sub>2</sub> is known to possess a high proton affinity [676 kJ/mol (Ref. 12)], about 15% higher than that of CO,<sup>13</sup> whose protonated species, HCO<sup>+</sup>, is one of the most abundant ions in the interstellar gas. Protonated sulfur dioxide has been suggested as a good candidate for astronomical detection,<sup>14</sup> and the neutral radical HSO<sub>2</sub> has been the subject of high-level theoretical calculations (see Ref. 15 and references therein). Besides a measurement of its proton affinity, the only other published study of the [H,S,O<sub>2</sub>]<sup>+</sup> system is that of Frank *et al.*,<sup>16</sup> who undertook quantum-chemical calculations on this ion as part of their neutralization-reionization mass spectrometry study of the hydroxysulfinyl and hydrogen sulfonyl radicals and dihydroxysulfane. Their calculations at the MP2 level of theory concluded that two O-protonated *cis*- and *trans*-planar forms of HOSO<sup>+</sup> (see Fig. 1) are almost isoenergetic (the *cis*-form being more stable by only about 2 kcal/mol). Protonation at the sulfur atom is much less favorable; it yields an isomer with C<sub>2v</sub> symmetry that is predicted to lie about 42 kcal/mol above *cis*-HOSO<sup>+</sup>.

Motivated by the recent discovery of HSCS<sup>+</sup> and HSCO<sup>+</sup> in this laboratory and a desire to characterize the structure and properties of protonated molecules closely related in structure and composition to CO<sub>2</sub>, OCS, and CS<sub>2</sub>, a combined theoretical and experimental study of HOSO<sup>+</sup> has been undertaken using coupled-cluster calculations and rotational spectroscopy. On the basis of vibrationally corrected rotational constants and dipole moments calculated quantum chemically, we report the laboratory detection of HOSO<sup>+</sup> in two distinct isomeric forms in a supersonic molecular beam by Fourier transform (FT) microwave spectroscopy. Four *a*-type rotational transitions, two from both the K<sub>a</sub>=0 and the K<sub>a</sub>=1 ladders, have been detected in the centimeter-wave range for the two isomers shown in Fig. 1. Double resonance spectroscopy at microwave or millimeter wavelengths has

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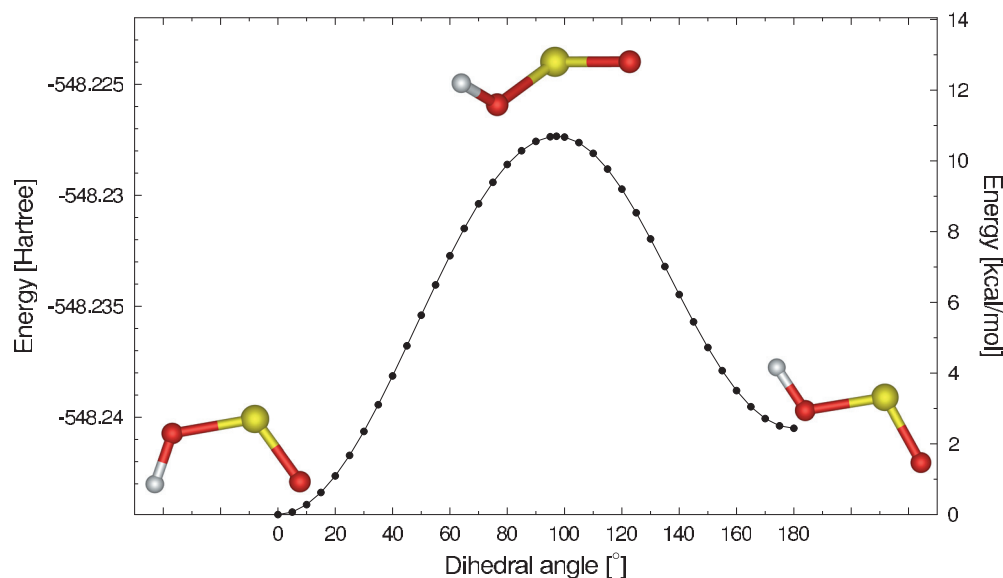


