A Molecular Beam Microwave Fourier Transform (MB-MWFT) Spectrometer with an Electric Discharge Nozzle

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We report on first experiments with our pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer using a special nozzle which allows high voltage discharges within the nozzle orifice. Under these conditions we observed low J rotational transitions in highly excited vibrational states of carbonyl sulfide and sulfur dioxide, and also rotational lines of the SO radical in the $^3\Sigma^-$ electronic ground state and both the vibrational ground and first excited state.

Introduction

Pulsed molecular beam microwave Fourier transform (MB-MWFT) spectroscopy is used in a number of laboratories because the low rotational temperature of the beam allows interesting experiments in the field of Van-der-Waals molecules. Additionally, the spectra of stable and unstable molecules are very clear since they are usually free of high rotational and highly excited vibrational states.

We found that the effectiveness of the cooling by beam expansion apparently depends inversely on the heights of the energy levels to be cooled, i.e. rotational states with energy differences of only a few cm^{-1} are cooled much better than vibrational states on the order of 500 cm^{-1} or above. In fact we have observed excited (stretching) vibrational state line intensities corresponding to statistically defined vibrational temperatures of more than 270 K. We tried to exploit this fact by exciting the molecules by an electric discharge at the moment when the gas enters the nozzle orifice, so that the vibrationally excited states may lose most of their rotational energy in the subsequent expansion while retaining the vibrational energy. As a result, a number of low J rotational transitions in vibrational states up to 6000 cm^{-1} (six thousand!) could be observed. Additionally, in the case of sulfur dioxide (SO_2) fragmentation of the molecule allowed us to observe rotational transitions of the SO radical in its $^3\Sigma^-$ electronic ground state and its ground and first excited vibrational state.

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Experimental

All measurements were carried out using our standard MB-MWFT spectrometer [1] with parallel molecular beam and resonator axes [2]. A General Valve Series 9 nozzle was modified to produce electric discharges within the nozzle orifice (Figure 1). The most important modification concerns the teflon poppet which was drilled along its axis. Subsequently a teflon coated 0.3 mm diameter wire was stripped, inserted into the hole and carefully glued. Then the wire was cut so that it finally stretched out 1 mm beyond the tip of the poppet. The wire serves as one electrode such that a discharge takes place between the wire tip and the walls of the 1.2 mm diameter orifice in the face plate of the nozzle which is at ground potential. From the bottom of the poppet the teflon coated wire is fed through the compression spring located inside the armature and through the coil assembly with its swagelok™ inlet port. There the wire leaves the gas inlet system through a high voltage feed-through and is connected via a 47 kΩ resistor to a high voltage power supply. The resistor is used for limiting the maximum current. It should be emphasized that this setup did not noticeably affect the performance of the spectrometer in its normal use.

Measurements

In order to get a first impression on the population of the vibrational states after an electric discharge took place we began our studies with a mixture of 1% carbonyl sulfide (OCS) in argon. A stagnation pressure of $7 \cdot 10^4$ Pa was used throughout. We used a

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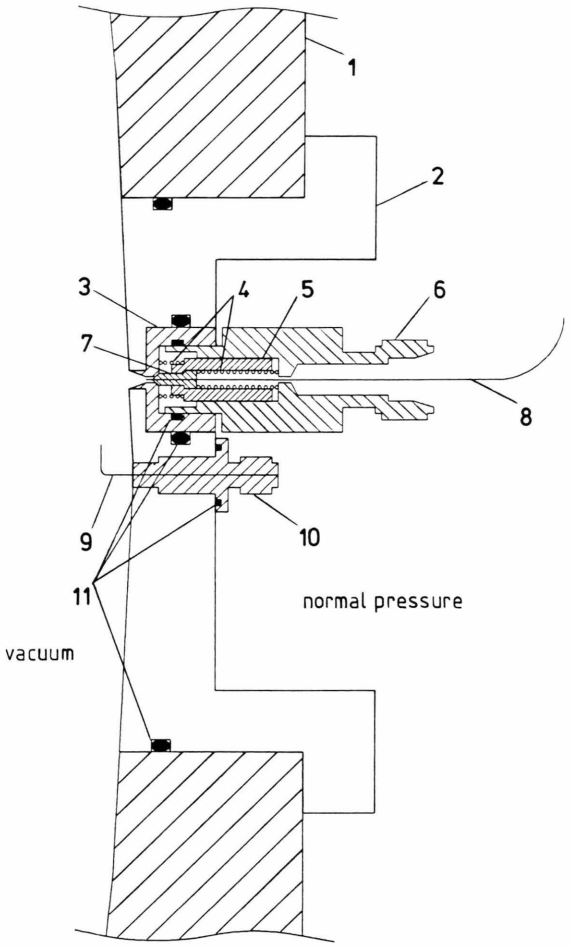

Fig. 1. Central part of one of two mirrors forming the Fabry-Perot cavity. 1 aluminum mirror, 2 stainless steel inset, 3 nozzle faceplate (home made), 4 springs, 5 armature, 6 solenoid assembly and gas inlet, 7 teflon poppet, 8 wrapping wire 0.3 mm diameter, 9 microwave antenna, 10 SMA connector, 11 O-rings. Parts 4–7 belong to the General Valve Series 9 nozzle.

voltage of 700 V DC to produce the discharge which could be observed as blue sparks when looking into the nozzle orifice. This voltage was considered as a compromise between a reliable discharge within the orifice and undesirable discharges within the coil assembly of the nozzle. All lines measured are compiled in Table 1. Only those transitions with low vibrational energies were also found without the discharge. Their intensity became dramatically stronger after the discharge was turned on. Several highly excited vibrational state transitions were measured for the first time with our apparatus. We found that vibrational states up to 6000 cm^{-1} are sufficiently populated to observe the rotational spectrum within a few minutes.

