High-resolution infrared spectroscopy of H₁₂C₁₃CD and H₁₃C₁₂CD in the 470-5200 cm⁻¹ spectral region

Filippo Tamassia, Elisabetta Cané, Gianfranco Di Lonardo, Luciano Fusina

► To cite this version:

Filippo Tamassia, Elisabetta Cané, Gianfranco Di Lonardo, Luciano Fusina. High-resolution infrared spectroscopy of H₁₂C₁₃CD and H₁₃C₁₂CD in the 470-5200 cm⁻¹ spectral region. *Molecular Physics*, 2008, 105 (17-18), pp.2321-2325. 10.1080/00268970701586373 . hal-00513131

HAL Id: hal-00513131

<https://hal.science/hal-00513131>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

High-resolution infrared spectroscopy of H₁₂C₁₃CD and H₁₃C₁₂CD in the 470-5200 cm⁻¹ spectral region

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2007-0179.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	06-Jul-2007
Complete List of Authors:	Tamassia, Filippo; Università di Bologna, Dipartimento di Chimica Fisica e Inorganica Cané, Elisabetta; Università di Bologna, Dipartimento di Chimica Fisica e Inorganica di Lonardo, Gianfranco; Università di Bologna, Dipartimento di Chimica Fisica e Inorganica Fusina, Luciano; Università di Bologna, Dipartimento di Chimica Fisica e Inorganica
Keywords:	H ₁₂ C ₁₃ CD, H ₁₃ C ₁₂ CD, High-resolution Fourier Transform Infrared Spectroscopy, Fundamental bands, Combination, Overtone, Hot bands

High-resolution infrared spectroscopy of
 $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ in the 470–5200 cm^{-1}
spectral region

Luciano Fusina, Elisabetta Cané, Filippo Tamassia and
Gianfranco Di Lonardo

Dipartimento di Chimica Fisica e Inorganica, Università di
Bologna

Viale del Risorgimento, 4. I-40136, Bologna, Italy

Number of pages : 12

Number of figures : 2

Number of tables : 3

Corresponding author: Filippo Tamassia

Dipartimento di Chimica Fisica e Inorganica, Università di
Bologna.

Viale del Risorgimento, 4. I-40136, Bologna, Italy.

Tel: (39)-051-2093703

Fax: (39)-051-2093690

e-mail: tamassia@ms.fci.unibo.it

Abstract

The fundamental ro-vibrational bands and the $2\nu_4 \leftarrow \text{GS}$, $2\nu_5 \leftarrow \text{GS}$, $2\nu_3 \leftarrow \text{GS}$, $\nu_4 + \nu_5 \leftarrow \text{GS}$, $\nu_3 + \nu_4 \leftarrow \text{GS}$, $\nu_3 + \nu_4 \leftarrow \nu_4$, $\nu_3 + \nu_5 \leftarrow \nu_5$, overtone, combination and hot bands of the two rare isotopologues of acetylene $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ have been detected by Fourier transform infrared spectroscopy (FTIR). The analysis of the data has provided very accurate rotational and vibrational parameters for the ground and for the vibrationally excited states.

Keywords $\text{H}^{12}\text{C}^{13}\text{CD}$ $\text{H}^{13}\text{C}^{12}\text{CD}$

High-resolution Fourier Transform Infrared Spectroscopy

Fundamental bands

Combination, Overtone, Hot bands

Introduction

Acetylene is a spectroscopically well known molecule. Its main isotopologues have been studied thoroughly and a large number of ro-vibrational parameters have been determined from very extensive sets of infrared data (see for example [1]).

For the two rare isotopomers, $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$, only one experimental work [2], published in 1975, was found in the literature. In this paper, the authors analyzed the rotational structure of some infrared bands, namely $\nu_5 \leftarrow \text{GS}$, $\nu_3 \leftarrow \text{GS}$, $\nu_3 + \nu_4 \leftarrow \nu_4$, and $\nu_3 + \nu_5 \leftarrow \nu_5$. However, because of the low resolution, the spectroscopic parameters were determined with poor precision.