FIG. 1. The total energy for the HOSO<sup>+</sup> system [CCSD(T)/cc-pV(T+d)Z] as a function of the dihedral angle. Each point corresponds to a 5° change in the dihedral angle, in which all other structural parameters were relaxed in the calculation of the total energy. Single point calculations of *trans*-HOSO<sup>+</sup> and the transition state energies relative to the *cis*-form (Table V) at the CCSD(T)/cc-pwCVQZ level of theory, which are corrected for zero-point vibrational effects, yield energy differences (2 and 9 kcal/mol, respectively), in very good agreement with those shown here.

been used to observe a third  $K_a=0$  line, to confirm the  $K_a=0$  line assignments, and to detect two low- $J$   $b$ -type transitions. With this data it has been possible to precisely determine the rotational constants for both isomers. For *cis*-HOSO<sup>+</sup>, our identification has been confirmed by the detection of rotational lines of DOSO<sup>+</sup> and HO<sup>34</sup>SO<sup>+</sup> at exactly the frequencies expected from the predicted molecular structure.

## II. QUANTUM CHEMICAL CALCULATIONS

In the present investigation, coupled-cluster theory,<sup>17</sup> specifically the coupled-cluster singles and doubles model augmented by a perturbative correction for triple excitations, CCSD(T),<sup>18</sup> has been used to calculate the molecular properties of *cis*- and *trans*-HOSO<sup>+</sup>, with the goal of facilitating the spectroscopic search for both isomers using Fourier transform microwave spectroscopy. The calculations were performed with the 2005 Mainz–Austin–Budapest version of ACESII.<sup>19</sup> Dunning’s hierarchies of correlation consistent polarized valence and polarized core-valence basis sets were used throughout: in the frozen-core approach,  $d$ -augmented correlation consistent basis sets cc-pV( $X+d$ )Z (Ref. 20) were used for the sulfur atom along with standard basis sets cc-pVXZ (Ref. 21) (with  $X=T$  and  $Q$ ) for hydrogen and oxygen [denoted as CCSD(T)/cc-pV( $X+d$ )Z in the following]. When considering all electrons in the correlation treatment, the cc-pwCVXZ ( $X=T$  and  $Q$ ) basis sets<sup>22</sup> were used. Equilibrium geometries were calculated, employing analytic gradient techniques.<sup>23</sup> The best equilibrium structures of *cis*- and *trans*-HOSO<sup>+</sup> have been calculated at the CCSD(T)/cc-pwCVQZ level of theory (Table I), which has been shown on several occasions to yield equilibrium structures of very high quality for molecules harboring second-row elements.<sup>24,25</sup> Harmonic and anharmonic force fields were calculated using analytic second-derivative techniques,<sup>26,27</sup>

followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force field.<sup>27,28</sup> Theoretical ground state rotational constants were then obtained from the relation

$$B_0^{qcc} = B_e^{qcc} - \frac{1}{2} \sum_i \alpha_i^{B,qcc}, \quad (1)$$

with corresponding equations for the  $A_0$  and  $C_0$  rotational constants, respectively. Here, the equilibrium rotational constants are obtained from the CCSD(T)/cc-pwCVQZ equilibrium structures and corrected for the effects of zero-point vibration ( $\frac{1}{2} \sum_i \alpha_i^{A,B,C,qcc} = \Delta A_0, \Delta B_0, \Delta C_0$ ) calculated at the CCSD(T)/cc-pV(Q+d)Z level of theory. In addition, the CCSD(T)/cc-pV(Q+d)Z force field calculation yields the quartic centrifugal distortion parameters. Theoretical spectroscopic parameters are summarized in Table II. The calculated harmonic and fundamental vibrational frequencies can be found in the supplementary electronic material.<sup>29</sup>

To study the *cis-trans* isomerization of HOSO<sup>+</sup> in more detail, a potential energy curve along the dihedral angle  $\tau_{\text{HOSO}}$  from 0° (*cis*) to 180° (*trans*) was calculated at the CCSD(T)/cc-pV(T+d)Z level of theory in steps of 5°, i.e., the dihedral angle was kept fixed in these calculations and all other structural parameters were varied (see Fig. 1). The transition state was also calculated directly at the CCSD(T)/cc-pwCVQZ level of theory (Table I), making use of the Cerjan–Miller algorithm<sup>30</sup> as implemented in ACESII.

TABLE I. Structural parameters of HOSO<sup>+</sup> [in Å and deg, CCSD(T)/cc-pwCVQZ].

