



MOLECULES OF ASTROPHYSICAL INTEREST: RECENT SUBMILLIMETER AND INFRARED SPECTRA

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Abstract—New developments in submillimeter technology are discussed: the use of new sweepers up to 180 GHz driven by backward wave oscillators. Spectroscopy in the terahertz region is carried out with BWOs. Detailed studies of line shifts and broadening are summarized.

I. INTRODUCTION

Laboratory studies provide basic spectroscopic information on spectra of atoms and molecules. In the past the main efforts concentrated on the measurement of highly precise transition frequencies, the determination of electric and magnetic dipole, and quadrupole moments and other spectroscopic properties. These data provided the pool from which astrophysicists could draw in the past for their impressive discoveries. However, with the advent of increased technical refinement, details in the line profiles and the dependence of the line center frequencies on pressure (foreign and self shift/broadening) can be revealed. The measurements of collisional phenomena reveal substantial information of intermolecular interactions under different physical conditions. These highly precise laboratory measurements along with traditional transition frequencies and assignments are of potential importance to planetary and astrophysical observations.

This paper reviews some recent laboratory studies and developments in molecular spectroscopy from the millimeter to the IR region. The results presented were obtained mostly in collaborative efforts between various laboratories, i.e. the Microwave Spectroscopy Laboratory of the Institute of Applied Physics, the Institute of Electronic Measurements KVARZ (both in Nizhny Novgorod, Russia), the Molecular Spectroscopy and the Time and Frequency Divisions, National Institute of Standards and Technology (NIST, Gaithersburg, Maryland and Boulder, Colorado, U.S.A.), the University of Cologne (Germany), and the Justus-Liebig University, Gießen (Germany).

II. MILLIMETER AND SUBMILLIMETER-WAVE SPECTROSCOPY

The use of Backward Wave Oscillators (BWOs) especially as high frequency radiation sources is generally well recognized, but has not yet been reported at this series of Conferences. BWOs together with an acoustic detector spectrometer are in long use at Nizhny Novgorod and provided for the first time recordings of continuous spectra in the millimeter- and most part of the submillimeter-wave region up to 1100 GHz. The sensitivities reached were between 10^{-8} and 10^{-10} cm^{-1} , depending largely on the power level of the BWO and the acoustic detector used.⁽¹⁾

However the lack of contact with laboratories engaged in astrophysical work and technical limitations associated with the metal-coated acoustic cell, limited our laboratory measurements to a relatively small number of chemically stable molecules. Some of those are of astrophysical interest, such as NH_3 and H_2O , especially in excited states. The scientific contacts with the University of Cologne have only recently opened the perspective of collaboration in the field of astrophysics.

In the present paper we shall describe some recent developments in submillimeter wave spectroscopy using BWOs as coherent radiation sources, although we are well aware of other

radiation sources such as klystrons and solid state sources, e.g. GUNN-oscillators. However BWOs have been used around 1 THz, a region which has not been reached by any other tunable source.

Continuous scans in the submillimeter wave range covering thousands of lines of acetaldehyde have been recorded in a joint work with NIST.⁽²⁾ For this work the BWO was stabilized to a tunable Fabry-Perot interferometer by an electronic feedback loop (Fig. 1) The tuning was achieved by means of moving one mirror of the interferometer, which in turn was also part of an He-Ne interferometer. Thus, the He-Ne fringes observed, gave precise information about the frequency tuning of the BWO between the lines of the reference spectrum recorded in another cell. The precise data of the submillimeter line positions are particularly important for non-rigid molecules, because the frequency positions of the transitions cannot be predicted from the lower frequency measurements with accuracies sufficient for astrophysical identifications. This statement is true for simple molecules such as the well-studied CH_3CN , CH_3OH , and many others, but it does hold in particular for molecular complexes, such as van-der-Waals molecules which are particularly amenable to large amplitude motions. Recently we have investigated in our Nizhny Novgorod laboratories simple molecular complexes such as HF-HF , HCl-HCl , $\text{H}_2\text{O-NH}_3$, and participated by new theoretical methods in analysing the spectra of H_3^+ , H_2D^+ and HD_2^+ .

