

Submillimeter-wave spectral lines of negative ions (SH^- and SD^-) identified by their Doppler shift

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For the first time submillimeter-wave transitions of an anion have been firmly identified. We observed one transition of SH^- ($J=1 \leftarrow 0$, 564 421.869 MHz) and two of SD^- ($J=1 \leftarrow 0$, 292 359.129 MHz; $J=2 \leftarrow 1$, 584 629.519 MHz) created in the positive column of an electric discharge set up in a mixture of H_2S and argon. By studying the Doppler shift brought about by the motion of charged species in the electric field of the discharge we were able to distinguish between positively and negatively charged ions and neutrals. We have hence shown that velocity modulation techniques commonly used for infrared spectroscopy could also be successfully applied for the study of ions in the submillimeter-wave region. © 1998 American Institute of Physics. [S0021-9606(98)00220-7]

INTRODUCTION

In this paper we will use the term “microwave” in its broadest sense to denote techniques first developed in the cm-wave region regardless of the actual frequency used. That is to say the use of coherent radiation generated by the oscillation of electrons in a resonant cavity and phase-locked against a reference oscillator. In recent years microwave spectroscopy has often been superseded by laser spectroscopy as a means of identifying and studying new molecular species. However, gas-phase microwave spectroscopy, which has been successively extended through the millimeter-wave, and submillimeter-wave region up to frequencies above 1 THz, still holds certain advantages. First, it remains the method by which the most precise approximations of molecular structure can be made. Second, it is the spectral region in which the identification of different molecular species in space is most often and most easily carried out. For example, the projected launching of the FIRST space based observatory working in the 0.3 to 3 THz region has given a new impetus to the research for new molecular species measured in this frequency range. Indeed the needs of astrophysicists for precise frequency predictions either in looking for new molecules in different regions of space or for identifying available astronomical spectra has provided much interesting work for microwave spectroscopists. A collaboration between these two scientific communities has already led to the astrophysical identification of a certain number of positive ions.^{1,2}

Despite the measurement of the microwave spectrum of several positive ions produced in the laboratory, no identi-

cation of microwave induced transitions of negative ions has previously been reported. This may be due to a combination of different factors. First, the simplest and most chemically stable anions are small light molecules. This means that the first rotational line is already high in frequency (by microwave standards) and the spectrum is sparse. Until recently the availability of suitable sources strong enough for the observation of such short-lived molecules limited microwave spectroscopy to below 500 GHz. SH^- for instance has no rotational transition in this frequency range and SD^- only the first rotational transition. However, the recent availability of Russian-constructed backward-wave-oscillator tubes now makes possible microwave measurements up to and exceeding 1 THz.^{3,4}

The second problem is to find the experimental conditions for producing anions in sufficient quantity to measure their rotational spectrum. As for all reactive molecules these conditions must be carefully optimized but are not necessarily the same at the pressures used for microwave spectroscopy as they are for those at the higher pressures used for infrared measurements. Even in optimum conditions the density of ions formed will be greatly inferior to that of the stable precursor molecules in the cell. Since these ions also have short lifetimes their time-averaged absorption signals will be weak. The choice of a first candidate negative ion was hence particularly important. One of us (S.C.) already had experience in producing the SD^- anion whose spectrum was measured in the infrared region by diode-laser spectroscopy.⁵ He had noticed that transitions of this ion were only of slightly lower intensity than those of the cation SD^+ when both of these ions were produced in the positive column of an electric discharge. We therefore decided to search first for this anion and for the parent hydrosulfide ion (SH^-) which has also been observed by infrared spectroscopy.^{6,7} The infrared results could then be used to narrow down the choice of experimental conditions and to predict transition frequencies to limit the frequency range to be searched.

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Even if optimum conditions can be found to produce a light anion and a suitable spectrometer is available for measuring its rotational transitions the major problem remains how to identify this ion from its very sparse spectrum. The lines of anions can be expected to be weak and have comparable or smaller intensities than lines of cations or of other reactive molecules even maybe those with isotopically less-abundant atoms or in excited vibrational or electronic states. The spectra of these latter may not be documented and are hence difficult to eliminate.

