

Methane as Carrier Gas for Molecular Beam Microwave Spectroscopy to Observe Transitions of Higher Rotational Energy Levels

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We report on an observation in molecular beam rotational spectroscopy: using Methane rather than rare gases as carrier extends the range of observable transitions towards levels of higher rotational energy.

Introduction

The combination of Fourier transform microwave (FTMW) spectroscopy with the technique of pulsed supersonic molecular beams (MB) by Balle and Flygare [1] resulted in a great improvement of rotational spectroscopy [2]. One advantage of the beam technique is the simplification of the rotational spectra observed in a static gas, which often, especially for asymmetric top molecules, are very dense by numerous rotational transitions in different vibrational states. Only transitions originating from low rotational energy levels are left, since the collisional cooling in the early stages of the beam expansion depopulates higher energy levels.

Thus, the initial assignment of the spectra also of rare isotopomers is much easier. This advantage converts to a disadvantage, if one is interested in effects produced by centrifugal distortion or methyl internal rotation. Here, the effects are more pronounced in high J transitions. It should be mentioned that the higher resolution [3] and precision of MB FTMW spectroscopy reveals these effects, compared to spectroscopy on static gases, already for lower J transitions. Nevertheless, the study of small effects still requires the observation for higher J transitions.

Recently, we were faced to investigate the centrifugal distortion in our effort to study the hyperfine structure of ^{33}S in thiirane, $\text{CH}_2 - \text{CH}_2$ [4].



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Usually, MB FTMW spectroscopy introduces the molecular sample in a carrier gas with a concentration of some percent. The rare gases helium, neon, and argon are the favoured carriers. Sometime ago we noticed that air, to 99% composed of the diatomic molecules oxygen and nitrogen, is also a suitable carrier gas, thus opening the possibility of air pollution measurements [5].

In this note we want to communicate the observation that methane, CH_4 , may be used to extend the accessible range of transitions demonstrated here for thiirane. A comparison is given in Figures 1 to 3. For the measurements of Figs. 1 to 3, which compare three rotational transitions, each observed in a beam with the carrier gases argon, helium and methane under equal spectrometer settings, the spectrometer was optimized for $J_{K-K+} = 5_{23} \leftarrow 5_{24}$ with argon. The number of experiment cycles was increased for higher J . This comparison shows that helium is superior to argon. Methane results in a signal to noise (S/N) ratio better than helium. The given S/N ratios are not very stable, but when the experiments were repeated for higher J transitions, methane was the best choice. We take this as a first indication that for special spectroscopic problems the choice of noble gases as carrier may not be the optimum.

For the transition $J_{K-K+} = 1_{01} \leftarrow 0_{00}$ with the lower energy level at zero, CH_4 was the inferior choice compared with He and Ar. It should be mentioned that the S/N-ratios could, for each carrier gas, be improved slightly by adjusting the spectrometer settings. In the recording of weaker lines a 10 MHz coherent perturbation appears and dominates.

An explanation of this observation is not easily straightforward, since the demonstrated effect may be