	$r_{\text{H-O}}$	$r_{\text{O-S}}$	$r_{\text{S-O}}$	$\alpha_{\text{HOS}}$	$\alpha_{\text{OSO}}$	$\tau_{\text{HOSO}}$
<i>cis</i> -HOSO <sup>+</sup>	0.9827	1.5192	1.4075	120.05	115.42	0.0
<i>trans</i> -HOSO <sup>+</sup>	0.9806	1.5282	1.4035	115.47	109.82	180.0
Transition state	0.9767	1.5107	1.5107	130.67	113.42	97.66

TABLE II. Spectroscopic constants (in MHz) and dipole moment components (in D) of *cis*- and *trans*-HOSO<sup>+</sup>.

Constant	Experimental <sup>a</sup>	<i>cis</i> -HOSO <sup>+</sup> — Calculated		
		Equilibrium <sup>b</sup>	Vib. Contrib. <sup>c</sup>	Ground vib. state
<i>A</i>	44 183.527(35)	44 160.7	−197.7	44 358.4
<i>B</i>	9 899.771 30(77)	9 952.1	+55.0	9 897.1
<i>C</i>	8 070.099 78(75)	8 121.7	+47.4	8 074.3
10 <sup>3</sup> <i>D<sub>J</sub></i>	7.52	7.52	...	...
10 <sup>3</sup> <i>D<sub>JK</sub></i>	−86.6	−86.6	...	...
<i>D<sub>K</sub></i>	1.00	1.00	...	...
10 <sup>3</sup> <i>d<sub>1</sub></i>	−2.29	−2.29	...	...
10 <sup>3</sup> <i>d<sub>2</sub></i>	−0.13	−0.13	...	...
<i>μ<sub>a</sub></i>		1.74		
<i>μ<sub>b</sub></i>		0.49		

Constant	Experimental <sup>a</sup>	<i>trans</i> -HOSO <sup>+</sup> — Calculated		
		Equilibrium <sup>b</sup>	Vib. contrib. <sup>c</sup>	Ground vib. state
<i>A</i>	44 766.215(35)	44 755.7	−257.1	45 012.8
<i>B</i>	9 961.720 64(93)	10 016.8	+60.9	9 955.9
<i>C</i>	8 131.957 2(13)	8 184.9	+48.5	8 136.4
10 <sup>3</sup> <i>D<sub>J</sub></i>	6.56	6.56	...	...
10 <sup>3</sup> <i>D<sub>JK</sub></i>	−64.5	−64.5	...	...
<i>D<sub>K</sub></i>	0.96	0.96	...	...
10 <sup>3</sup> <i>d<sub>1</sub></i>	−1.92	−1.92	...	...
10 <sup>3</sup> <i>d<sub>2</sub></i>	−0.12	−0.12	...	...
<i>μ<sub>a</sub></i>		3.16		
<i>μ<sub>b</sub></i>		2.47		

<sup>a</sup>Uncertainties (1σ) are in units of the last significant digit.<sup>b</sup>Rotational constants obtained at the CCSD(T)/cc-pwCVQZ level of theory. Centrifugal distortion constants calculated at the fc-CCSD(T)/cc-pV(Q+d)Z level.<sup>c</sup>fc-CCSD(T)/cc-pV(Q+d)Z.

### III. EXPERIMENTAL DETAILS

The centimeter-wave spectrum of protonated sulfur dioxide was detected using a supersonic molecular beam discharge source in combination with a FT microwave spectrometer, both of which have been described in detail elsewhere.<sup>31</sup> This technique has been proven to be particularly successful for the detection of small protonated molecules such as HNCCN<sup>+</sup>, HC<sub>3</sub>NH<sup>+</sup>, etc.,<sup>32</sup> and the aforementioned HSCO<sup>+</sup> and HSCS<sup>+</sup> and other positively and negatively charged and neutral carbon molecules, as well as silicon- and sulfur-bearing species, whose rotational spectra are greatly simplified at the very low rotational temperature that is achieved in a supersonic beam expansion. Protonated ions are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve.