The problem of identifying ions has been solved in the infrared region by a velocity-modulation technique developed by Saykally and co-workers 15 years ago.⁸ The polarity of the two electrodes generating the discharge is modulated and the generated ions are hence moved back and forward along the discharge cell. This results in a modulation of the frequency of the exciting radiation seen by the ions due to a Doppler shift. By demodulating at the same frequency, lines due to noncharged species are eliminated and positive and negative ions can be discriminated by the relative sign of the first-derivative signal obtained. This has become a standard technique in infrared spectroscopy of ions.⁹ However, in the microwave region we are not aware of any published work referring to the successful use of velocity modulation.

The concentration of cations is expected to be highest in the negative glow region of a discharge.¹⁰ A magnetically extended-negative-glow is hence often employed for the generation of cations but the weakness of the electric field probably leads to an insignificant Doppler shift. The same is true of hollow-cathode discharges. The concentration of anions is, however, accepted to be greatest in the positive column of a discharge.¹⁰ We hence decided to search for SD^- and SH^- in the positive column and to see if we could distinguish neutrals, positive, and negative ions by the Doppler shift of their transition frequencies.

EXPERIMENT

The Lille microwave spectrometer^{11,12} works on the simple concept of absorption spectroscopy comprising a variable-frequency source (phase-locked to a reference oscillator), an absorption cell and an extremely low-noise helium-cooled InSb detector (QMC Instruments, London). Reactive molecules are created *in situ* by setting up a discharge in the absorption cell. We use a flow system to constantly provide fresh precursor gas and to remove final discharge products. The simple design allows a very wide frequency coverage and belies a large sensitivity enhanced by the use of frequency modulation and phase-sensitive detection.

In these experiments microwave power was provided by Russian constructed BWO tubes (ISTOK Research and Production, Fryazino) phase locked against a 78-118 GHz synthesizer (KVARZ, Nizhnii Novgorod) as described in previous articles.^{13,3}

The anions were produced in a positive-column discharge set up in a mixture of H_2S (or D_2S) at a concentration of 4% in argon. The total pressure in the cell, measured at room temperature, was 0.1 mbar. Typical discharge conditions were 3 kV and 100 mA. The discharge cell can be cooled by flowing liquid nitrogen through an outer jacket.

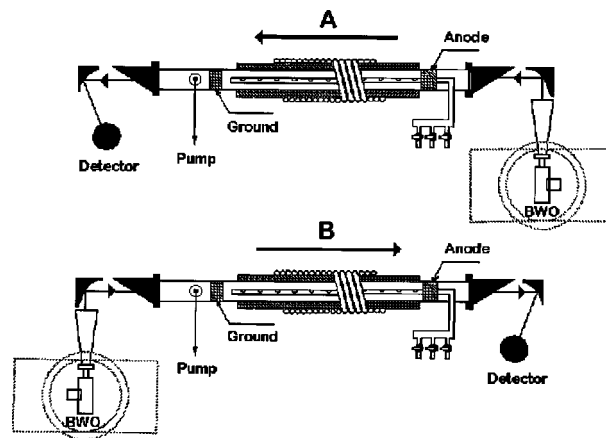


FIG. 1. Schematic diagram of experimental setup showing discharge cell, discharge polarity, microwave source and detector. In two successive sets of experiments the position of the detector and source are interchanged so that the electric field is in the same direction (A) or opposite direction (B) to the propagation of microwave energy.

The anion lines could be seen at room-temperature but were stronger with cooling. Cooling also helped to eliminate a number of parasite lines.

The technique of velocity modulation was not envisaged when the Lille discharge cell was designed. Due to the larger cell dimensions and lower pressures employed in microwave spectroscopy a diffusion pump is connected directly to the cell in order to provide sufficient pumping speed. The setup requires that the electrode closest to the pump be held at earth potential to prevent arcing. We were hence not able to change electrode polarities. In order to test if the movement of ions in the electric field between the two electrodes creates a measurable Doppler shift we hence proceeded in the following manner. One set of measurements was first taken with the setup A shown in Fig. 1. The millimeter-wave source and detector were then exchanged so that the sense of radiation propagation was reversed, and a second set of frequency measurements taken with the setup B.