Very recently, Hardwick and coworkers [3] recorded a diode laser spectrum of these two species around 6500 cm^{-1} . They detected the $2\nu_1$ overtone band and fitted their data together with the ν_3 and ν_5 bands of Ref. [2] to improve the values of the ground state parameters B_0 and D_0 . In addition, precise values of the ν_0 band origin and of the rotational and centrifugal distortion constants for the $\nu_1=2$ states were determined for both isotopomers.

Here, we present a high-resolution study of all the fundamental bands and of some overtone, combination and hot

bands of $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ in the spectral region up to 5200 cm^{-1} .

Experimental details

The spectra of $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ were accidentally observed while recording the FTIR spectra of C_2HD and $\text{H}^{13}\text{C}^{12}\text{CH}$. In the former case the sample contained the ^{13}C isotope in natural abundance, while in the latter case the studied isotopomers were due to accidental deuterium exchange with the wall of the cell. Details about the experiments, including the calibration procedure, can be found in Refs. [4-6].

The bands are generally weak or very weak and can be seen thanks to the excellent S/N ratio of the spectra. The worst case is shown in figure 1, containing the ν_4 Q-branch of both isotopomers in the region of 500 cm^{-1} , where the HgCdTe detector has a very poor response. One of the best recordings is shown in figure 2. It displays the Q branch of the ν_5 band of $\text{H}^{13}\text{C}^{12}\text{CD}$, at 674.2 cm^{-1} , which is probably the strongest feature in the whole spectrum. The ν_5 Q branch of

the other isotopomer at 677.9 cm^{-1} falls among the very strong lines of the Q branch of the same band of $^{12}\text{C}_2\text{HD}$.

[insert Figs 1 and 2 about here]

Results and discussion

Table 1 lists all the bands that we have identified for both isotopomers, the upper state G_c^0 term values, the range of J values assigned in the P , Q and R sub-branches, the number of fitted transitions, and the standard deviation of the least-squares fits. Information about the $2\nu_1$ bands reported recently [3] are also included for completeness.

[insert Table 1 about here]

Most of the fundamental infrared bands of $\text{H}^{13}\text{C}^{12}\text{CD}$ are slightly more intense than the bands of the other species by a factor from 5 to 10%. However, it is difficult to make accurate considerations about the intensity of the bands, because the transitions observed are very weak and the S/N ratio generally is smaller than 10. A probable explanation could be a small difference between the transition moments of the two molecules. To confirm this hypothesis it would be

necessary to perform very accurate intensity calculations at an anharmonic level.

As observed in the spectra of $^{12}\text{C}_2\text{HD}$ [4,5] and $^{13}\text{C}_2\text{HD}$ [7], the fundamental bands of the studied molecules do not show evident anomalies, due to systematic or accidental resonances (see figures 1 and 2). Therefore, all the data could be fitted using the basic Hamiltonian of a linear molecule with centrifugal distortion corrections up to the quartic term. In fact, the strong anharmonic resonances present in other isotopologues (i.e. 3/245 in $^{12}\text{C}_2\text{H}_2$ [8,9] and 1/255 in $^{13}\text{C}_2\text{H}_2$ [10]) are not effective here because of the large energy difference between the interacting states.

For the bending modes, the ℓ -doubling parameters q_v and q_v' were included. The ro-vibrational energy term values are given by

$$T^0(v, J) = G_c^0(v) + B_v J(J+1) - D_v [J(J+1)]^2 \mp \frac{1}{2} \{ q_v [J(J+1)] + q_v' [J(J+1)]^2 \} \quad (1)$$

with the $-$ and $+$ signs related to the e and f levels, respectively and $G_c^0 = G_v^0 - B_v k^2 - D_v k^4$, with G_v^0 the pure vibrational term value and $k = \ell_4 + \ell_5$.