At Nizhny Novgorod precise measurements of line positions, pressure broadening, and pressure shifts have been performed with a phase-locked BWO and an acoustic detector system, which provided the observed lines with a very high signal to noise ratio. The recorded spectra are relatively free from interference problems, since the acoustic detection registers only the power absorbed by the molecules averaged over the oversized cell. In "conventional" microwave detection, the change of the total power is registered. Therefore the acoustic detection does not respond to power level fluctuations, unless the molecule is absorbing which results principally in straight baselines. The remaining interference caused by power feedback (i.e. fringes) and its effect on the apparent position of the line center is removed, by shifting the location of the cell, which to first order influences the power pattern. This way the remaining baseline ripple is hopefully averaged out by taking the mean of several such scans. This measurement method was used for obtaining highly precise values for absolute line positions and line shift/broadening of several mm/submm transitions of the CO molecule.⁽³⁾ These results were obtained in a collaborative effort together with

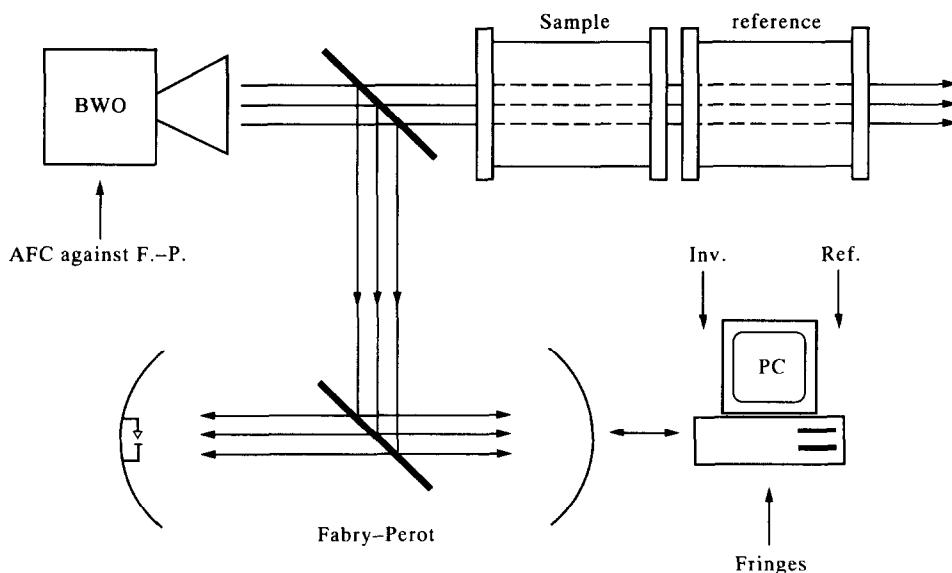


Fig. 1. Experimental arrangement of the Nizhny Novgorod Millimeter Wave spectrometer with Backward Wave Oscillators (BWO) and acoustic detector. Shown here is the version with a tunable Fabry-Perot interferometer (see text).

NIST and were used to interpret the observed winds in the Venus atmosphere. Accuracies of 1–2 kHz for the transition frequencies and also of 1–2 kHz/Torr for the lineshifts due to collisions with CO₂ were achieved for the first time. These data permitted the decrease of the errors of the laboratory measurements by approximately one order of magnitude.

Another significant development in the use of BWOs is a series of millimeter-wave synthesizers which, by three individual units, cover continuously the frequency region from 58 up to 178 GHz. They deliver CW power up to tens of milliwatts. The frequency of these sources is phase-locked to an internal quartz oscillator which can be stabilized on a standard radio signal of an external atomic clock. All settings of the instrument i.e. frequency increments, number of frequency steps per second, etc. and the data acquisition can be computer controlled. At millimeterwave frequencies the smallest frequency step is 100 Hz. The stability of the output signal in frequency, amplitude and phase allows subtraction of the background spectrum, recorded separately with an empty absorption cell. The difference spectrum shows a surprisingly flat baseline. As a first example we present OCCCS spectra recorded with this type of synthesizer in the frequency region between 78 and 118 GHz. This work was jointly done with the University Giessen (Germany) by employing a free space absorption cell equipped with a liquid He-cooled InSb bolometer. It is for the first time that such a wide and sensitive spectral scan has become possible, resulting in a large number of observed and also assigned lines of many different vibrational states.⁽⁴⁾ The measured frequency range covers the rotational spectrum of the linear molecule OCCCS starting at $J = 28 \leftarrow 27$ up to $J = 41 \leftarrow 40$ (Fig. 2).

About 5000 pure rotational lines have been recorded. The spectrum is dominated by ground state transitions, and associated low-lying excited states, particularly the ν_7 vibration around 78 cm⁻¹. Rotational satellites of hotbands up to $\nu_7 = 9$ and many combination bands add to the complexity. In this study a sensitivity level around 10⁻⁸ cm⁻¹ for a 120 ms time constant was reached, with no additional noise from the source.

