

On the Measurement of Rotational Spectra of Monodeuterated Asymmetric Top Molecules in Natural Abundance Demonstrated for Monofluorobenzene

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We report on the measurement of rotational transitions of monodeuterated fluorobenzene in natural abundance to show the feasibility of the investigation of monodeuterated asymmetric top molecules without the necessity of isotopic enrichment.

Introduction

A fundamental application of microwave or rotational spectroscopy of molecules is the determination of their structure. Because the analysis of an asymmetric top spectrum provides three rotational constants or moments of inertia, at most three structural parameters can be determined. Therefore the spectra of isotopomers are investigated and used for the structure determination under the assumption that the structure is unchanged upon substitution of isotopes or at least changed only to a small extent. For details see Chapt. XIII of Gordy and Cook [1] and citations therein. One method, the r_s substitution method, introduced by Costain [2] on the basis of equations given by Kraitchman [3], requires in principle the single substitution of each atom in the molecule for the determination of a complete structure from the differences in the moments of inertia. More elaborate structure determinations [4] also rely on the experimental moments of inertia for a sufficient set of isotopomers. A survey of determined structures is given in [5]. For many molecules the preparation of the different isotopomers is a difficult and possibly expensive task. We intend to show that this preparation work can be reduced, since the investigation of many deuterated asymmetric top molecules is becoming feasible in natural abundance.

Over the past years, molecular beam (MB) Fourier transform microwave (FTMW) spectroscopy was in-

troduced [6] and considerably improved [7 - 11]. It was noticed that the rotational spectra of many isotopomers can be recorded in natural abundance, assigned and evaluated. This is a consequence of the increased sensitivity compared to MW absorption spectroscopy techniques and the fact, that only lower levels of the rotational energy ladder are populated in a supersonic jet expansion, thus both simplifying the otherwise dense spectra as well as significantly enhancing the remaining transitions. As examples for the observation of rotational spectra of isotopomers containing, in natural abundance, carbon- ^{13}C (1.107 %) [12], sulfur- ^{33}S (0.76 %) [13], nitrogen- ^{15}N (0.3663 %) [14] and other isotopes with higher natural abundance, such as ^{10}B , ^{34}S , may be mentioned. Since many molecules contain hydrogen, H, we tackled the problem to record rotational spectra of fairly heavy asymmetric tops with deuterium, D, in natural abundance (0.01492 %). Sometimes hydrogen is situated in equivalent positions in the molecule so that the natural abundance increases by the number of equivalent positions. In general, the measurement of deuterated isotopomers of a small linear, prolate symmetric top or even near prolate asymmetric top molecules is an easier task, since the partition sum is rather small in these cases.

Experimental

We used our MB FTMW spectrometer [11] in a new version and a new arrangement of the microwave circuits [15] with a reduced noise figure. To demonstrate the progress in sensitivity we present in Fig. 1 the

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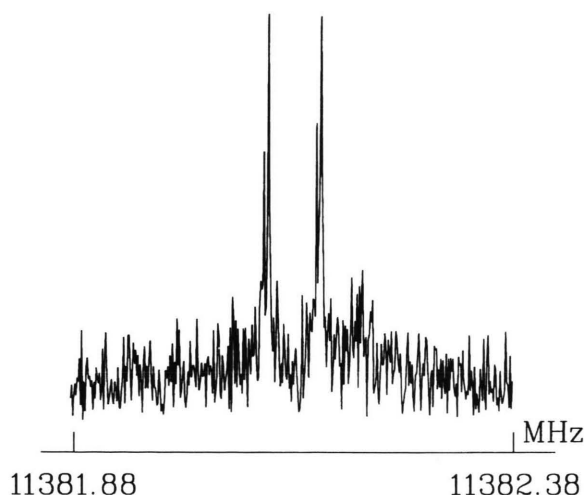


Fig. 1. Fourier transform amplitude spectrum of the $J=1-0$ transition of $^{18}\text{O}^{13}\text{C}^{32}\text{S}$ in natural abundance (0.0022%) of *one* single transient emission signal. This transition was used to check the spectrometer for sensitivity. The wide doublet results from the Doppler effect due to the parallel arrangement of the molecular beam and the resonator axis [8], while the narrow doublet is due to the ^{13}C -spin-rotation coupling ($\nu = 11382.1239$ MHz and $\nu = 11382.1288$ MHz, resp.). Experimental conditions: one experiment cycle; 10 ns sampling interval; 8 k data points in the time domain; 4 k spectral points.