For most of the other bands, the fits improved considerably if higher-order centrifugal distortion terms were added in the model. In general, the sextic coefficient H could always be fitted; in some cases even the octic constant L could be determined. Usually, if the set of data includes transitions with J lower than 40, as in all the studied bands, only D is necessary to obtain good quality fits. This is confirmed by the fits of the fundamental bands. When higher-order terms are required, it might be the symptom of a resonance affecting the vibrational levels of the band considered. Since the discrepancies between observed and calculated values increase for increasing J 's, it is reasonable to assume that the resonance terms include a rotational dependence. Although we believe that the determined H and L are not effective distortion constants, we chose to fit them where necessary, in order to have comparable standard deviation of the fit for all bands. This way, the sets of parameters obtained from the analysis can be used to predict with good precision ro-vibrational transitions not observed in our spectra.

An example of a ro-vibrational resonance is evident in the pattern of the $\nu_3 + \nu_4 \leftarrow \nu_4$ band of $\text{H}^{12}\text{C}^{13}\text{CD}$. The upper state (Π symmetry) is perturbed by a Coriolis interaction with the $\nu_2 + \nu_4 + \nu_5$ state (Σ^+ symmetry). By using x_{24} and x_{25} from $^{12}\text{C}_2\text{HD}$

[5], we calculated a vibrational term value of 3024 cm^{-1} for the Σ^+ state of $\text{H}^{12}\text{C}^{13}\text{CD}$ and 3014 cm^{-1} for the Σ^+ state of $\text{H}^{13}\text{C}^{12}\text{CD}$. The energy separation between Π and Σ^+ states is 25 cm^{-1} for $\text{H}^{12}\text{C}^{13}\text{CD}$ and 67 for $\text{H}^{13}\text{C}^{12}\text{CD}$, calculated using the term values in table 1 for the Π states. The different energy gap would explain why a rotational perturbation is evident for the $\text{H}^{12}\text{C}^{13}\text{CD}$ species only.

It has to be pointed out that for the vibrational levels involving a double excitation of the bending modes, $2\nu_4 \leftarrow \text{GS}$, $2\nu_5 \leftarrow \text{GS}$, $\nu_4 + \nu_5 \leftarrow \text{GS}$, we detected only the Σ^+ states. Transitions involving the other Δ component of the manifold, and also the Σ^- state in the case of $\nu_4 + \nu_5$, were too weak to be observed from either $\nu_4=1$ or $\nu_5=1$ and are not allowed from the ground state. Therefore, ℓ -type rotational and vibrational interactions between different levels of a manifold are not considered. This can account for the anomalous values of the centrifugal distortion constants for these vibrational states.

Initially, the wavenumbers for each band were fitted to upper and lower state ro-vibrational parameters, in order to check the correctness of the assignments and to extend the data set. Identical unitary weights were assigned to all the

transitions, except for the overlapped or very weak lines, which were given zero weight.

Once the single fits were satisfactory, all the data of each isotopomer were fitted together to provide a unique determination of the ground state parameters. The analysis consisted of the following steps. i) The combination differences (GSCD) from all the bands in table 1 starting from the ground state were fitted simultaneously to the best values of B_0 and D_0 . A total of 231 and 210 GSCD were fitted with a standard deviation of 35×10^{-5} and $39 \times 10^{-5} \text{ cm}^{-1}$ for $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$, respectively. ii) The single band fits (excluding the hot bands) were performed again constraining the ground state parameters to the values determined in step i). iii) For the hot bands, B_4 , D_4 , B_5 and D_5 were fixed to the values obtained in step ii). In each fit all the transition wavenumbers that differed from their calculated values by more than 0.001 cm^{-1} were excluded from the data set in the final cycle of the least-squares procedure. The spectroscopic parameters obtained in the final fits are listed in table 2.

[insert Table 2 about here]

The quality of the fits is very satisfactory, and the parameters show a remarkable improvement with respect to the previous work. They allow the calculation of the harmonic wavenumbers and the anharmonic constants listed in table 3 for both molecules. These values are consistent with the corresponding ones calculated from the parameters reported for $^{12}\text{C}_2\text{HD}$ [11] and $^{13}\text{C}_2\text{HD}$ [7].