RESULTS

The results are summarized in Table I. We first tested a known positive ion, SH_3^+ , also created in the hydrogen sulfide discharge, to see if we could observe a difference in the frequency measured with the two experimental setups A and B. As can be seen from Fig. 2(a), a line measured around 587 GHz was shifted by about 230 kHz between the two setups. We repeated the measurement eight times for each setup. Figure 2(b) summarizes the results and shows that the shift is much greater than the spread of frequencies from successive results with the same configuration. It should be noted that the small spread of results for one configuration does not indicate the absolute accuracy of our measurements only the reproducibility of the frequency measurement under the same experimental conditions. These conditions were kept the same for the two sets of measurements. In order to check that the frequency difference was really due to a Doppler shift we also measured a nearby transition of H_2S (with the

TABLE I. Comparison of the Doppler shift between the two experimental setups for neutral, positively and negatively charged species. The mean (unshifted) frequency is also given.

Molecule		Measured center frequency (MHz)	Comparison with previous results or predictions	Frequency shift (kHz) between setups A and B
H ₂ S	7 ₅₂ ←7 ₄₃	555 253.983	555 253.972 ^a	<5
N ₂ H ⁺	6←5	558 966.528	558 965.7 ^b	+36
SH ₃ ⁺	2←1; K=0	586 805.343	586 805.550 ^c	+228
SH ⁻	1←0	564 421.869	564 409.5 ^d ; 564 416.8 ^e	-220
SD ⁻	1←0	292 359.129	292 367.8 ^f	-120
SD ⁻	2←1	584 629.519	584 640.8 ^f	-131

^aMeasurement. Reference 14.^bMeasurement. Reference 15.^cMeasurement. Reference 16.^dPrediction using infrared measurements from Ref. 6.^ePrediction using infrared measurements from Ref. 7.^fPrediction using infrared measurements from Ref. 5.

discharge running). The results showed as expected (since the molecule is neutral) no observable frequency difference between the setups A and B.

Prior to these measurements we had already scanned more than 200 MHz around the predicted frequency for the first rotational transition of SH⁻. We had tested all the lines which could not be identified as belonging to known molecules and rejected those which appeared to arise from long-lived or paramagnetic species. We were left with a small number of lines which were good candidates as being due to the SH⁻ ion but between which we could not distinguish.

We then set about measuring the frequency of each one of these candidate lines several times with the setup A and several times with the setup B, without changing discharge conditions. We found one line (and one line only) which had a frequency shift (-220 kHz) opposite to that of SH₃⁺ and which we hence identified as belonging to the negative ion.

For SD⁻ two transitions were available in our operating range, the first rotational transition predicted around 292 GHz and the second around 584 GHz. In both cases we repeated the experimental procedure above (after replacing H₂S by D₂S) and found one single line close to the predic-