Fourier transform amplitude spectrum of carbonylsulfid, $^{18}\text{O}^{13}\text{C}^{32}\text{S}$, with a natural abundance of 0.0022% derived from a single transient emission signal (one experiment cycle) with a signal to noise (S/N) ratio of 6. Isotomers with minor abundance require more experiment cycles.

As asymmetric top test molecule we have chosen monofluorobenzene, $\text{C}_6\text{H}_5\text{F}$, as this molecule was investigated earlier with all its isotopomers using isotopically enriched samples [16, 17]. The deuterium isotopomers have been recently investigated by MB FTMW spectroscopy [17]. Fluorobenzene was supplied by Aldrich, Steinheim, and was used without further purification. Using the ^{13}C isotopomers [16] we adjusted the experimental parameters (*i. e.* polarizing power, MW pulse width, molecular pulse width, delay between molecular and MW pulse, delay between MW pulse and data acquisition, beam nozzle operation, and the alignment of the MW antennae) until we were able to record the corresponding transition in one experiment cycle. The sample was prepared in a storage container by mixing 2.5 % of fluorobenzene in neon as carrier gas at 200 kPa total pressure. For spectroscopy, the backing pressure was varied

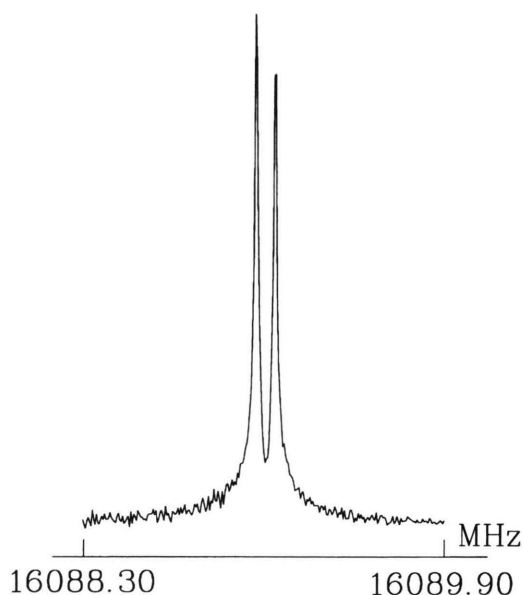


Fig. 2. 1.6 MHz section of the Fourier transform amplitude spectrum of the $J_{K_a K_c} = 4_{04} - 3_{03}$ transition of fluorobenzene-2- ^{13}C digitizing *one* transient emission signal after optimization of the spectrometer. Experimental conditions: $\nu = 16089.1043$ MHz; *one* experiment cycle; 10 ns sampling interval; 16 k data points in the time domain; 8 k spectral points.

between 100 and 140 kPa. The quality of such an optimized signal is demonstrated for the $J_{K_a K_c} = 4_{04} - 3_{03}$ transition of fluorobenzene-2- ^{13}C , with 2.214 % natural abundance in Figure 2. By reproducing a number of the transitions reported in Table 1 to 3 of [17] of fluorobenzene- $n\text{-D}_1$, $n=2,3,4$, we noticed that transitions with low K_a -quantum number and unresolvable D-hfs can be recorded with a tolerable number of experiment cycles. The $J_{K_a K_c} = 4_{04} - 3_{03}$ transition is an example for those transitions. These transitions for the fluorobenzene-2 D_1 , and 3 D_1 were *not reported* in [17], but the rotational parameters of Table 4 of [17] allowed a good prediction of the frequencies of these transitions. To demonstrate the possibility to locate the transitions with a frequency scan [10], such as is typically used in the process of recording of a yet unassigned spectrum, we also present such a scan from 15886.5 to 15900 MHz for the 2 D_1 isotopomer and from 15752.3 to 15758.3 MHz for the 3 D_1 isotopomer in the inserts of Figs. 3 and 4. For these scans 10 ns sample intervals, 2 K data points per transient emission, and 512 experiment cycles per polarization frequency setting at a repetition rate of 5 Hz were used. The polarization frequency stepwidth of