[insert Table 3 about here]

The assigned transitions for all the analyzed bands, together with the corresponding observed-calculated values obtained using the parameters in table 2, are available from the authors.

Conclusions

The infrared spectrum of $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ has been detected in the 470–5200 cm^{-1} spectral region. All the fundamental bands and some overtone, combination and hot bands have been analyzed. The spectroscopic parameters were determined with great accuracy from single band fits.

The transitions of the $2\nu_1$ bands reported recently [3] were fitted using our new ground state constants for completeness. The values of the determined parameters for the $\nu_1=2$ states (see table 2) are, as expected, very close to those given in table 2 of [3].

Acknowledgements

The authors acknowledge the Università di Bologna and the Ministero della Ricerca e dell'Università (PRIN 'Trasferimento di energia e di carica al livello molecolare') for financial support.

References

- [1] A. Fayt, S. Robert, G. Di Lonardo, L. Fusina, F. Tamassia, M. Herman, *J. Chem. Phys.*, **126**, 114303 (2007).
- [2] S. Ghersetti, A. Baldacci, S. Giorgianni, R. H. Barnes, K. Narahari Rao, *Gazz. Chim. It.*, **105**, 875 (1975).
- [3] J. L. Hardwick, Z. T. Martin, M. J. Pilkenton, E. N. Wolf, *J. Mol. Spectrosc.*, **243**, 10 (2007).
- [4] L. Fusina, F. Tamassia, G. Di Lonardo, *Mol. Phys.*, **103**, 2613 (2005).
- [5] L. Fusina, E. Canè, F. Tamassia, G. Di Lonardo, *Mol. Phys.*, **103**, 3263 (2005).
- [6] G. Di Lonardo, A. Baldan, G. Bramati, L. Fusina, *J. Mol. Spectrosc.*, **213**, 57 (2002).
- [7] L. Fusina and G. Di Lonardo, to be published.
- [8] R. D'Cunha, Y. A. Sarma, V. A. Job, G. Guelachvili, K. Narahari Rao, *J. Mol. Spectrosc.*, **157**, 358 (1993).
- [9] J. Vander Auwera, D. Hurtmans, M. Carleer, M. Herman, *J. Mol. Spectrosc.*, **157**, 337 (1993).
- [10] G. Di Lonardo, P. Ferracuti, L. Fusina, E. Venuti, *J. Mol. Spectrosc.*, **164**, 219 (1994).
- [11] M. Herman, C. Depiesse, G. Di Lonardo, A. Fayt, L. Fusina, D. Hurtmans, S. Kassı, M. Mollabashi, J. Vander Auwera, *J. Mol. Spectrosc.*, **228**, 499 (2004).

Table Captions

Table 1

Vibrational assignments and term values G_v^0 (in cm^{-1}) of the vibration-rotation bands for $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$

Table 2

Vibrational assignments, band centres, rotational and distortion parameters (in cm^{-1}) of $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ ^a

Table 3

Vibrational parameters (in cm^{-1}) for $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ ^a

Captions for figures.

Figure 1.

The Q -branch of the $\nu_4 \leftarrow GS$ band for $H^{12}C^{13}CD$ and $H^{13}C^{12}CD$. Experimental conditions: $H^{13}C^{12}CH$ sample, pressure 1.33 kPa, absorption path length 6.0 m, resolution 0.005 cm^{-1} , acquisition time 110 h.

Figure 2.

The Q -branch of the $\nu_5 \leftarrow GS$ band for $H^{13}C^{12}CD$. Experimental conditions: $^{12}C_2HD$ sample, pressure 0.266 kPa, absorption path length 0.18 m, resolution 0.004 cm^{-1} , acquisition time 25 h.

