Doctoral Thesis

Pulsed microwave Fourier transform spectroscopy of molecules with small electric dipole moments

Author(s):
Oldani, Markus

Publication Date:
1985

Permanent Link:
https://doi.org/10.3929/ethz-a-000339319

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Pulsed Microwave Fourier Transform Spectroscopy of Molecules with Small Electric Dipole Moments

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH
for the degree of Doctor of Natural Sciences

presented by

MARKUS OLDANI
Dipl. Chem. ETH Zürich
born December 14, 1955
citizen of Baden, Switzerland

accepted on the recommendation of

Prof. Dr. A. Bauder, examiner
Prof. Dr. M. Quack, co-examiner
Dr. A.G. Robiette, co-examiner

Zurich 1985
Summary

Microwave Fourier transform (MWFT) spectroscopy has been applied for the first time to observe rotational transitions of so called "nonpolar" molecules. It is shown that the method is well suited to the observation of those spectra. In conventional Stark modulation spectroscopy, prohibitively high Stark fields would be required to observe transitions of "nonpolar" molecules. The MWFT-method, however, makes no use of the Stark effect but acquires its sensitivity from the multichannel advantage and the superheterodyne detection technique. As the information on the J value of a transition is not available with a MWFT-spectrometer, the assignment of the transitions is more problematic than in conventional microwave spectroscopy. The proper assignment is established solely on the internal consistency of the data. The search range in a single experiment is limited to a few MHz for "nonpolar" molecules. Hence, reliable predictions for the transition frequencies are necessary in order to avoid tedious searches.

Pure rotational spectra of methane, methane-d$_4$ and silane-$^{28}$Si in their ground vibrational state have been observed. Microwave spectra have been predicted on the basis of previous work with sensitivity enhanced Stark spectroscopy or with double resonance methods. In contrast to earlier investigations, transitions have been measured irrespective of the order of their Stark effect and of their symmetry species $A_1$-$A_2$, $E$-$E$, and $F_1$-$F_2$. The measured data have been used to
obtain tensorial centrifugal distortion constants of the molecules by the least squares fit method. In all three cases the accuracy of the constants up to eighth order in J has been improved compared to previous results due to a larger and better balanced data set. In addition, the influence of the tenth order constants has been attained for methane-d₄.

Rotational transitions of methane-d₄ and silane-²⁸Si in their F₂ degenerate vibrational excited state v₄ have been located. The microwave spectra have been predicted from previous high resolution infrared data. For methane-d₄, eleven Q-branch transitions within the v₄ = 1 state have been measured. Seventeen rotational transitions of silane-²⁸Si in the v₄/v₂ dyad have been observed. Some of the transitions in the excited state of methane-d₄ are stronger than the ground state transitions. The larger dipole moment in the excited state compensates for the small Boltzmann factor of approximately 10⁻³. The measured data of methane-d₄ have been combined with high resolution infrared data in a least squares fit of the spectroscopic parameters of the v₄ / v₂ dyad. Due to their higher absolute precision compared with the infrared data, the microwave data contributed considerably to the determination of the v₄ parameters.

Pure rotational spectra of benzene-d₁ and benzene-1,2-d₂ have been observed. For both molecules a set of three R-branch and 17 Q-branch transitions has been observed and assigned. Spectroscopic parameters have been calculated from the measured data. The rotational constants of both species
have been used to calculate the substitution coordinate of the hydrogen nucleus. The formulae of Kraitchman for single substitution and of Chutjian or Nygaard for symmetrical double substitution yielded the same result within the experimental accuracy.

Under conditions of low sample pressure and high microwave power, the MWFT-method allows high resolution measurements of weak transitions. This has been demonstrated by the observation of the deuterium nuclear quadrupole hyperfine splitting of the $0(0,0)-1(0,1)$ pure rotational transition of benzene-$d_1$. The $Q_{aa}$ quadrupole coupling constant has been determined from the line splitting. It compares well with results obtained from ab initio calculations but it differs significantly from results obtained by NMR methods.
Zusammenfassung


Berechnung der molekularen, tensoriellen Zentrifugalverzerrungskonstanten nach der Methode der kleinsten Quadrate benützt. Konstanten bis zur achten Ordnung in \( J \) wurden in die Rechnung miteinbezogen. Bei allen drei Molekeln konnte die Genauigkeit der Konstanten dank einem größeren und besser ausgeglichenen Datensatz verbessert werden im Vergleich mit den Resultaten früherer Arbeiten. Im Falle von Methan-\( \text{d}_4 \) konnte der Einfluss der Konstanten zehnter Ordnung bestimmt werden.

Rotationsübergänge von Methan-\( \text{d}_4 \) und Silan-\( ^{28}\text{Si} \) in ihren vibrationsangeregten Zuständen \( v_4 \) (\( P_2 \)) wurden beobachtet. Die Mikrowellenspektren wurden auf der Basis früherer Arbeiten mit hochauflösender Infrarotspektroskopie berechnet. Bei Methan-\( \text{d}_4 \) wurden elf Q-Zweig Übergänge im \( v_4 = 1 \) Zustand gemessen. In der \( v_4 / v_2 \) Dyade von Silan-\( ^{28}\text{Si} \) wurden 17 Rotationsübergänge gefunden. Das Dipolmoment von Methan-\( \text{d}_4 \) im vibratorisch angeregten Zustand \( v_4 \) ist größer als jenes im Grundzustand, so dass der Boltzmann-Faktor von etwa \( 10^{-3} \) bei gewissen Übergängen kompensiert wird. Einige Übergänge im vibratorisch angeregten Zustand sind deshalb intensiver als die Grundzustands-Übergänge. Die gemessenen Daten von Methan-\( \text{d}_4 \) wurden zusammen mit den Daten aus Infrarot-Messungen zur Berechnung der \( v_4 / v_2 \)-Parameter benützt. Es zeigte sich, dass die Mikrowellendaten dank ihrer höheren Genauigkeit wesentlich zur Bestimmung der \( v_4 \)-Parameter beitrugen.

Reine Rotationsspektren von Benzol-\( \text{d}_1 \) und Benzol-\( 1,2-\text{d}_2 \) wurden beobachtet. Bei beiden Molekeln wurden drei R-Zweig-

Bei tiefem Probendruck und hoher Mikrowellenleistung erlaubt die MWFT-Methode schwache Übergänge mit hoher Auflösung zu messen. Dies wurde durch die Messung der Deuterium-Kernquadrupol-Hyperfeinstruktur des $0(0,0) - 1(0,1)$ Überganges von Benzol-$d_1$ gezeigt. Aus der Aufspaltung wurde die $x_{aa}$ Kopplungskonstante bestimmt. Sie liegt im Bereich der mit ab-initio-Rechnungen ermittelten Resultate, unterscheidet sich jedoch signifikant von den aus NMR-Messungen erhaltenen Werten.