A search for the fundamental rotational transition (1<sub>0,1</sub> → 0<sub>0,0</sub>) of *cis*-HOSO<sup>+</sup> was undertaken first using SO<sub>2</sub> heavily diluted (0.2%) in hydrogen. Before doing so, however, the experimental conditions (e.g., gas duration, discharge voltage, etc.) were first optimized by monitoring a low-*J* line (the 2<sub>0,2</sub> → 1<sub>0,1</sub> transition at 22.5 GHz) of HSCO<sup>+</sup>, a closely related species with similarly high proton affinity [628 kJ/mol for OCS (Ref. 33) versus 676 kJ/mol for SO<sub>2</sub>], whose rotational spectrum was recently detected using the same apparatus.<sup>34</sup> As before, the strongest line of this ion was observed with OCS diluted in H<sub>2</sub> to ≤0.2% and a dis-

charge potential of 800 V. Other experimental parameters were similar to those previously reported: a total flow rate of about 20 cm<sup>3</sup> min<sup>−1</sup> at standard temperature and pressure, with a stagnation pressure behind the valve of 2.5 kTorr and a 6 Hz pulse rate of the nozzle.

The search for the rotational spectrum of *cis*-HOSO<sup>+</sup> was based on the high-level calculations described in Sec. II. The predicted transition frequencies in the *K<sub>a</sub>*=0 ladder are expected to be accurate to much better than ±1%, an uncertainty that amounts to a search of at most ±180 MHz near 18.0 GHz, the predicted frequency of the 1<sub>0,1</sub> → 0<sub>0,0</sub> line. Several surveys covering this frequency range were initially undertaken without success; the only observed line is from <sup>34</sup>SO<sub>2</sub> [the 5<sub>2,4</sub> → 6<sub>1,5</sub> transition (Ref. 35)], which nearly coincides in frequency (within 1 MHz) to that predicted for *cis*-HOSO<sup>+</sup>. By carefully adjusting the experimental conditions to reduce somewhat the intensity of this strong, unwanted background line, we eventually detected a new line (see Fig. 2), only produced in the presence of the discharge, that lies very close in frequency, i.e., about 1 MHz (<0.01%) below the theoretical prediction (see Table III for experimental transition frequencies).

A second discharge-dependent line (2<sub>0,2</sub> → 1<sub>0,1</sub>) was soon found at higher frequency at precisely the expected frequency to better than 0.006% on the assumption that the 18.0 GHz line arises from *cis*-HOSO<sup>+</sup>. Two additional lines from the *K<sub>a</sub>*=1 ladder were subsequently found within ±10 MHz

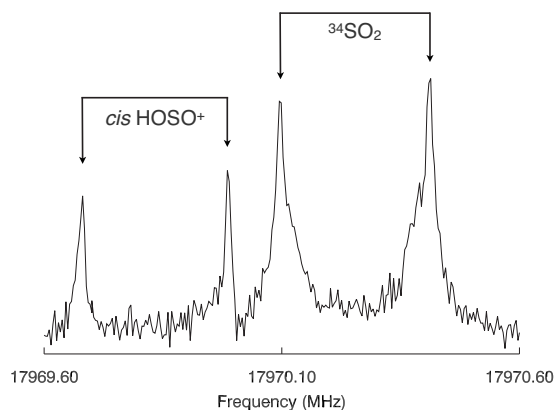


FIG. 2. The fundamental rotational transition of the *cis*-isomer of protonated sulfur dioxide, the result of 2.5 min of integration. The unrelated line lying slightly higher in frequency is the  $5_{2,4} \rightarrow 6_{1,5}$  transition of  $^{34}\text{SO}_2$ . Each transition has a double-peaked line shape, owing to the Doppler shift of the supersonic molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Pérot cavity.

of predictions made by scaling the theoretical rotational constants of *cis*-HOSO<sup>+</sup> to those measured.

The search for the analogous transitions of *cis*-HO<sup>34</sup>SO<sup>+</sup> in natural abundance, and *cis*-DOSO<sup>+</sup> using D<sub>2</sub> instead of H<sub>2</sub> as the expansion gas, was subsequently performed. Because of the low natural abundance of  $^{34}\text{S}$  (4.2%), only the fundamental transition was observed for this isotopic species. For both isotopic species, the search was based on theoretical rotational constants (see Sec. II) scaled by the ratio of the measured rotational constants to those calculated for the normal isotopic species. Such scaling generally predicts the frequencies of the isotopic lines (see Table IV) to better than 1% of the frequency shift from lines of the normal species, so a search of only a few megahertz in the vicinity of 17.2 GHz was required for the detection of *cis*-DOSO<sup>+</sup>.