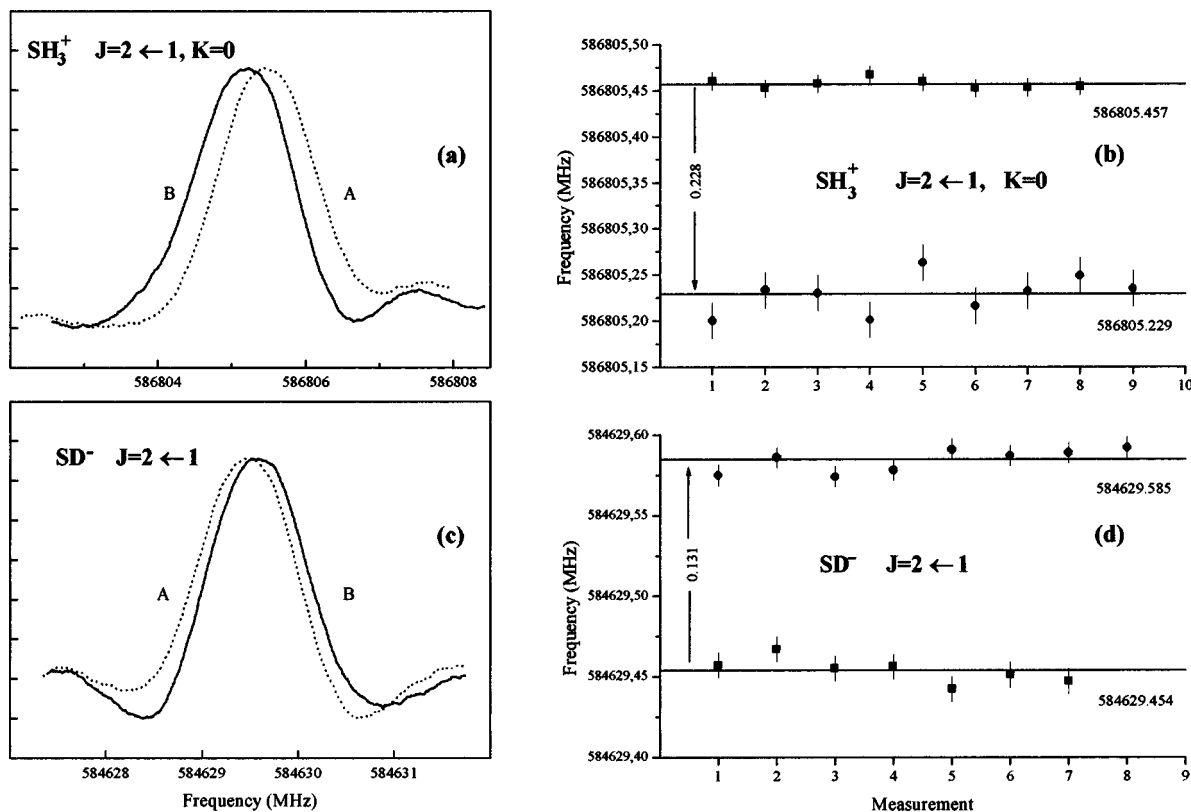


FIG. 2. The Doppler shift of transition frequencies of the negative ion SD⁻ (c) and (d) is opposite to that of the positive ion SH₃⁺ (a) and (b). In the left-hand figures dotted (A) and solid (B) traces show spectral lines recorded with detector and source interchanged. The right-hand figures show measured frequencies, from successive experiments. The shift between setups A (■) and B (●) can be seen to be much greater than the spread of results for one setup. For neutral molecules no such shift was observed.

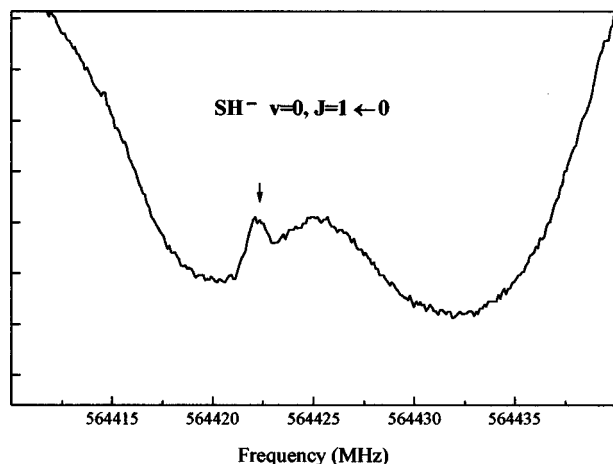


FIG. 3. Single scan of 30 MHz showing absorption of SH^- compared to noise, and baseline variation due to standing waves set up in cell. For this scan we used frequency modulation at 40 kHz with phase-sensitive detection (PSD) at twice the modulation frequency and 100 ms time constant.

tions which shifted in the same direction as the line attributed to SH^- . Figures 2(c) and 2(d) illustrate that this shift is opposite to that observed for a positive ion.

In order to see if this Doppler-shift test could generally be applied to ions formed by positive column discharge in other gas mixtures and to further test the validity of the results we applied the same technique to the known molecular ion N_2H^+ . We obtained a shift opposite to that of the anions and in the same direction seen for the cation SH_3^+ .

