Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Spectroscopy 233 (2005) 93–97

Journal of MOLECULAR SPECTROSCOPY

www.elsevier.com/locate/jms

Rotational spectra of the deuterated carbon chain molecules: C_3D, C_4D, C_3HD, and C_4HD

Eunsook Kim *,[1], Satoshi Yamamoto

Department of Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Received 20 January 2005; in revised form 17 May 2005

Abstract

The rotational spectra of the deuterated carbon chain molecules, C_3D, C_4D, C_3HD, and C_4HD, have been measured with the Fourier transform microwave (FTMW) spectrometer. The C_3D and C_4D radicals are produced by discharging the DCCD gas diluted in Ar. On the other hand, the gaseous mixture of HCCH, DCCD, and HCCD diluted in Ar is used for producing C_3HD and C_4HD. For C_3D, the molecular constants are determined from a joint least-squares analysis with the previously published millimeter- and submillimeter-wave data by considering the vibronic interaction between the $^2\Pi$ ground state and the low-lying $^2\Sigma$ vibronic state. The molecular constants of C_4D are determined by use of the conventional Hamiltonian of the $^2\Sigma$ radical, while the effective rotational constant and centrifugal distortion constant are derived for C_3HD and C_4HD. In the present study, the hyperfine interaction constants of the deuterium nuclei in C_3D and C_4D are determined accurately. In particular, the nuclear quadrupole interaction constant, eQq, of the C_3D radical is found to be significantly smaller than those of C_2D and C_4D, indicating that C_3D has a floppy motion of the CCD bending mode due to the large Renner–Teller effect.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Carbon chain molecule; Microwave spectrum; Hyperfine interaction

1. Introduction

Rotational spectra of various carbon chain molecules have been detected in radioastronomical observations in collaboration with laboratory spectroscopic studies since detection of cyanopolyynes [1]. For example, the rotational spectra of the linear carbon chain radicals, C_nH ($n = 2$–8), have been detected in interstellar molecular clouds, and hence, laboratory spectroscopic studies of longer carbon chain radicals have been motivated in relation to radioastronomical observations [2]. The existence of such highly unsaturated linear carbon chains in space has promoted extensive studies on chemical processes in interstellar molecular clouds [3–5].

Deuterated linear carbon chain radicals, C_2D and C_4D, have also been detected in interstellar molecular clouds [6,7], and a high deuterium fractionation ratio has been reported for these radicals especially in cold clouds. For example, the observed abundance ratio of C_4D/C_4H is reported to be 4.3×10^{-3} in TMC-1 [7], the ratio being much higher than the cosmic D/H ratio of 1.65×10^{-5} [8]. The deuterium fractionation ratio provides us with valuable information on production pathways of molecules as well as physical conditions of interstellar molecular clouds.

To study the deuterium fractionation in further detail, accurate transition frequencies of various deuterated carbon chain radicals are indispensable. For this purpose, we have observed the rotational spectral lines of several deuterated carbon chain molecules, C_3D,

---

* Corresponding author. Fax: +81 3 5841 4178.

E-mail addresses: kim@taurus.phys.s.u-tokyo.ac.jp (E. Kim), yamamoto@phys.s.u-tokyo.ac.jp (S. Yamamoto).

[1] Present address: Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

0022-2852/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2005.05.010

C_4D, C_3HD, and C_4HD, with the Fourier transform microwave (FTMW) spectrometer [9]. Note that the rotational spectra of the C_5D and C_6D radicals were reported by Hirota et al. [10] and Linnartz et al. [11], respectively.

2. Experiment

A Balle–Flygare type Fourier transform microwave (FTMW) spectrometer was used in combination with a pulsed discharge nozzle [9]. The pulsed discharge nozzle was set to be perpendicular to the cavity axis. A high voltage pulse of 1.5 kV synchronized with opening of the nozzle was applied to the discharge electrodes attached to the nozzle. The earth magnetic field was compensated by using three Helmholtz coils placed perpendicular to one another. The C_3D and C_4D radicals were produced by discharging DCCD gas diluted in Ar, while for measurements of the C_3HD and C_4HD lines, a gaseous mixture of HCCH, DCCD, and HCCD diluted in Ar was used as a sample gas. The DCCD gas was prepared by a reaction of CaC_2 and D_2O, and the gaseous mixture of HCCH, DCCD, and HCCD by a reaction of CaC_2 and a mixture of D_2O (50%) and H_2O (50%).