Following the detection of *cis*-HOSO<sup>+</sup>, a search was undertaken for the *trans*-isomer. Employing a similar search strategy to that for the *cis*-species, four rotational lines were assigned to this isomer (Table III). The lines of *trans*-HOSO<sup>+</sup> are generally three to five times weaker than those of the corresponding *cis* lines, which is qualitatively consistent with the calculated relative energies and protonated OCS.

TABLE III. Measured rotational transitions of the two isomeric forms of protonated sulfur dioxide (in MHz).

$J'_{K'_a K'_c} \rightarrow J_{K_a K_c}$ <sup>a</sup>	HOSO <sup>+</sup>			
	<i>cis</i>	O–C <sup>b</sup>	<i>trans</i>	O–C <sup>b</sup>
$1_{0,1} \rightarrow 0_{0,0}$	17 969.837	–4	18 093.653	1
$2_{1,2} \rightarrow 1_{1,1}$	34 110.247	–3	34 357.704	2
$2_{0,2} \rightarrow 1_{0,1}$	35 868.210	7	36 116.877	–1
$1_{1,0} \rightarrow 1_{0,1}$ <sup>c</sup>	36 112.603	2	36 633.431	12
$2_{1,1} \rightarrow 1_{1,0}$	37 769.444	–2	38 017.106	0
$1_{1,1} \rightarrow 0_{0,0}$ <sup>c</sup>	52 252.779	–10	52 897.313	–10
$3_{0,3} \rightarrow 2_{0,2}$ <sup>c</sup>	53 624.380	–18	53 999.971	6

<sup>a</sup>Unless otherwise noted, estimated measurement uncertainties are 2 kHz.

<sup>b</sup>Residuals in kHz.

<sup>c</sup>Line frequencies determined by fitting Gaussian line profiles to the double resonance spectra (e.g., Fig. 3). Estimated measurement uncertainties are 50 kHz.

TABLE IV. Measured rotational frequencies and spectroscopic constants of *cis*-DOSO<sup>+</sup> (in MHz).

$J'_{K'_a K'_c} \rightarrow J_{K_a K_c}$ <sup>a</sup>	$F' \rightarrow F$	<i>cis</i> -DOSO <sup>+</sup>
$1_{0,1} \rightarrow 0_{0,0}$	1 → 1	17 222.333
$1_{0,1} \rightarrow 0_{0,0}$	2 → 1	17 222.364
$1_{0,1} \rightarrow 0_{0,0}$	0 → 1	17 222.400
$2_{0,2} \rightarrow 1_{0,1}$	...	34 355.243
$2_{1,2} \rightarrow 1_{1,1}$	...	32 543.881
$2_{1,1} \rightarrow 1_{1,0}$	...	36 345.799

Constant	Experimental <sup>b</sup>	Predicted
<i>A</i>	38 939.11(80)	39 092.5 <sup>c</sup> /38 943.9 <sup>d</sup>
<i>B</i>	9 561.710 90(77)	9 557.8 <sup>c</sup> /9 560.4 <sup>d</sup>
<i>C</i>	7 660.680 22(78)	7 664.1 <sup>c</sup> /7 660.1 <sup>d</sup>
$\chi_{aa}$	–0.085 4(37)	–0.115
$\chi_{bb}$	0.244	0.244
$10^3 D_J$	7.55	7.55
$10^3 D_{JK}$	–73.29	–73.29
$D_K$	0.68	0.68
$10^3 d_1$	–2.42	–2.42
$10^3 d_2$	–0.15	–0.15

<sup>a</sup>Estimated measurement uncertainties are 2 kHz.

<sup>b</sup>Uncertainties ( $1\sigma$ ) are in units of the last significant digit.

<sup>c</sup>Calculated equilibrium rotational constants [CCSD(T)/cc-pwCVQZ] corrected for the zero-point vibrational effects [CCSD(T)/cc-pV(Q+d)Z].

<sup>d</sup>Calculated ground state rotational constants scaled by the main isotopic species in which the calculated constants are scaled to those measured.