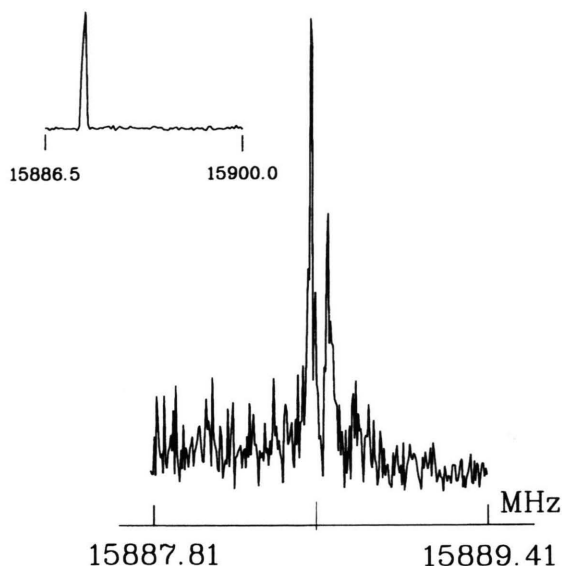


Fig. 3. Upper left: frequency scan from $\nu = 15886.5$ MHz to $\nu = 15900.0$ MHz used to locate the fluorobenzene-2D $J_{K_a K_c} = 4_{04} - 3_{03}$ transition. Experimental conditions: 512 experiment cycles; 10 ns sampling interval; 2 k data points; 0.15 MHz frequency step width. Right: 1.6 MHz section of the high resolution spectrum of the same transition. Experimental conditions: $\nu = 15886.6169$ MHz; 1024 experiment cycles; 10 ns sampling interval; 32 k data points in the time domain; 16 k spectral points.

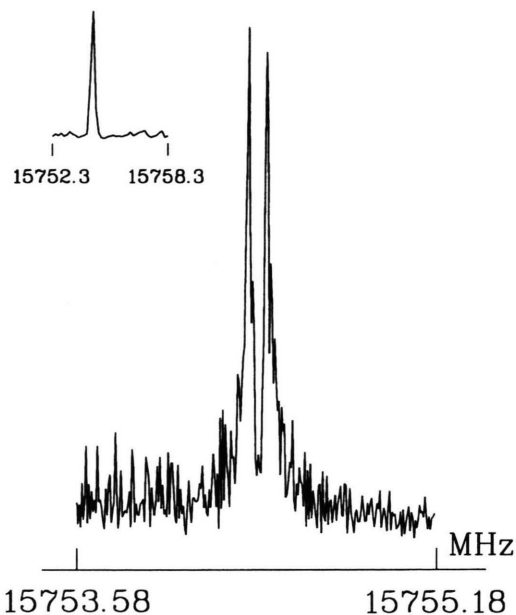


Fig. 4. Upper left: frequency scan from $\nu = 15752.3$ MHz to $\nu = 15758.3$ MHz used to locate the fluorobenzene-3D $J_{K_a K_c} = 4_{04} - 3_{03}$ transition. Right: 1.6 MHz section of the high resolution spectrum of the same transition. $\nu = 15754.3810$ MHz. Experimental conditions: see Fig. 3 for both recordings.

the scans was 0.15 MHz. In Figs. 3 and 4 we give the subsequently recorded transitions with 10 ns sample interval, 16 K data points per transient emission signal and 1024 experiment cycles at 15888.617 MHz and 15754.381 MHz. These lines fit with a standard deviation of 2 kHz and 6 kHz, respectively, to a Watson A centrifugal distortion analysis [18] using the lines in Tables 2 and 3 of [17]. A similar standard deviation was obtained when only the transitions given in [17] are used. So we are rather sure of the assignment. An additional line at 15888.718 MHz was excluded as the standard error of the fit deteriorated by a factor of 7. The $J_{K_a K_c} = 4_{04} - 3_{03}$ of fluorobenzene-4D₁ given in [17] could be recorded under the same settings with an *S/N* ratio of about 25.

Conclusion

We demonstrated that for a fairly asymmetric top molecule it is possible to record rotational spectra of monodeuterated isotopomers in natural abundance

using a sensitive and well adjusted MB FTMW spectrometer. To our knowledge, measurements of this kind were not reported hitherto. Even though a general application is still a challenge, this result is encouraging since such asymmetric top molecules exhibit rather large partition functions compared to near prolate asymmetric top, prolate symmetric top, or even linear molecules. With the improvement of the sensitivity of the MB FTMW spectrometers, a wide field of structure determination and of the analysis of deuterium nuclear quadrupole couplings may be opened without the necessity for possibly difficult and expensive chemical preparations.

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