Table 1

Vibrational assignments and term values G_C^0 (in cm^{-1}) of the vibration-rotation bands for $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$

$\text{H}^{12}\text{C}^{13}\text{CD}$					
Transition	Symmetry	G_C^0 ^a	Transitions Assigned	Fitted data	σ ($\times 10^5$) ^b
$\nu_1 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	3 333.979	$\text{P}_{\text{e-e}}(1-37); \text{R}_{\text{e-e}}(0-40)$	64	40
$\nu_2 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 837.675	$\text{P}_{\text{e-e}}(1-34); \text{R}_{\text{e-e}}(0-30)$	61	27
$\nu_3 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	2 551.578	$\text{P}_{\text{e-e}}(1-32); \text{R}_{\text{e-e}}(0-33)$	58	22
$\nu_4 \leftarrow \text{GS}$	$\Pi \leftarrow \Sigma^+$	511.511	$\text{P}_{\text{e-e}}(2-19); \text{R}_{\text{e-e}}(0-20); \text{Q}_{\text{f-e}}(3-24)$	54	38
$\nu_5 \leftarrow \text{GS}$	$\Pi \leftarrow \Sigma^+$	677.867	$\text{P}_{\text{e-e}}(2-32); \text{R}_{\text{e-e}}(0-35); \text{Q}_{\text{f-e}}(1-30)$	89	29
$2\nu_1 \leftarrow \text{GS}$ ^c	$\Sigma^+ \leftarrow \Sigma^+$	6 565.491	$\text{P}_{\text{e-e}}(1-28); \text{R}_{\text{e-e}}(1-25)$	48	31
$2\nu_3 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	5 058.135	$\text{P}_{\text{e-e}}(1-24); \text{R}_{\text{e-e}}(0-23)$	44	45
$2\nu_4 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 020.534	$\text{P}_{\text{e-e}}(1-32); \text{R}_{\text{e-e}}(0-30)$	51	59
$2\nu_5 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 342.278	$\text{P}_{\text{e-e}}(1-38); \text{R}_{\text{e-e}}(0-36)$	63	38
$\nu_4 + \nu_5 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 193.519	$\text{P}_{\text{e-e}}(1-33); \text{R}_{\text{e-e}}(0-31)$	51	23
$\nu_3 + \nu_4 \leftarrow \nu_4$	$\Pi \leftarrow \Pi$	3 048.569	$\text{P}_{\text{e-e}}(9-28); \text{R}_{\text{e-e}}(7-25)$ $\text{P}_{\text{f-f}}(7-27); \text{R}_{\text{f-f}}(9-25)$	41	52
$\nu_3 + \nu_5 \leftarrow \nu_5$	$\Pi \leftarrow \Pi$	3 226.748	$\text{P}_{\text{e-e}}(2-30); \text{R}_{\text{e-e}}(1-24)$ $\text{P}_{\text{f-f}}(3-30); \text{R}_{\text{f-f}}(1-25)$	77	42
$\text{H}^{13}\text{C}^{12}\text{CD}$					
Transition	Symmetry	G_C^0 ^a	Transitions Assigned	Fitted data	σ ($\times 10^5$) ^b
$\nu_1 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	3 319.251	$\text{P}_{\text{e-e}}(1-39); \text{R}_{\text{e-e}}(0-34)$	63	40
$\nu_2 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 826.181	$\text{P}_{\text{e-e}}(1-35); \text{R}_{\text{e-e}}(0-31)$	62	28
$\nu_3 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	2 579.287	$\text{P}_{\text{e-e}}(1-36); \text{R}_{\text{e-e}}(0-39)$	67	26
$\nu_4 \leftarrow \text{GS}$	$\Pi \leftarrow \Sigma^+$	516.490	$\text{P}_{\text{e-e}}(4-21); \text{R}_{\text{e-e}}(2-23); \text{Q}_{\text{f-e}}(1-23)$	50	45
$\nu_5 \leftarrow \text{GS}$	$\Pi \leftarrow \Sigma^+$	674.169	$\text{P}_{\text{e-e}}(2-30); \text{R}_{\text{e-e}}(0-35); \text{Q}_{\text{f-e}}(1-30)$	90	17
$2\nu_1 \leftarrow \text{GS}$ ^c	$\Sigma^+ \leftarrow \Sigma^+$	6 536.336	$\text{P}_{\text{e-e}}(1-25); \text{R}_{\text{e-e}}(0-23)$	41	41
$2\nu_3 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	5 113.397	$\text{P}_{\text{e-e}}(2-26); \text{R}_{\text{e-e}}(1-24)$	39	40
$2\nu_4 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 030.333	$\text{P}_{\text{e-e}}(1-31); \text{R}_{\text{e-e}}(0-34)$	53	51
$2\nu_5 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 335.235	$\text{P}_{\text{e-e}}(1-34); \text{R}_{\text{e-e}}(0-36)$	64	28
$\nu_4 + \nu_5 \leftarrow \text{GS}$	$\Sigma^+ \leftarrow \Sigma^+$	1 194.400	$\text{P}_{\text{e-e}}(1-13); \text{R}_{\text{e-e}}(0-8)$	17	38
$\nu_3 + \nu_4 \leftarrow \text{GS}$	$\Pi \leftarrow \Sigma^+$	3 080.559	$\text{P}_{\text{e-e}}(3-25); \text{R}_{\text{e-e}}(3-17); \text{Q}_{\text{f-e}}(1-21)$	37	53
$\nu_3 + \nu_4 \leftarrow \nu_4$	$\Pi \leftarrow \Pi$	3 080.558	$\text{P}_{\text{e-e}}(3-25); \text{R}_{\text{e-e}}(1-26)$ $\text{P}_{\text{f-f}}(3-25); \text{R}_{\text{f-f}}(2-20)$	72	39
$\nu_3 + \nu_5 \leftarrow \nu_5$	$\Pi \leftarrow \Pi$	3 250.573	$\text{P}_{\text{e-e}}(2-28); \text{R}_{\text{e-e}}(1-26)$ $\text{P}_{\text{f-f}}(3-26); \text{R}_{\text{f-f}}(1-24)$	69	33