The same type of synthesizer was used jointly together with NISTs (Gaithersburg) cooled beam, Electric Resonance Optothermal Spectrometer—EROS, to investigate the broad band spectrum of the heavy water dimer (D₂O)₂ with a resolution less than 100 kHz as determined by the time of flight broadening.⁽⁵⁾

As an example of the use of high frequency BWOs, we present a recent recording of the bandhead of the $K_a = 4 - 3$ Q-branch of HSSH near 1 THz (Fig. 3). By replacing in the Cologne submillimeter wave spectrometer,⁽⁶⁾ the normally used radiation sources with the Russian-made BWOs, a sensitive method has been opened for spectroscopy in the Terahertz region. The power output of the high frequency BWOs is limited to a few milliwatts, which is more than enough to drive the liquid He operated InSb-detector of the Cologne spectrometer, but it is barely sufficient for the acoustic detector used in the Nizhny Novgorod spectrometers. Observation of the 'Q₃-branch of HSSH permitted to derive that the K-doubling of the $K_a = 3$ levels is inverted,⁽⁶⁾ i.e. the order of the levels is reversed from the normal order as given by the asymmetry splitting. Anomalous K-doubling has been observed earlier for the $K_a = 2$ levels of HSSH.⁽⁷⁾ BWOs used in this fashion, may also be employed as local oscillators in heterodyne receivers for radioastronomical applications.

III. PRESSURE BROADENING AND PRESSURE SHIFT MEASUREMENTS

In the quest to obtain reliable and consistent data on pressure shifts and broadening parameters of molecular lines, considerable effort has been invested to carry out highly precise measurements both in the submillimeter and IR region. This data is required for a detailed discussion of intermolecular forces and for astrophysical applications of planetary atmospheres.

At the moment, these measurements seem to proceed in accuracy the prediction based on existing theories, such as the Anderson theory. In this light the results of some recent highly precise laboratory measurements will be discussed.