The lines of HOCS<sup>+</sup> are systematically three times weaker than those of HSCO<sup>+</sup>, presumably because this isomer is also less stable, calculated to lie 5 kcal/mol above HSCO<sup>+</sup>.<sup>34</sup>

#### IV. DOUBLE RESONANCE SPECTROSCOPY

Double resonance (DR) techniques have been widely used in molecular rotational spectroscopy as a tool to confirm assignments of complex spectra and to measure transitions lying outside the frequency range of the microwave spectrometer.<sup>36–42</sup> One of the first authors to use a Balle–Flygare type<sup>43</sup> FT microwave spectrometer in a DR experiment was Martinache *et al.*<sup>44</sup> More recently, several groups<sup>45,46</sup> have implemented slightly different variants of DR spectroscopy, allowing them to study van der Waals complexes and other transient species.

Because so few lines of HOSO<sup>+</sup> are accessible in the frequency range of our FT microwave spectrometer, and to be certain of the present assignments, double resonance experiments have been performed to confirm that the two  $K_a = 0$  lines of each isomer share a common rotational level and therefore arise from a common carrier. Our double resonance experiments employ a coaxial molecular beam in which the FT spectrometer is tuned in frequency to the higher *J*-rotational line (i.e., the  $2_{0,2} \rightarrow 1_{0,1}$  transition near 34 GHz; the so-called “signal,” following the notation of Jäger and Gerry<sup>45</sup>) for both HOSO<sup>+</sup> isomers, while microwave radiation generated from a second frequency synthesizer (the so-called “pump” operating between 1 and 26 GHz) propagates perpendicular to the molecular beam near the beam waist of the Fabry–Pérot cavity. Pump radiation is coupled into the cavity by means of a horn in combination with a collimating



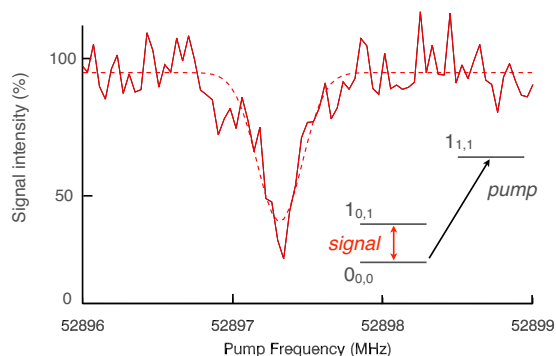


FIG. 3. The fundamental  $b$ -type transition  $1_{1,1} \rightarrow 0_{0,0}$  of *trans*-HOSO<sup>+</sup> recorded by double resonance spectroscopy. A schematic diagram indicating the two transitions that share a common energy level is shown in the inset. The spectrum was recorded in 40 kHz steps, in which the intensity at each step is a coverage of 100 signal pulses (17 s of integration at the 6 Hz repetition rate of the nozzle); the total integration time was approximately 20 min. Three spectra have been coaveraged to determine the frequency reported in Table III. Frequencies were obtained by fitting Gaussian line profiles (shown as dashed red) to the double resonance spectra.

lens; the timing is adjusted so that this radiation is only present during the signal free induction decay. A DR spectrum is then recorded by monitoring the signal intensity as the pump is tuned in frequency through the lower- $J$  transition (i.e., the  $1_{0,1} \rightarrow 0_{0,0}$  near 18 GHz). If the two transitions share a common level, the signal intensity may either increase or decrease, the sign depending on whether polarization or population effects are dominant.<sup>45</sup>

DR spectroscopy has also been used here to extend the frequency range of our HOSO<sup>+</sup> measurements, enabling line frequencies for the  $3_{0,3} \rightarrow 2_{0,2}$  transitions of both isomers to be precisely determined (Table III). In this variant, tunable radiation up to 60 GHz is produced by coupling the output of a second synthesizer into a frequency quadrupler. A spectrum is then recorded by monitoring the intensity of the  $2_{0,2} \rightarrow 1_{0,1}$  transition near 34 GHz with the FT microwave spectrometer as the pump is swept across the predicted frequency of the  $3_{0,3} \rightarrow 2_{0,2}$  transition.