The low-J rotational transitions of the C_3D and C_4D radicals were readily observed with the aid of the molecular constants reported by Yamamoto et al. [12] and Woodward et al. [13], respectively. The optimum stagnation pressure for production of C_3D and C_4D was 600-800 Torr with the DCCD concentration of 0.5% in Ar. Under this condition, the $J = \frac{3}{2}$–$\frac{1}{2}$ and $J = \frac{5}{2}$–$\frac{3}{2}$ transitions in the $^2\Pi_{\frac{1}{2}}$ state of C_3D were observed in the frequency regions of 29.4 and 49 GHz. Fig. 1 shows an example of the observed rotational spectrum of C_3D in the 49 GHz region; three hyperfine component lines of the $J = \frac{5}{2}$–$\frac{3}{2}$ transition in the $^2\Pi_{\frac{1}{2}}$ state were observed. The spectrum was obtained by integrating 1500 free induction decay signals with a repetition rate of 5 Hz. For the C_4D radical, the low-N rotational transitions were observed in the frequency range from 8 to 27 GHz. Fig. 2 shows an example of the observed spectrum of C_4D ($N = 2 - 1$, $J = \frac{5}{2}$–$\frac{3}{2}$), where the hyperfine splitting from the deuterium nuclei is clearly resolved. This spectrum was obtained by integrating 100 free induction decay signals with a repetition rate of 5 Hz. The measured frequencies for C_3D and C_4D were listed in Tables 1 and 2, respectively.

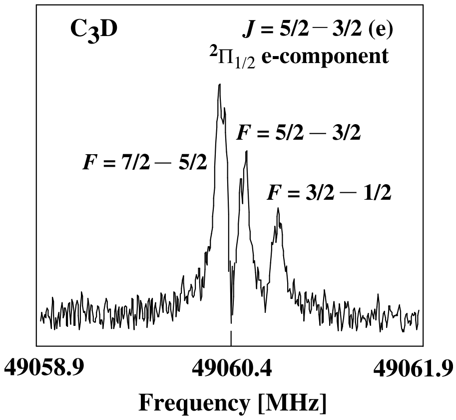

Fig. 1. An example of the observed spectral lines of the $J = \frac{5}{2}$–$\frac{3}{2}$ (*e*) transition of C_3D. The hyperfine components due to the deuterium nuclei are resolved.

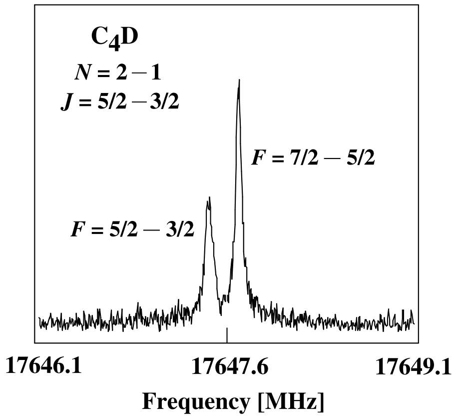

Fig. 2. An example of the observed spectral lines of the $J = \frac{5}{2}$–$\frac{3}{2}$ transition of C_4D. The hyperfine components due to the deuterium nuclei are resolved.

On the other hand, the rotational spectra of the C_3HD and C_4HD molecules were searched for on the basis of the rotational constants calculated from the molecular structures of C_3H_2 and C_4H_2, respectively [14,15]. A few low-J rotational transitions with $K_a = 0$ were observed each for C_3HD and C_4HD around the predicted frequencies. The optimum stagnation pressure was about 700 Torr with the 0.5% concentration of HCCH, DCCD, and HCCD in Ar. Table 3 lists the observed transition frequencies of C_3HD and C_4HD. Hyperfine splittings due to the D nucleus were not resolved in the present study.

3. Results and discussion

The observed transition frequencies of the C_3D radical were analyzed in combination with the millimeter- and submillimeter-wave data in the $^2\Pi$ ground state and the low-lying $^2\Sigma$ vibronic state reported by Yamamoto et al. [12]. The weight of the FTMW data to those of the absorption spectroscopy was taken to be 25 by considering the relative accuracy of the frequency measurements. According to Yamamoto et al. [12], the strong vibronic interaction exists between the ground state and the $v_4(^2\Sigma^{\mu})$ vibronic state for C_3D, since the $v_4(^2\Sigma^{\mu})$ state is located in energy between $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$.

Download English Version:

https://daneshyari.com/en/article/9589400

Download Persian Version:

https://daneshyari.com/article/9589400

Daneshyari.com