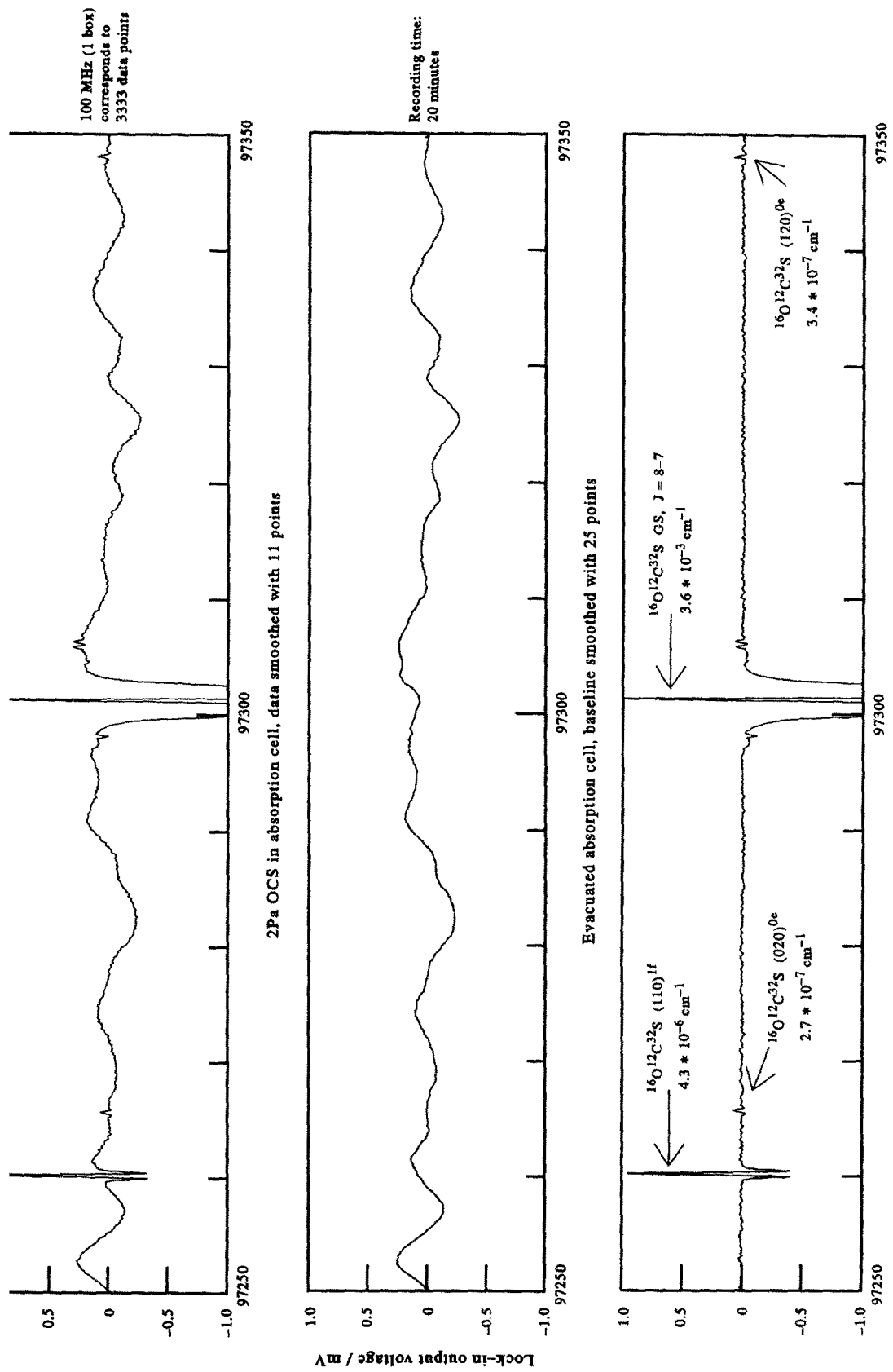


Fig. 2(a). Overview spectrum of OCS (nat. abundance), frequency/MHz. OCCS spectra observed with the Gießen millimeter wave spectrometer employing a Russian made sweeper unit, and baseline subtraction.

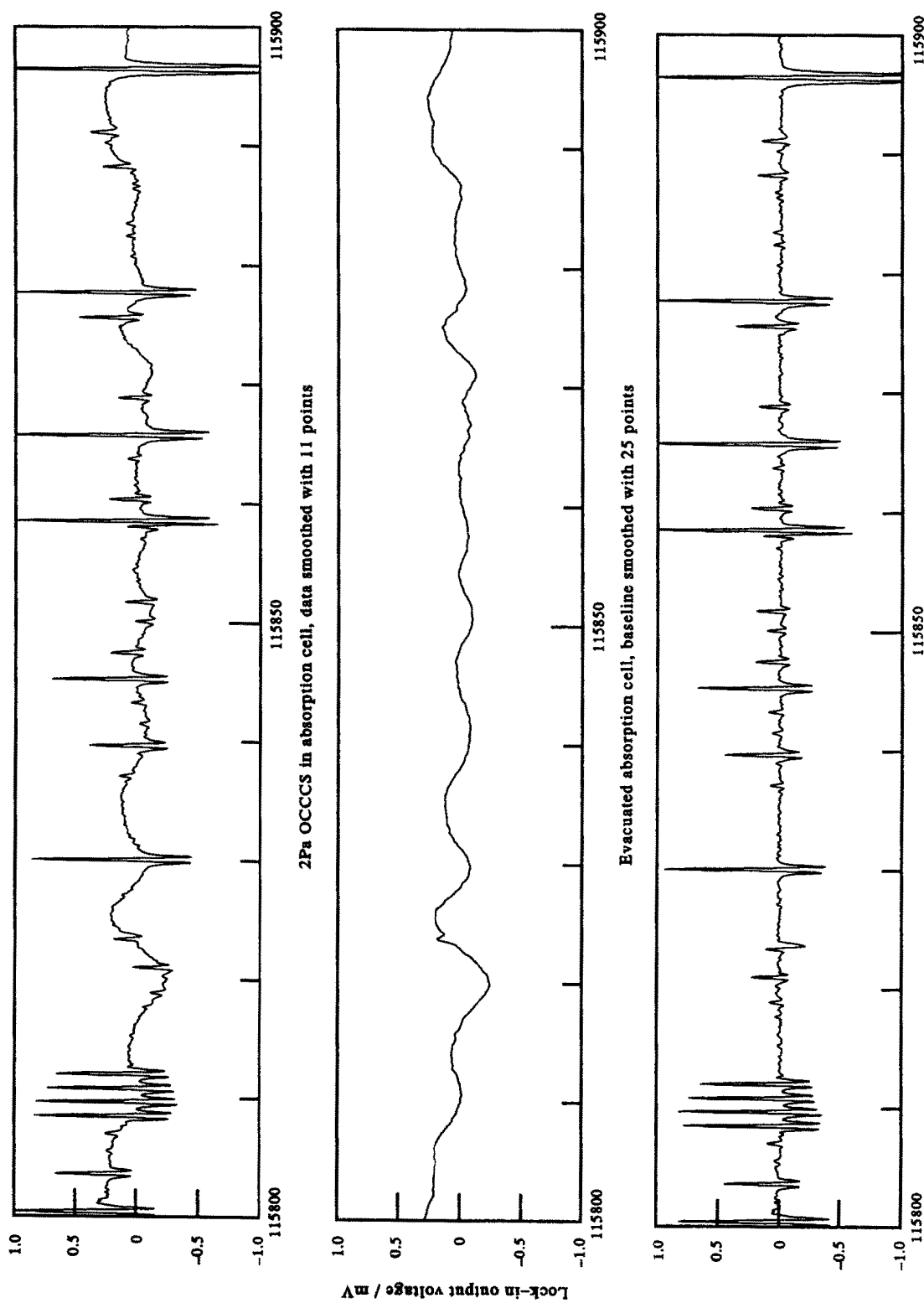


Fig. 2(b). Overview spectrum of OCCC, frequency/MHz. OCCC spectra observed with the Gießen millimeter wave spectrometer employing a Russian made sweeper unit, and baseline subtraction.