Employing a similar setup, two  $b$ -type transitions have been detected for both isomers: the fundamental  $1_{1,1} \rightarrow 0_{0,0}$  transition near 52 GHz was detected by monitoring the intensity of the  $1_{0,1} \rightarrow 0_{0,0}$  transition (see Fig. 3) and the  $1_{1,0} \rightarrow 1_{0,1}$  transition near 36 GHz was detected by monitoring the intensity of the  $2_{0,2} \rightarrow 1_{0,1}$  transition. The sign of the double resonance signals—a decrease in signal intensity—is just as expected. Because the lowest- $J$  levels have comparable populations in our rotationally cold molecular beam, the primary effect of the pump radiation is to partially destroy the coherence of the free induction decay, which diminishes the signal intensity; this behavior is similar to that described by Suma *et al.*<sup>47</sup>

## V. RESULTS AND ANALYSIS

Both *cis*- and *trans*-HOSO<sup>+</sup> are closed-shell asymmetric top rotors fairly close to the prolate symmetric limit ( $\kappa = -0.899$  for *cis* and  $\kappa = -0.902$  for *trans*), with  $a$ - and  $b$ -type transitions. The  $a$ -type spectrum is predicted to be more intense for both isomers, particularly for *cis*-HOSO<sup>+</sup>, owing to

the threefold larger dipole moment along the  $a$ -axis (1.74 D versus 0.49 D along the  $b$ -axis). The  $K_a = \pm 1$  rotational ladders lie only 2.6 K above ground and are efficiently populated in our rotationally cold molecular beam ( $T_{\text{rot}} \sim 3$  K), and, as a result, the rotational spectrum of *cis*-HOSO<sup>+</sup> does not consist of a single series of closely-related harmonic lines from  $K_a = 0$ , as it does for the recently detected HSCS<sup>+</sup> or HSCO<sup>+</sup> ions. Those measured for the normal species are summarized in Table III; those of *cis*-DOSO<sup>+</sup> are given in Table IV.

A standard asymmetric top Hamiltonian<sup>48</sup> was used to reproduce the measured transition frequencies of both isomers and *cis*-DOSO<sup>+</sup>. Using only the three rotational constants and fixing the centrifugal distortion terms to their calculated values, it was possible to reproduce the seven transition frequencies of the normal isotopic species of *cis*-HOSO<sup>+</sup> and *trans*-HOSO<sup>+</sup> to the measurement uncertainties; for *cis*-DOSO<sup>+</sup>, one component of the deuterium quadrupole coupling tensor ( $\chi_{aa}$ ) is needed as well to achieve a satisfactory fit. The derived spectroscopic constants for both isomers are summarized in Table II, along with the corresponding theoretical values; those for *cis*-DOSO<sup>+</sup> are given in Table IV.

The spectroscopic and chemical evidence for the present identifications is compelling. For both isomers, the three rotational constants are within 0.1% of those predicted from the high-level coupled-cluster calculations (Table II) in Sec. II. The observed lines also pass several other tests: they are only found in the presence of an electrical discharge through a gas containing H<sub>2</sub> and SO<sub>2</sub>, as expected, and the lines of the normal isotopic species disappear when H<sub>2</sub> is replaced by D<sub>2</sub> as the buffer gas, indicating a hydrogen-containing molecule. Like other recently detected ions, all lines assigned to HOSO<sup>+</sup> or its isotopic species disappear when a permanent magnet is brought near the molecular beam. The origin for this effect is that a static magnetic field produces a Lorentz force on fast-moving charged particles, which, in turn, increases the collisional cross section and therefore linewidth for light ions such as protonated carbonyl sulfide<sup>32</sup> and the butadiyne anion, C<sub>4</sub>H<sup>-</sup>.<sup>49</sup> In addition, the double resonance experiments described in Sec. IV confirm that the  $K_a = 0$  lines do not arise from chance coincidence; they are instead from two transitions of the same molecules that share a common rotational state.

Confirmation of the *cis*-HOSO<sup>+</sup> assignment is also provided by isotopic substitution: lines of the deuterium isotopic species were observed within 0.006% of those calculated from the molecular structure, yielding individual rotational constants that again agree within 0.09% of those predicted theoretically. In addition, the resolved hyperfine structure in the fundamental rotational transition of *cis*-DOSO<sup>+</sup> establishes that the carrier contains deuterium; the very close agreement of the measured quadrupole coupling constant  $\chi_{aa} = -85(4)$  kHz to that predicted from theory ( $-115$  kHz) leaves little doubt that *cis*-DOSO<sup>+</sup> is the carrier of the observed lines. Finally, the detection of the fundamental rotational transition of HO <sup>34</sup>SO<sup>+</sup> (17 925.2 MHz) in natural abundance with the expected intensity within 0.006% of that predicted from the molecular structure provides further evi-

TABLE V. The total energies of HOSO<sup>+</sup> and HSO<sub>2</sub><sup>+</sup> species (hartrees) and the zero-point vibrational energy (ZVPE) and the corresponding relative energy (kcal/mol).