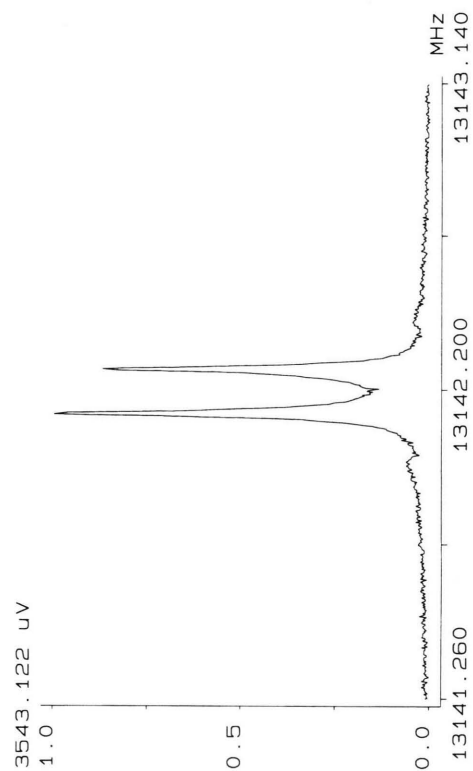


Fig. 1b

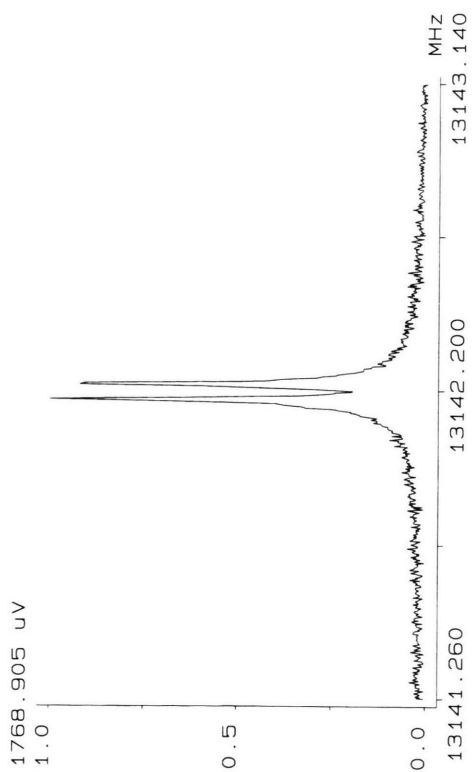


Fig. 1a

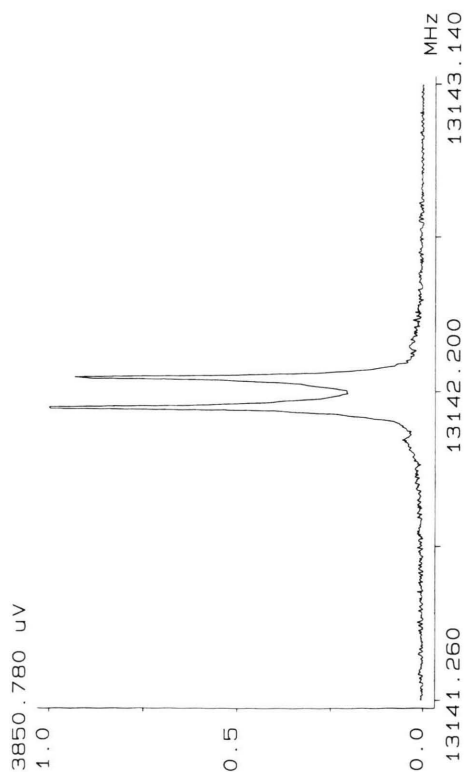


Fig. 1c

Fig. 1. Amplitude spectrum of the rotational transition $J_{K+} = 5_{2,3} \leftarrow 5_{2,4}$, $\nu = 13142.193$ MHz observed with the carrier gases Ar (1a), He (1b), CH_4 (1c) containing $\approx 1\%$ thiirane. The S/N ratios are approximately: 38, 53, 102. 512 experiment cycles. Energy of lower level: $E(5_{2,4}) \approx 11 \text{ cm}^{-1}$.