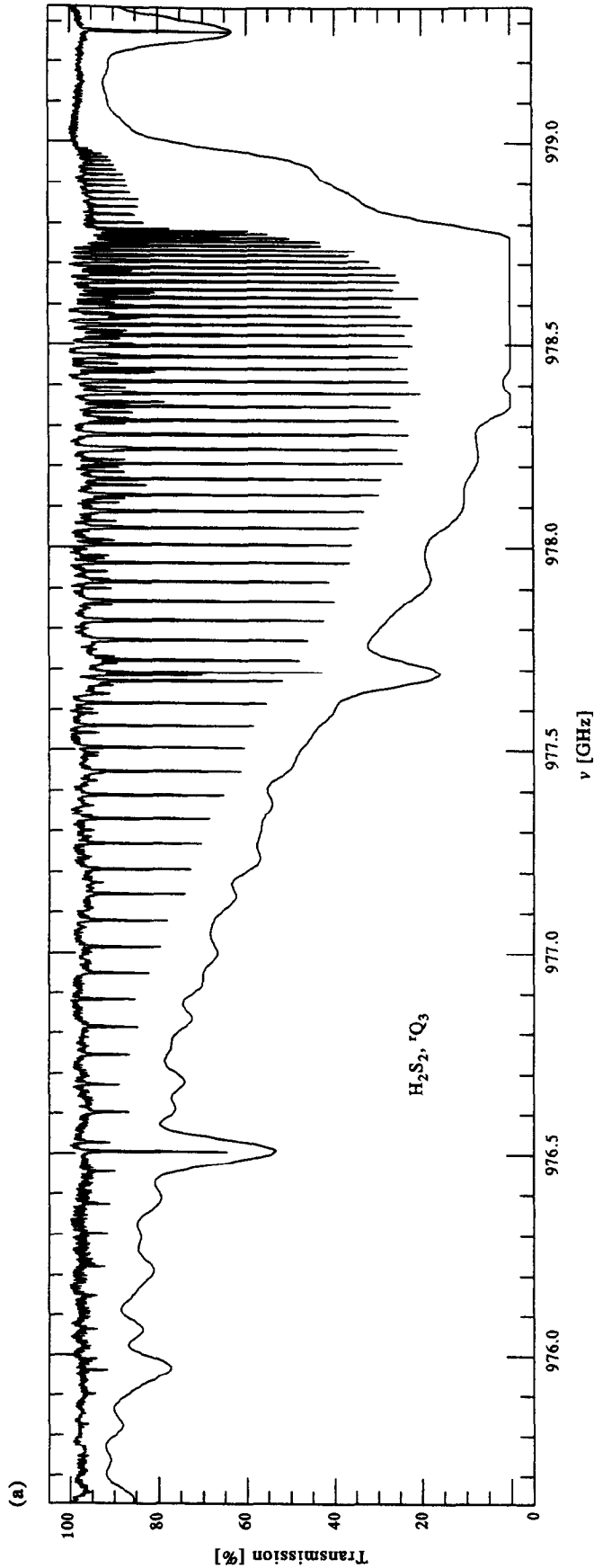


Fig. 3(a). ${}^1\text{Q}_3$ -branch of HSSH recorded with the Cologne submillimeter spectrometer and with the Gießen high resolution Fourier-Transform spectrometer (lower trace).