	Total energy <sup>a</sup>	ZPVE <sup>b</sup>	Relative energy
<i>cis</i> -HOSO <sup>+</sup>	−548.806 858	11.27	0.0
<i>trans</i> -HOSO <sup>+</sup>	−548.803 048	11.27	2.4
Transition state	−548.790 417	10.18 <sup>c</sup>	9.2
HSO <sub>2</sub> <sup>+</sup> (S-protonated)	−548.740 561	10.47	40.8

<sup>a</sup>CCSD(T)/cc-pwCVQZ.

<sup>b</sup>CCSD(T)/cc-pV(T+d)Z.

<sup>c</sup>From harmonic force field.

dence that the assigned lines arise from *cis*-HOSO<sup>+</sup> with the structure shown in Fig. 1 and no other molecules.

## VI. DISCUSSION

At the highest level of theory employed here, the energy difference between *cis*- and *trans*-HOSO<sup>+</sup> is only 2.4 kcal/mol (see Table V), but both are well-defined minima on the potential energy surface, separated by a transition state that is located about 9 kcal/mol above *cis*-HOSO<sup>+</sup> (see Fig. 1 and Table V). The next most stable isomer is the S-protonated C<sub>2v</sub>-form HSO<sub>2</sub><sup>+</sup>, but this one is considerably higher in energy, lying about 41 kcal/mol above *cis*-HOSO<sup>+</sup>.

The CCSD(T)/cc-pV(Q+d)Z calculation of anharmonic force fields also provides fundamental vibrational frequencies for *cis*- and *trans*-HOSO<sup>+</sup> that may support future investigations in the infrared. For both molecules, the  $\nu_3$  modes at 1029 cm<sup>−1</sup> (*cis*) and 949 cm<sup>−1</sup> (*trans*) are predicted to be the strongest with intensities of a few hundred km/mol<sup>−1</sup>.<sup>29</sup> From a calculation of the harmonic force field of the transition state at the CCSD(T)/cc-pV(T+d)Z level of theory, an imaginary frequency is found for  $\omega_4$ .

Because SO<sub>2</sub> possesses a high fractional abundance in some astronomical sources, it has a high proton affinity, and because ion-molecule reactions play an important role in interstellar chemistry, protonated derivatives of the form HSO<sub>2</sub><sup>+</sup> would appear to be the natural candidates for astronomical detection, especially since the most stable isomers are calculated to be highly polar. Now that precise laboratory rest frequencies are available to guide astronomical searches in the centimeter-wave band, the search for protonated SO<sub>2</sub> should probably be undertaken first in cold, dark dust clouds [e.g., TMC-1 and L183 (Ref. 3)] where sulfur dioxide has already been found using large sensitive single-dish radio telescopes, such as the NRAO 100 m Green Bank Telescope. In some sources, the millimeter lines rather than the centimeter-wave lines may be the most intense, and thus it is desirable to soon measure the rotational spectrum of both isomers above 60 GHz, to better constrain the centrifugal distortion parameters, and to prepare an accurate frequency catalog so that astronomical search can then be performed with confidence in the (sub)millimeter band with large single-dish observatories or powerful interferometers such as the upcoming Atacama Large Millimeter Array, ALMA, in the near future. If both isomers can be detected in space, comparisons of the relative column densities may provide

insight into the formation mechanism because very low collision energies and temperatures characterize most astronomical sources.

Other protonated molecules might be detectable with the present techniques. Among the most promising would appear to be protonated SO and isocyanic acid, H<sub>2</sub>NCO<sup>+</sup>. The fundamental rotational transition of HSO<sup>+</sup> (42.8 GHz) lies just above the frequency ceiling of our FT microwave spectrometer, but the detection of the same transition of DSO<sup>+</sup> (40.2 GHz) should be possible owing in part to its large calculated *a*-dipole moment (2.8 D). H<sub>2</sub>NCO<sup>+</sup> is calculated to have a sizable proton binding energy (782 kJ/mol), a structure with C<sub>2v</sub> symmetry,<sup>50</sup> and a substantial dipole moment [4.3 D (Ref. 51)].

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