Figure 3 depicts a single scan of 30 MHz showing the $J=1 \leftarrow 0$ transition of SH^- and which gives some idea of the relative size of the line, noise and background. The background is due to accidental multiple reflections; a well known problem in microwave absorption spectroscopy which has been minimized in Lille by the use of Brewster-angle windows at the entrance and exit to the cell. The line is shifted slightly to high frequency because of the relatively large time-constant (100 ms) used to decrease the noise. Line frequency measurements, used to determine the Doppler shifts, were made with a lower time-constant and calculated after separate accumulation of up and down-scans. Successive results were taken with different backgrounds (obtained by moving slightly the position of the detector) in order to verify that the background could not accidentally be the cause of the shifts attributed to the ion movement. The fre-

quency shifts quoted in Table I are the differences between the mean of the series of results for setup A and for setup B. The measured center frequencies are the mean of the two series and hence suppose that the shifts are symmetric.

DISCUSSION

Although we scanned a relatively large region around the predictions from the infrared data the measured transitions were finally quite close. As can be seen in Table I the line of SH^- was found only 5 MHz lower than predictions based on the latest infrared measurements.⁷ The first and second transitions of SD^- were found, respectively, about 9 and 11 MHz lower than predictions. It should be noted that although the infrared measurements were invaluable in indicating the frequency region where the search for the microwave transitions should be made they were not sufficient alone to identify the microwave transitions. We found other nonidentified lines equally close to the predictions, stronger in intensity than the lines finally attributed to the anions and which could not be excluded as candidates without the Doppler-shift test.

In later work on N_2H^+ we discovered that although the direction of the Doppler shift was always the same for a particular ion, the size of the shift depended strongly on experimental conditions. Cooling produced higher shifts indicating higher ion mobility. The largest shifts and ion mobilities were seen with small discharge currents (<10 mA). This may help to explain why these Doppler-shifts have not been commonly reported in the microwave region as ions are often created using currents of several 100 mA. A study of ion mobilities at the lower pressures used for microwave spectroscopy would be interesting but is outside the scope of this article.

The measured line of SH^- , as expected, fits well with the infrared data^{6,7} and, as can be seen in Table II, its inclusion improves somewhat the rotational constants, especially B_e , at the expense of a very slight increase in the standard deviation of the vibrational constants. Revised molecular constants for SD^- are given in Table III. First work on this ion indicated that although the infrared lines⁵ fitted well, the $v_1 \leftarrow 0$, $P(5)$ transition had a larger deviation than the others. This transition was subsequently remeasured at 1784.442 cm^{-1} , using the infrared diode-laser spectrometer in Prague, having been incorrectly attributed in the previous

TABLE II. The addition of one measured rotational transition of SH^- to previous infrared data improves somewhat the fitted rotational constants. The standard deviation of the vibrational constants slightly increases.

Molecular constants cm^{-1}	Reference 6	Reference 7	Inclusion of microwave measurement
ω_e	2 645.634(40)	2 645.641 3(12)	2 645.643 0(16)
$\omega_e x_e$	52.155(15)	52.155 93(44)	52.156 30(51)
B_e	9.562 70(20)	9.562 849(53)	9.562 918(14)
α_e	0.296 76(14)	0.296 750(28)	0.296 784(30)
$10^4 \times \gamma_e$	0.52(21)	0.439(96)	0.474(75)
$10^4 \times D_e$	5.012(39)	4.990 0(51)	4.991 0(27)
$10^6 \times \beta_e$	-2.6(15)	-3.046(91)	-3.17(12)
$10^6 \times H_e$	0.032(11)	0.013 5(16)	0.012 8(14)

TABLE III. After the inclusion of two measured rotational transitions of SD^- to previous infrared data we were able to determine three new fitted molecular constants and decrease the standard deviation of B_e and D_e . The standard deviation of the previously determined vibrational constants slightly increased.