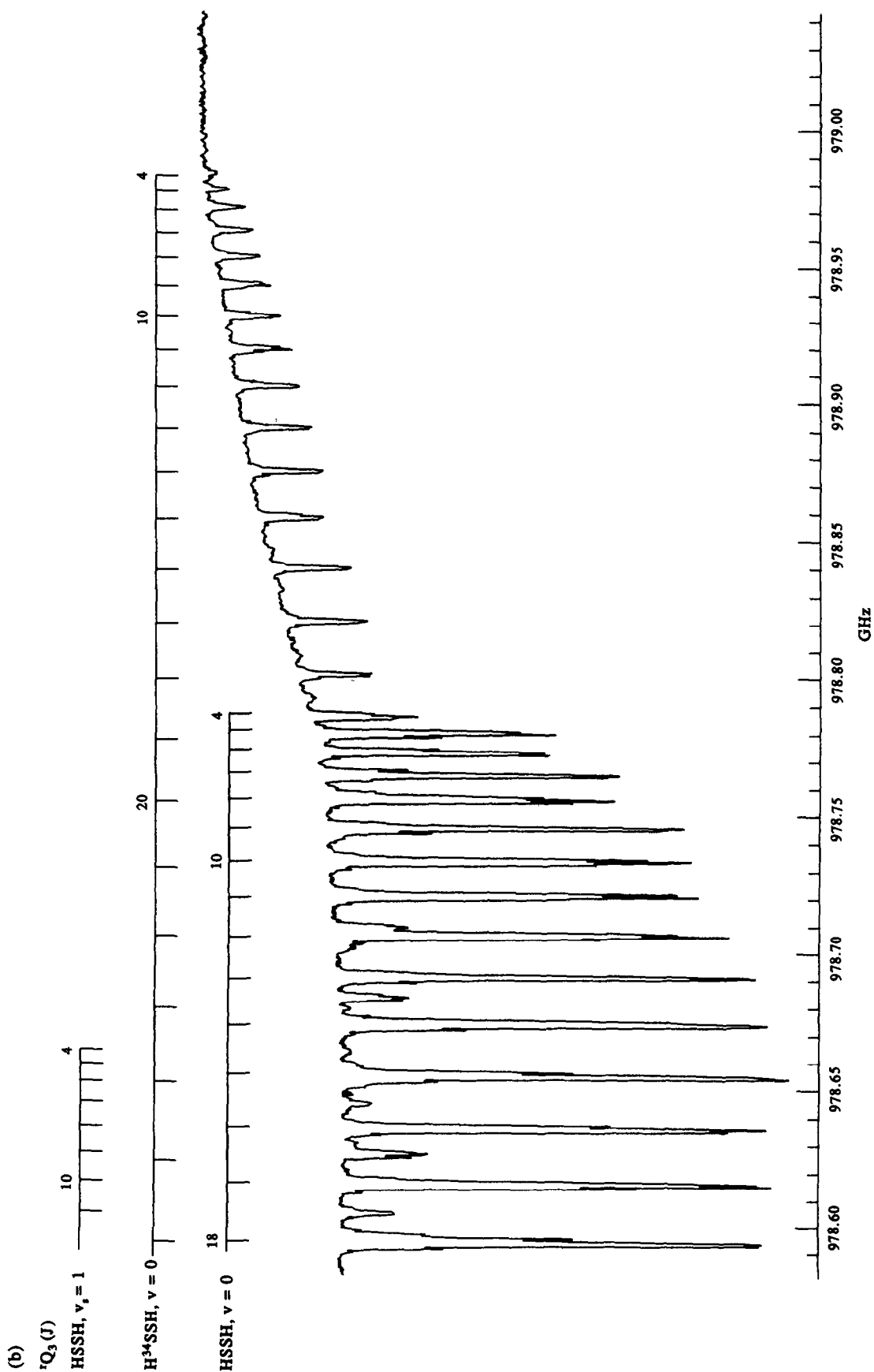


Fig. 3(b). Band head of the 1Q_3 -branch of HSSH, with the $H^{34}SSH$ species and the first excited stretching state.

Probably the most important developments in the area of high resolution IR-spectroscopy during recent years was the advent of wavelength-stabilized diode lasers, whose performance was considerably improved by a new shock-isolated laser mount.⁽⁸⁾ The resulting increase in frequency resolution yield measurement accuracies comparable to values more familiar from microwave spectroscopy. In the IR, line shifts due to pressure can now be determined routinely to 5–15 kHz/Torr, whereas in the microwave region the best measurements are performed with 1–2 kHz/Torr.^(3,11) Effects of line-center shifts and line broadening in dependence of pressure can now be investigated with hitherto unknown accuracy.

However this development was paralleled by a significant increase in measurement accuracy in high resolution Fourier-Transform spectroscopy. Now FT and tunable diode laser measurements are about compatible in terms of accuracy, with TDs having the edge by about a factor of three. In the following two new directions of studies will be considered:

- (a) The validity of Ritz' combination principle for the transition frequencies of pressure broadened and shifted lines, and
- (b) The additivity of line shifts caused by different foreign gases and by different mixing ratios.

(a) Ritz' combination principle: pressure shifted lines

Very often an initial and a final energy level can be connected via different intermediate energy levels, i.e. by sets of transitions which form different paths in the energy level scheme. Measurement of these sets of transitions and their associated lineshifts necessarily require a broad range of frequencies normally spanning the region from millimeter to IR wavelengths, and the measurement accuracies are required to match each other.