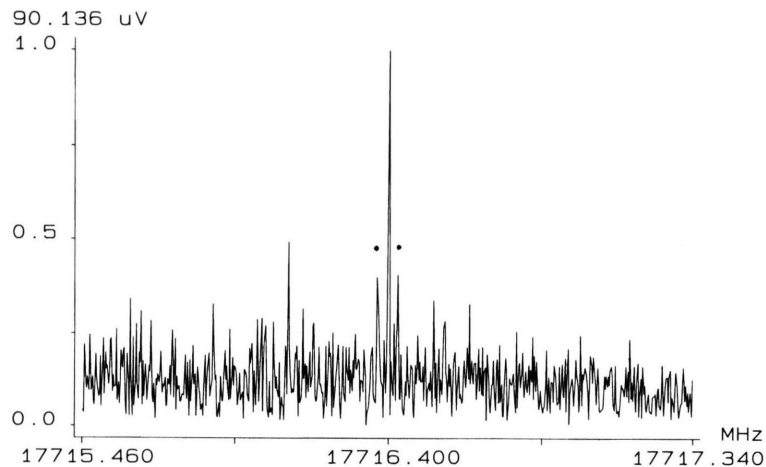


Fig. 2a

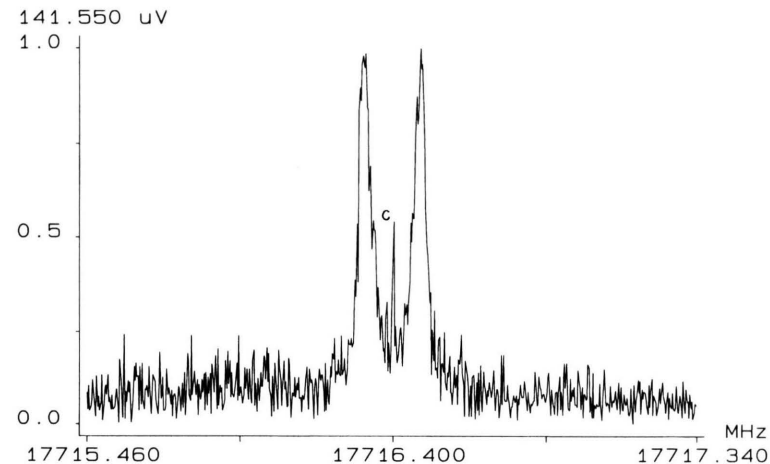


Fig. 2b

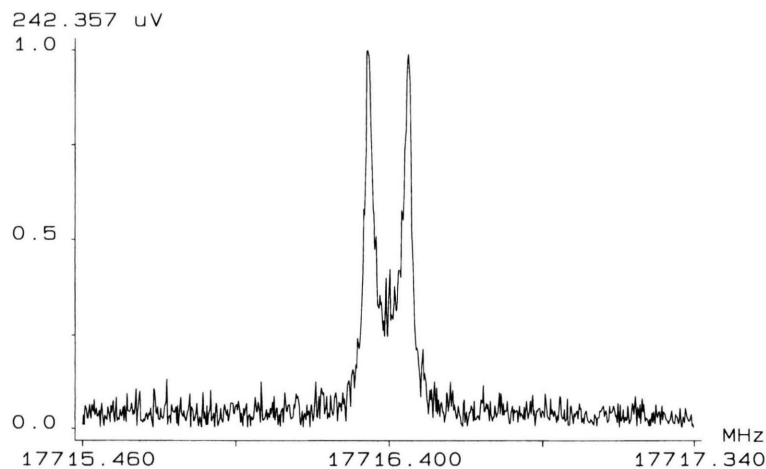


Fig. 2c

Fig. 2. Rotational transition $J_{K-K^+} = 11_{4,7} \leftarrow 11_{4,8}$, $\nu = 17716.395$ MHz with the same carrier gases and $\sim 1\%$ substance. The S/N ratios are approximately: 3, 10, 18, 2096 cycles. $E(11_{4,8}) \approx 48.4$ cm $^{-1}$. The lines marked with “●” correspond to the Doppler doublet of the transition. The line marked with “c” is a coherent perturbation.