Molecular constants cm^{-1}	Reference 5	Inclusion of microwave data
ω_e	1 899.150 0(24)	1 898.639 9(38)
$\omega_e x_e$	26.649 6(12)	26.242 8(21)
B_e	4.931 54(11)	4.931 358(11)
α_e	0.109 960(40)	0.110 255(22)
$10^4 \times \gamma_e$	—	1.57(20)
$10^4 \times D_e$	1.356 9(44)	1.210 5(17)
$10^6 \times \beta_e$	—	-4.75(39)
$10^6 \times H_e$	—	3.16(28)

work to a nearby stronger line. This discrepancy was not discernible before inclusion of the microwave data.

The next transition of SD^- lies around 877 GHz, that of SH^- around 1.1 THz. Although we possess BWO tubes capable of working in this region we do not yet have sufficient sensitivity to detect reactive species in such low concentration. The future acquisition of an inhomogeneously tuned InSb bolometer (QMC Instruments) should make these measurement possible and open the way to the study of other light cations.

CONCLUSION

We have shown that negative ions can be created at the low pressures used for microwave spectroscopy. We have demonstrated that Doppler shifts similar to those already observed in infrared spectroscopy can be used for classing microwave lines as originating from neutral, positively, or negatively charged species. It is, however, important to use the right discharge conditions in order to observe these shifts. Our results indicate a possible source of error in microwave measurements of ions if this shift is not taken into account. They also suggest that it may be possible to use velocity-modulation techniques, currently employed in infrared work, even at relatively low microwave frequencies. The high precision of microwave measurements could facilitate the study of ion mobilities.

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- ¹J. L. Destombes, C. Demuynck, and M. Bogey, *Philos. Trans. R. Soc. London, Ser. A* **324**, 147 (1988).
- ²F. J. Lovas, *J. Phys. Chem. Ref. Data* **21**, 181 (1992).
- ³M. Bogey, S. Civiš, B. Delcroix, C. Demuynck, A. F. Krupnov, J. Quiguer, M. Yu. Tretyakov, and A. Walters, *J. Mol. Spectrosc.* **182**, 85 (1997).
- ⁴S. P. Belov, F. Lewen, Th. Klaus, and G. Winnewisser, *J. Mol. Spectrosc.* **174**, 606 (1995).
- ⁵Z. Zelinger, A. Bersch, M. Petri, W. Urban, and S. Civiš, *J. Mol. Spectrosc.* **171**, 579 (1995).
- ⁶M. Gruebele, M. Polak, R. J. Saykally, *J. Chem. Phys.* **88**, 1698 (1986).
- ⁷M. Elhanine, R. Farrenq, G. Guelachvili, and M. Morillon-Chapey, *J. Mol. Spectrosc.* **129**, 240 (1988).
- ⁸C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).
- ⁹See, for example, R. J. Saykally, *Science* **239**, 157 (1988).
- ¹⁰A. von Engel, *Ionized Gases* (Clarendon, Oxford, 1965).
- ¹¹M. Bogey, H. Bolvin, M. Cordonnier, C. Demuynck, J. L. Destombes, and A. G. Császár, *J. Chem. Phys.* **100**, 8614 (1994).
- ¹²J. L. Destombes, M. Bogey, M. Cordonnier, C. Demuynck, and A. Walters in *Molecules and Grains in Space*, Conference Proceedings No. 312, edited by I. Nenner (American Institute of Physics, New York, 1994), p. 268.
- ¹³G. Winnewisser, A. F. Krupnov, M. Yu. Tretyakov, M. Liedke, F. Lewen, A. H. Saleck, R. Schieder, A. P. Shkaev, and S. V. Volokhov, *J. Mol. Spectrosc.* **165**, 294 (1994).
- ¹⁴S. P. Belov, K. M. T. Yamada, G. Winnewisser, L. Poteau, R. Bocquet, J. Demaison, O. Polyansky, and M. Yu. Tretyakov, *J. Mol. Spectrosc.* **173**, 380 (1995).
- ¹⁵W. C. Ho, C. J. Pursell, D. P. Weliky, and T. Oka, *J. Chem. Phys.* **93**, 87 (1990).
- ¹⁶S. K. Lee, H. Ozeki, S. Saito, and S. Yamamoto, *Chem. Phys. Lett.* **224**, 21 (1994).