The first experiment towards tackling this line shift problem was performed on ammonia in 1982⁽⁹⁾ with the result that the additivity of the line shift was proved to hold within the experimental error limits. However these early measurements lacked the completeness required for settling the question. Figure 4 summarizes the results of recent measurements for two different paths involved. The ground state and excited state splittings in ammonia were measured in Nizhny Novgorod and Boulder,⁽¹⁰⁾ whereas the interconnecting ro-vibrational transitions were measured to high precision in Cologne. The problem now encountered and to be settled is twofold: (i) from the experimental side it has to be cleared first of all that the measurements do provide the accuracy required, to prove that the effect of non-additivity of lines does exist. To this end the sensitivity and measurement accuracy with the Cologne TDL-Spectrometer, were greatly increased by introducing the method of signal averaging and by employing multiple reflection cells of Herriott type. With this improved experimental system, further studies of the ammonia problem are in progress. (ii) If it should turn out that the line shifts do not behave additive, a more fundamental problem is encountered in the sense that the reconstruction of energy levels according to Ritz' combination principle for pressure broadened lines may have some limitation.

(b) Additivity of line shift: foreign gas perturbers

It was found in the Cologne laboratory by Giesen *et al.*⁽¹¹⁾ that the shift of two measured water lines caused by pure air does not agree with the weighted mean of the shift measured by the collision of pure nitrogen and oxygen. Such an astonishing result was obtained for the two water vapor transitions $13_{2,12}$ – $14_{1,13}$ and $9_{5,5}$ – $10_{6,4}$ for which a full set of measurements (air, nitrogen and oxygen lineshifts and broadenings) exists. This seems undoubtedly to be very interesting, but this experimental result, not yet understood, requires a more thorough investigation and extension to other transitions with different J values. So far the "additivity" of lineshifts was taken for granted. In some papers shifts of lines by air were not measured but rather calculated as weighted mean from measurements of pressure lineshifts by the two pure gases, oxygen and nitrogen. Undoubtedly

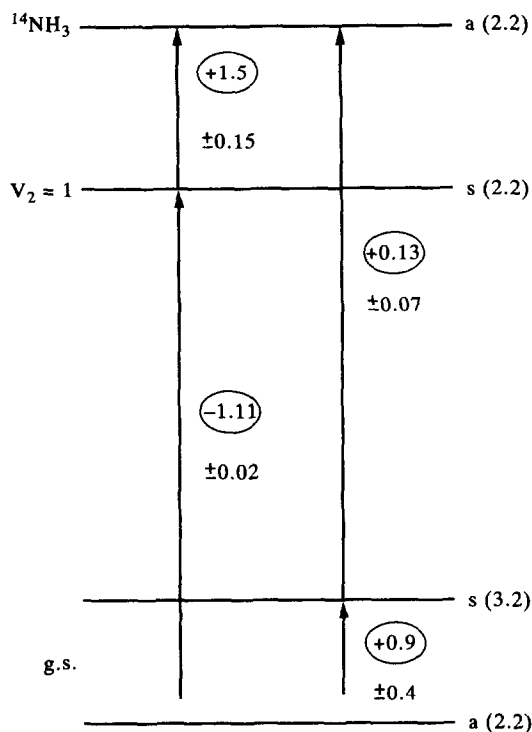


Fig. 4. A part of the vibration-rotation energy diagram of NH_3 , where the levels are connected by two different paths. Values in circles are measured lineshift parameters in MHz/Torr.