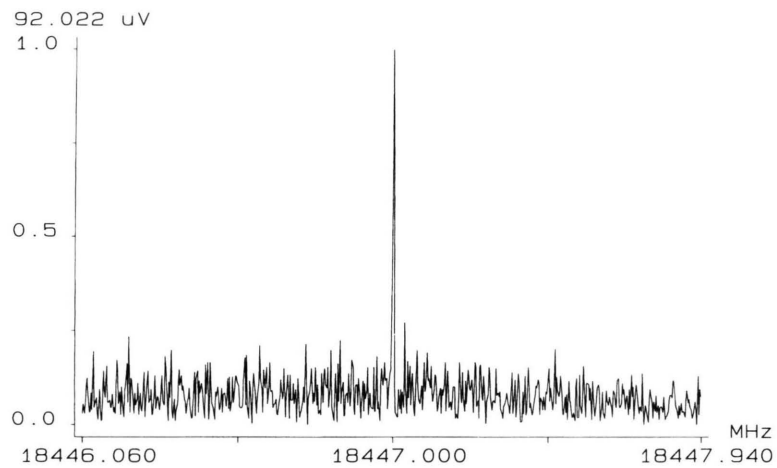


Fig. 3a

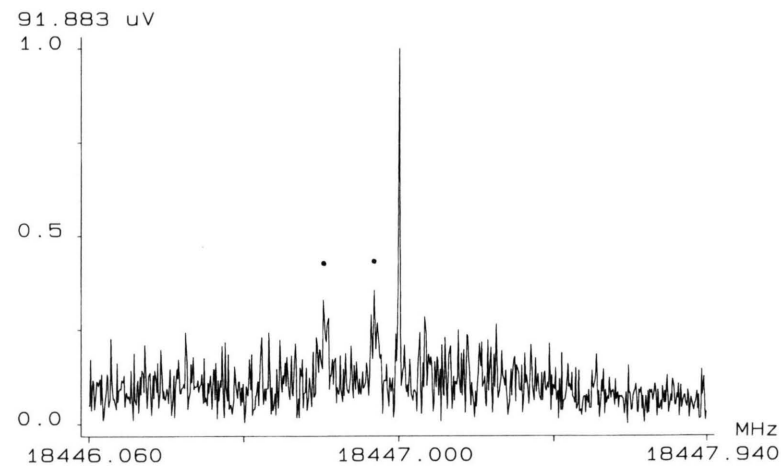


Fig. 3b

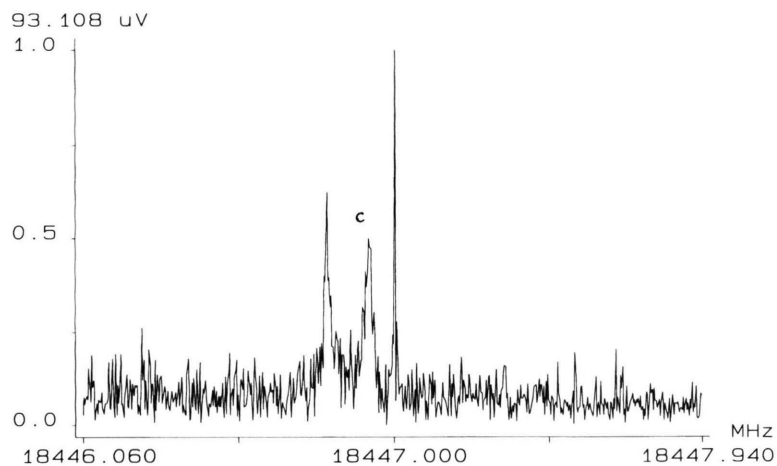


Fig. 3c

Fig. 3. Rotational transition $J_{K-K^+}=14_{5,9} \leftarrow 14_{5,10}$, $\nu=18446.52$ MHz for the same samples. The S/N ratios are: n/a , 3.5, 6.5, 4096 cycles. $E(14_{5,10}) \approx 77$ cm⁻¹. The lines marked with "•" correspond to the Doppler doublet of the transition. The narrow line marked with "c" at the left is a coherent perturbation.

caused by a different efficiency of the collisional cooling for those carrier gases as well as by the degree of complexation by carrier atoms (or molecules), which changes the total number of the molecular species under investigation.

The questions are open for further studies which should be extended also to other carrier gas molecules, preferably without a permanent dipole moment and an extremely small polarizability. The strategy for the investigation of the rotational spectrum of a molecule will be to first choose a noble gas as carrier for assignment and investigation of effects more pronounced in low J transitions, such as nuclear quadrupole cou-

pling, and afterwards to select a different gas like methane as carrier to access higher energy levels.

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