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PRESSURE BROADENING OF HYDROGEN SULFIDE†

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Abstract—Microwave measurements of the self-broadening parameters of four pure rotational transitions of H_2S have been carried out in the millimeter and submillimeter wavelength region. The resulting parameters are (in MHz torr^{-1}): $1_{1,0}-1_{0,1}$, 7.18 ± 0.5; $2_{2,0}-2_{1,1}$, 6.78 ± 0.5; $2_{1,1}-2_{0,2}$, 9.10 ± 0.5; $3_{3,0}-3_{2,1}$, 7.76 ± 0.5. In addition, Anderson theory calculations have been carried out for these transitions and are found to be in good agreement.

INTRODUCTION

BECAUSE H_2S is a light asymmetric rotor without transitions in the conventional microwave region, we have used high resolution millimeter and submillimeter microwave techniques[1] to measure the self-broadening parameters of four pure-rotational transitions of H_2S in the region between 150 and 400 GHz. To the best of our knowledge, these results are the first experimental measurements of the pressure broadening parameters of H_2S. We have also carried out Anderson theory[2] calculations and find them to be in good agreement with our experimental values.

These results are of both theoretical and practical importance. H_2O is the only other light asymmetric species for which experimental line-broadening data have been reported and some of these data are in substantial conflict with theoretical predictions.[3] H_2S is both a minor constituent of the atmosphere and one of the principal molecular components of the interstellar medium.

EXPERIMENTAL TECHNIQUE AND RESULTS

We have discussed in previous publications the techniques for producing and detecting millimeter and submillimeter microwave energy.[1] Our pressure-broadening measurement technique follows closely the double modulation scheme of RUSK.[4] Figure 1 shows an outline of our apparatus. Millimeter wave energy in the 50–60 GHz region was produced by an OKI 55V11 klystron. A small amount of this energy was compared with an accurate local frequency standard and the rest coupled onto a crystal harmonic generator. The resultant harmonic energy in the 150–400 GHz region was transmitted by quasi-optical techniques through the sample cell and detected by a 1.6°K InSb photodetector. The pressure-broadened line acted as a discriminator for the small 10 kHz FM modulation that was applied to the tube. The resulting 10 kHz signal was amplified by the tuned amplifiers of a PAR HR-8 lock-in and displayed on an oscilloscope. A cathetometer and oil manometer were used to monitor pressure. Although H_2S is well behaved and reaches equilibrium pressure rapidly, measurements were made both in series of increasing and decreasing pressure and on different days to avoid possible systematic effects. Because rotational transitions of light asymmetric rotors are such strong absorbers in the millimeter and submillimeter spectral region, we used absorption cell lengths as short as 10 cm. Even so, it was necessary to include a correction for the large absorption by[5]

$$\Delta\nu = \sqrt{(3)}\delta\nu\left(1-\frac{1}{4}a_0l+\frac{5}{32}(a_0l)^2-\cdots\right), \tag{1}$$

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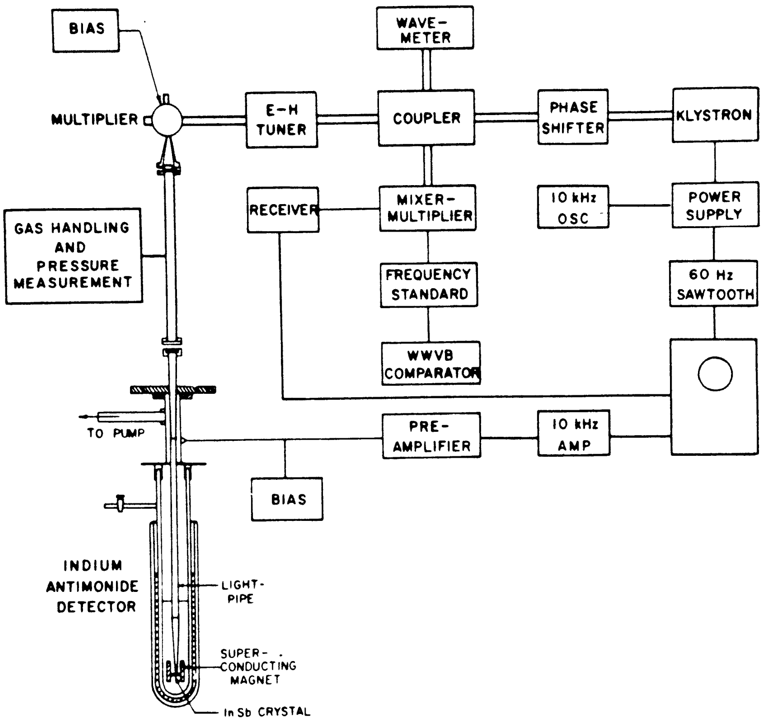

Fig. 1. Submillimeter wave pressure broadening system.

where a_0 is the absorption coefficient, l the cell length, $2\delta\nu$ the distance between the inflection points on our oscilloscope and $\Delta\nu$ the pressure broadened linewidth. Our preliminary report[6] on these data does not include this correction. Figures 2–5 show the experimental data and Table 1 contains the parameters calculated from these data. The uncertainties listed are approximately four times the statistical uncertainties of the fits of the experimental data points and somewhat larger than the corrections for large absorption.