^a The upper state vibrational term value G_C^0 (in cm^{-1}) is : $G_C^0 = G_v^0 - B_v k^2 - D_v k^4$.

^b σ (in cm^{-1}) is the standard deviation of the fit.

^c From Ref. [3].

Table 2

Vibrational assignments, band centers, rotational and distortion parameters (in cm^{-1}) of $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ ^a

$\text{H}^{12}\text{C}^{13}\text{CD}$							
Transition	ν_c	B	$D \times 10^6$	$H \times 10^9$	$L \times 10^{12}$	$q \times 10^3$	$q_J \times 10^8$
GS		0.97527102 (68)	1.09732 (49)				
$\nu_1 \leftarrow \text{GS}$	3333.9792335 (942)	0.970505543 (345)	1.087398 (230)				
$\nu_2 \leftarrow \text{GS}$	1837.6751570 (653)	0.971041721 (364)	1.098274 (368)				
$\nu_3 \leftarrow \text{GS}$	2551.5776674 (541)	0.968975550 (290)	1.090351 (285)				
$\nu_4 \leftarrow \text{GS}$	511.510777 (108)	0.97762407 (118)	1.11441 (249)			4.35234 (145)	-4.177 (387)
$\nu_5 \leftarrow \text{GS}$	677.8671580 (600)	0.976627955 (356)	1.111464 (405)			3.411419 (498)	-1.9658 (692)
$2\nu_1 \leftarrow \text{GS}$	6565.4907266 (847)	0.965686571 (693)	1.08555 (102)				
$2\nu_3 \leftarrow \text{GS}$	5058.134860 (155)	0.96280448 (298)	1.5901 (133)	0.7283 (157)			
$2\nu_4 \leftarrow \text{GS}$	1020.533817 (223)	0.98029082 (397)	6.3481 (187)	3.0908 (307)	-0.7350 (161)		
$2\nu_5 \leftarrow \text{GS}$	1342.278145 (110)	0.978274890 (920)	1.88616 (177)	0.057632 (899)			
$\nu_4 + \nu_5 \leftarrow \text{GS}$	1193.5187946 (707)	0.97891281 (117)	-2.48538 (441)	-1.44993 (435)			
$\nu_3 + \nu_4 \leftarrow \nu_4$	2537.05814 (129)	0.9716912 (105)	1.4829 (256)	0.2266 (194)		4.38197 (143)	-5.910 (257)
$\nu_3 + \nu_5 \leftarrow \nu_5$	2548.880819 (106)	0.970296153 (709)	1.101996 (923)			3.371040 (807)	-1.857 (136)
$\text{H}^{13}\text{C}^{12}\text{CD}$							
Transition	ν_c	B	$D \times 10^6$	$H \times 10^9$	$L \times 10^{12}$	$q \times 10^3$	$q_J \times 10^8$
GS		0.96719254 (82)	1.08061 (58)				
$\nu_1 \leftarrow \text{GS}$	3319.2513516 (945)	0.962706329 (409)	1.071087 (328)				
$\nu_2 \leftarrow \text{GS}$	1826.1807529 (686)	0.963020202 (353)	1.079919 (336)				
$\nu_3 \leftarrow \text{GS}$	2579.2870423 (584)	0.960662849 (230)	1.075481 (166)				
$\nu_4 \leftarrow \text{GS}$	516.489900 (136)	0.96968717 (146)	1.12312 (292)			4.24063 (174)	-4.665 (432)
$\nu_5 \leftarrow \text{GS}$	674.1694345 (342)	0.968417887 (198)	1.092803 (219)			3.376613 (279)	-2.0143 (375)
$2\nu_1 \leftarrow \text{GS}$	6536.336499 (120)	0.95773432 (119)	1.09870 (220)				
$2\nu_3 \leftarrow \text{GS}$	5113.397080 (137)	0.95408708 (117)	1.08665 (187)				