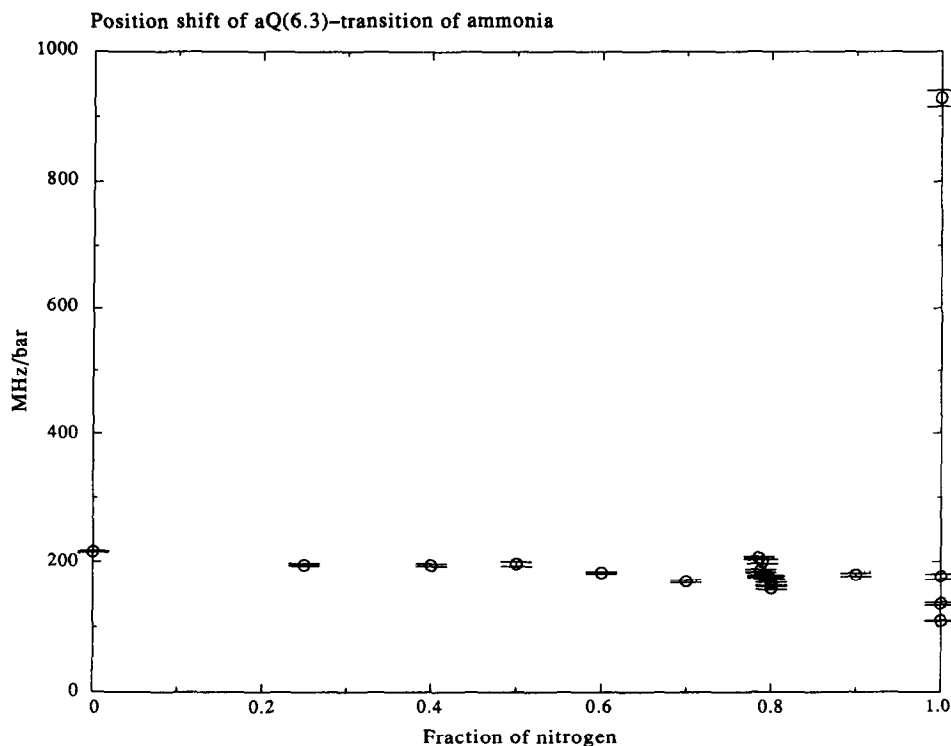


Fig. 5. A preliminary result of line shift measurements for the a Q(6,3) transition of ammonia in dependence of the N_2/O_2 mixing ratio. At the 80% fraction of nitrogen, the different measured points represent air with different water content. At the 100% nitrogen mark, the very top point represents the recorded position shift, obtained for pure H_2O as foreign gas. The lower two points represent the Co and He (lowest point). (M. Fabian 1993, Cologne, private communication.)

elucidation of this question of the validity of this procedure and the magnitude and origin of these deviations is of interest both from a point of view of "pure" and "applied" science.

In this context, it seemed interesting to look at already published results of similar measurements⁽¹²⁻¹⁴⁾ carried out by FT-technique. Indeed, some of the data of these papers show for pure gases the aforementioned differences between measured and as weighted mean calculated lineshifts. This difference is sometimes well outside three times the standard deviation listed in Refs.⁽¹²⁻¹⁴⁾ A statistical analysis of these data clearly shows—for all three papers—that the deviations of the air-shifts from the weighted average of the N₂- and O₂-shifts do not follow the normal Gaussian distribution, suggesting that these deviations do not originate from the statistical errors. For the a-Q(6,3) transition of ammonia very recently completed measurements in Cologne show that the pressure shifts behave linearly on the N₂/O₂ mixing ratio within experimental error (Fig. 5). This work is now in progress at the University of Cologne by using the wavelength-stabilized TDLs.⁽¹⁵⁾ Similar measurements in the submillimeter wave region are planned in Nizhny Novgorod.

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REFERENCES

1. A. F. Krupnov, *Modern Microwave Spectroscopy* (Edited by G. Chantry), pp. 217–256. Academic Press, London (1979).
2. S. P. Belov, M. Yu. Tretyakov, I. Kleiner and J. T. Hougen, *J. molec. Spectrosc.* In press
3. S. P. Belov, M. Yu. Tretyakov and R. D. Suenram, *Astrophys. J.* **393**, 848–851 (1992).
4. V. Wagener, M. Winnewisser, A. A. Uljanov, O. P. Pavlovsky, G. M. Altschuller, O. G. Anikin, A. F. Krupnov, E. N. Karyakin and V. P. Kazakov, Paper WF 05 at the 1993 Columbus Conference.
5. G. T. Fraser, R. D. Suenram and E. N. Karyakin, *J. molec. Phys.* In press.
6. M. Liedtke, R. Schieder, K. M. T. Yamada, G. Winnewisser, S. P. Belov and A. F. Krupnov, *J. molec. Spectrosc.* In press.
7. G. Winnewisser, *J. Chem. Phys.* **56**, 2944–2954 (1972).
8. N. Anselm, K. M. T. Yamada, R. Schieder and G. Winnewisser, *J. molec. Spectrosc.* In press
9. S. P. Belov, V. P. Kazakov, A. F. Krupnov, V. N. Markov, A. A. Melnikov, V. A. Skvortso and M. Yu. Tretyakov, *J. molec. Spectrosc.* **94**, 264–282 (1982).
10. K. Evenson and L. Zink, private communication.
11. T. Giesen, R. Schieder, G. Winnewisser and K. M. T. Yamada, *J. molec. Spectrosc.* **153**, 406–418 (1992).
12. C. P. Rinsland, M. A. H. Smith, V. Malathy Devi and D. C. Benner, *J. molec. Spectrosc.* **150**, 173–183 (1991).
13. C. P. Rinsland, M. A. H. Smith, V. Malathy Devi and D. C. Benner, *J. molec. Spectrosc.* **150**, 640–646 (1991).
14. C. P. Rinsland, M. A. H. Smith, V. Malathy Devi and D. C. Benner, *J. molec. Spectrosc.* **156**, 507–511 (1992).
15. M. Fabian, private communication.
16. K. M. T. Yamada, M. Harter and T. Giesen, *J. molec. Spectrosc.* **157**, 84–89 (1993).