ANDERSON THEORY CALCULATIONS

In a monumental work, BENEDICT and KAPLAN,[7] have calculated the pressure-broadening parameters of H_2O for a wide variety of transitions. We have followed their general procedures, which are based on TSAO and CURNUTTE'S[8] extension of Anderson's theory,[2] to calculate self-broadening parameters for comparison with our experimentally determined values. As a check of our computer programs, we have also calculated the line-broadening parameters of several H_2O transitions and find our results to be in excellent agreement with those of BENEDICT and KAPLAN.[7]

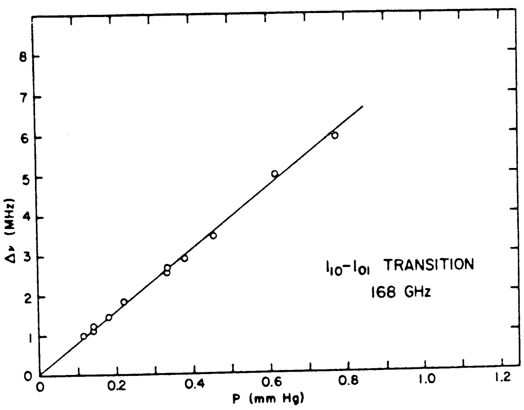

Fig. 2. Experimental data for the $1_{1,0} - 1_{0,1}$ transition.

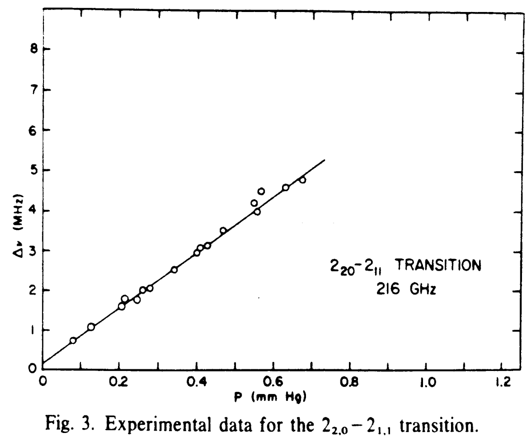

Fig. 3. Experimental data for the $2_{2,0}-2_{1,1}$ transition.

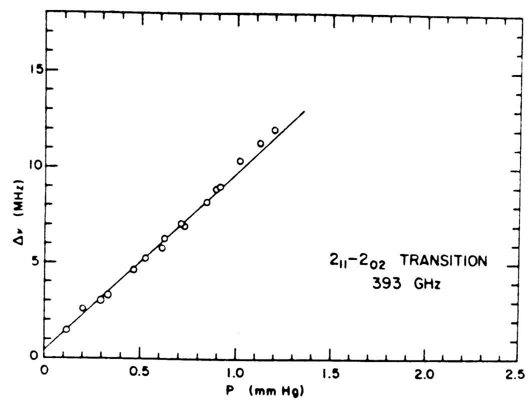

Fig. 4. Experimental data for the $2_{1,1}-2_{0,2}$ transition.

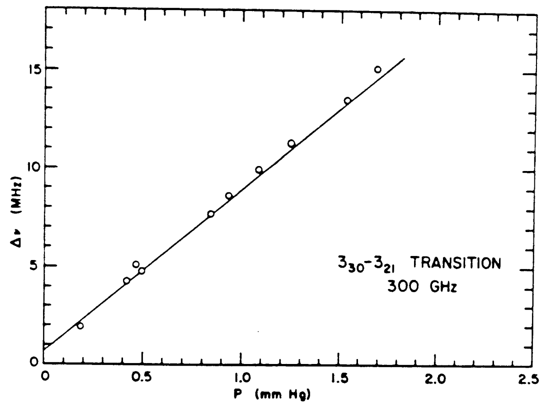

Fig. 5. Experimental data for the $3_{3,0}-3_{2,1}$ transition.

For all of our calculations, we have used the transition frequencies which resulted from our distortion analysis of the microwave rotational spectrum of H_2S.[9] The dipole moment of H_2S was taken to be 0.974 D[10] and rigid rotor transition moments were used. These moments should differ little from the exact transition moments for the strong rotational transitions which dominate the calculation. The upper limit on the energy of states included was determined by the requirement that the calculated parameters not change significantly with the addition of higher energy transitions. Table 1 shows that the results of our calculations are in good agreement with our experimental values.

Table 1. Hydrogen sulfide line broadening parameters

Transition	Line Frequency (GHz)	Experimental[a] Broadening Data (MHz/Torr)	Corrected Self Broadening Parameter (MHz/Torr)	Anderson Theory Value (MHz/Torr)
$1_{1,0}-1_{0,1}$	168	7.80	7.18 ± 0.5	6.58
$2_{0,2}-2_{1,1}$	216	9.69	9.10 ± 0.5	7.21
$2_{2,0}-2_{1,1}$	393	7.14	6.78 ± 0.5	6.99
$3_{3,0}-3_{2,1}$	300	8.52	7.76 ± 0.5	7.14

[a] Line widths measured at 300° K.

DISCUSSIONS

Until this work, H_2O was the only light asymmetric rotor for which comparison could be made of experimental and theoretical pressure-broadening parameters. Unfortunately, only the microwave measurements of the $3_{1,3}-2_{2,0}$[4] and $6_{1,6}-5_{2,3}$[11] transitions are in good agreement with the theoretical predictions. Several i.r. measurements all gave results that are about 50% higher than the values of BENEDICT and KAPLAN.[3] The good agreement between our microwave results and theory, coupled with the fact that the apparent discrepancies in H_2O are all based on lower resolution i.r. measurements, would indicate that Anderson's theory is capable of giving good results for pure rotational transitions of light asymmetric species. Recent microwave work by NERF[12] on the somewhat heavier H_2CO leads to the same conclusion.

TEJWANI and YENUNG[13] have recently carried out Anderson's theory calculations on H_2S with and without the inclusion of higher order interactions. Their results are in general agreement with ours (~10%) although the differences are substantially greater than the differences between our H_2O calculations and those of Benedict and Kaplan.

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