Table 1. List of measured $J''-J'=1-0$ lines of OCS in vibrationally excited states. Asterisks in the last column indicate transitions which were, to our knowledge, observed for the first time.

v_1	v_2^l	v_3	Frequency/ MHz	Approximate Vibrational energy/ cm^{-1}
0	2^0	0	12 200.3779	1047
0	4^0	0	12 229.6140	2105
1	2^0	0	12 168.7776	1892
1	0	1	12 057.8379	2918
2	0	0	12 089.7474	1711
3	0	0	12 052.0227	2600
4	0	0	12 013.4578	3400*
5	0	0	11 973.9717	4300*
6	0	0	11 933.4912	5100*
7	0	0	11 891.9314	6000*
0	0	1	12 090.1165	2062
0	0	2	12 017.7366	4101
0	0	3	11 946.4320	6200*

Table 2. List of all measured lines of SO_2 in vibrationally excited states (rotational quantum numbers $1,1,1-2,0,2$ except $v_3=1$: $3,0,3-2,1,2$). The asterisk in the last column indicates a transition which was, to our knowledge, observed for the first time.

v_1	v_2	v_3	Frequency/ MHz	Approximate Vibrational energy/ cm^{-1}
1	0	0	12 522.7154	1151.7
2	0	0	12 787.1284	2303.4
1	1	0	13 729.1477	1665
0	1	0	13 457.3470	512
0	2	0	14 714.0731	1029
0	3	0	16 030.7989	1535
0	4	0	17 411.9737	2060*
0	0	1	8 622.3296	1360

We continued our experiments with some measurements on SO_2 as a simple example for an asymmetric top molecule. A sample of 1% SO_2 in argon and a stagnation pressure of $7 \cdot 10^4$ Pa was used. We also observed vibrationally excited states without any difficulties. A list of observed transitions is given in Table 2.

The line widths of excited vibrational state transitions were entirely comparable to ground state line widths. This means that, for OCS and SO_2, there is no evidence for intramolecular vibrational relaxation within this energy range.

In a third experiment we investigated whether our new nozzle can also be used for the production of free

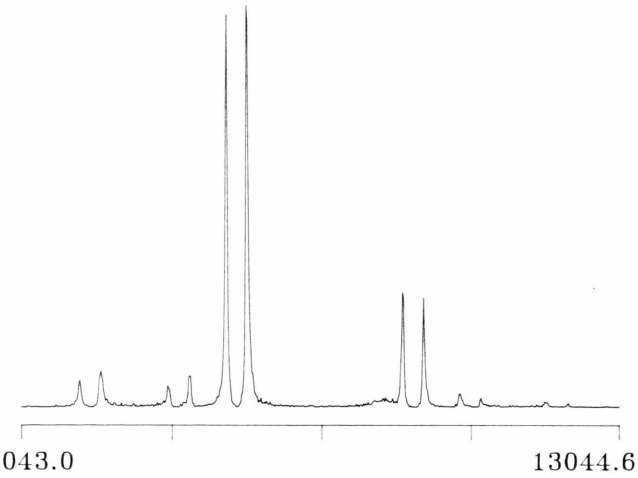

Fig. 2. Zeeman pattern of the $J'', K''-J', K'$ $1,2-1,1$ transition of the SO radical in its vibrational and electronic ($^3\Sigma^-$) ground state. The Zeeman effect is caused by the earth magnetic field. Each component of the pattern appears as a Doppler doublet with a separation of 55 kHz. Recording conditions: polarizing pulses at 13 043.7 MHz with 1 μs length and 0.1 mW pulse power, 100 ns sample interval 4 k = 4096 data points, 4000 averaging cycles, $8 \cdot 10^4$ Pa (0.8 atm).

radicals. Therefore we tried to find the well known $J'', K''-J', K' = 1,1-1,2$ line of the SO radical in the $^3\Sigma^-$ electronic ground state. Indeed we observed a Zeeman multiplet (Fig. 2) caused by the earth magnetic field. In order to verify that the multiplet really originates from a free radical in the triplet state we produced an additional external magnetic field on the order of 10^{-5} T (0.1 Gauss) by a current loop with 16 turns and 1.2 m diameter wound around the entire apparatus and a current of 1 A. The splittings of the multiplet shifted significantly. Finally the same rotational transition was measured in the first vibrationally excited state.

Outlook

We have shown that it is possible to observe rotational transitions in highly excited vibrational states by MB-MWFT spectroscopy when an electric discharge nozzle is used. In combination with the extremely high resolution of MB-MWFT spectroscopy, interesting future applications like intramolecular relaxation studies are possible. We have also shown that the same arrangement can be used to generate free radicals by fragmentation of stable precursors. We are convinced that in future this setup will allow for the detection of a number of new radicals by MB-MWFT spectroscopy. We also consider the use of this setup for ion spectroscopy.

Acknowledgement

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[1] U. Andresen, H. Dreizler, J.-U. Grabow, and W. Stahl, Rev. Sci. Instrum. **61,** 3694 (1990).
[2] J.-U. Grabow and W. Stahl, Z. Naturforsch. **45a,** 1043 (1990).