$2\nu_4 \leftarrow \text{GS}$	1030.332576(176)	0.97245466(424)	5.5820(247)	2.1279(497)	-0.2924(320)		
$2\nu_5 \leftarrow \text{GS}$	1335.2350713(762)	0.969930196(644)	1.85600(125)	0.049101(641)			
$\nu_4 + \nu_5 \leftarrow \text{GS}$	1194.400158(202)	0.9707206(210)	-7.202(479)	-45.76(256)			
$\nu_3 + \nu_4 \leftarrow \text{GS}$	3080.559094(211)	0.96331578(211)	1.14531(425)			4.27541(253)	-7.823(658)
$\nu_3 + \nu_4 \leftarrow \nu_4$	2564.067740(101)	0.963313617(887)	1.12730(150)			4.26905(104)	-5.605(225)
$\nu_3 + \nu_5 \leftarrow \nu_5$	2576.4035694(866)	0.961842202(680)	1.08482(104)			3.348872(802)	-1.874(158)

^aThe standard deviation (1σ) is indicated in parentheses in the unit of the last quoted digit.
Rotational ground state constants were constrained during the fitting procedure.

Table 3

Vibrational parameters (in cm^{-1}) in $\text{H}^{12}\text{C}^{13}\text{CD}$ and $\text{H}^{13}\text{C}^{12}\text{CD}$ ^a

	$\text{H}^{12}\text{C}^{13}\text{CD}$	$\text{H}^{13}\text{C}^{12}\text{CD}$
$\tilde{\omega}_1^0$	3385.21310(21)	3370.33445(23)
$\tilde{\omega}_3^0$	2574.08790(20)	2601.87554(19)
$\tilde{\omega}_4^0$	514.70989(33)	519.75289(34)
$\tilde{\omega}_5^0$	686.54850(17)	682.65817(11)
x_{11}^0	-51.23387(10)	-51.08310(11)
x_{33}^0	-22.510237(95)	-22.588502(90)
$x_{44}^0 - g_{44}^0$	-2.22149(16)	-2.29330(16)
$x_{55}^0 - g_{55}^0$	-7.704713(81)	-7.520317(51)
x_{34}^0	-14.5195(13)	-15.21930(12)
x_{35}^0	-2.69685(12)	-2.88347(10)
$x_{45}^0 - g_{45}^0 + r_{45}^0$	2.18661(14)	1.80272(25)

^a The standard deviation (1σ) is indicated in parentheses in the unit of the last quoted digit.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36