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## High-resolution infrared spectroscopy of H<sub>12</sub>C<sub>13</sub>CD and H<sub>13</sub>C<sub>12</sub>CD in the 470-5200 cm<sup>-1</sup> spectral region

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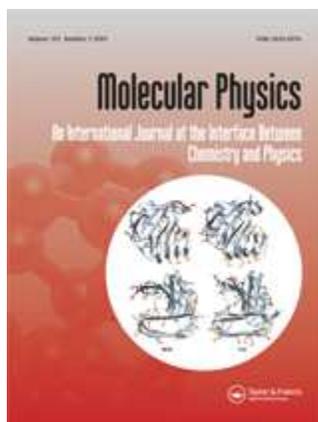
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### High-resolution infrared spectroscopy of H<sub>12</sub>C<sub>13</sub>CD and H<sub>13</sub>C<sub>12</sub>CD in the 470-5200 cm<sup>-1</sup> spectral region

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Keywords:	H <sub>12</sub> C <sub>13</sub> CD, H <sub>13</sub> C <sub>12</sub> CD, High-resolution Fourier Transform Infrared Spectroscopy, Fundamental bands, Combination, Overtone, Hot bands



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3 **High-resolution infrared spectroscopy of**  
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6  **$H^{12}C^{13}CD$  and  $H^{13}C^{12}CD$  in the 470–5200  $cm^{-1}$**   
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10 **spectral region**  
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17 Luciano Fusina, Elisabetta Cané, Filippo Tamassia and  
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**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  $6500 \text{ cm}^{-1}$ . They detected the  $2\nu_1$  overtone band and fitted their data together with the  $\nu_3$  and  $\nu_5$  bands of Ref. [2] to improve the values of the ground state parameters  $B_0$  and  $D_0$ . In addition, precise values of the  $\nu_0$  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  $5200\text{ cm}^{-1}$ .

### 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  $\text{C}_2\text{HD}$  and  $\text{H}^{13}\text{C}^{12}\text{CH}$ . In the former case the sample contained the  $^{13}\text{C}$  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  $\nu_4$  Q-branch of both isotopomers in the region of  $500\text{ cm}^{-1}$ , 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  $\nu_5$  band of  $\text{H}^{13}\text{C}^{12}\text{CD}$ , at  $674.2\text{ cm}^{-1}$ , which is probably the strongest feature in the whole spectrum. The  $\nu_5$  Q branch of

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3 the other **isotopomer** at  $677.9 \text{ cm}^{-1}$  falls among the very  
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5 strong lines of the Q branch of the same band of  $^{12}\text{C}_2\text{HD}$ .  
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10 **[insert Figs 1 and 2 about here]**  
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## 12 13 14 15 **Results and discussion**

16  
17 Table 1 lists all the bands that we have identified for both  
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19 **isotopomers**, the upper state  $G_c^0$  term values, the range of  $J$   
20  
21 values assigned in the  $P$ ,  $Q$  and  $R$  sub-branches, the number  
22  
23 of fitted transitions, and the standard deviation of the  
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25 least-squares fits. Information about the  $2\nu_1$  bands reported  
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27 recently [3] are also included for completeness.  
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34 **[insert Table 1 about here]**  
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39 Most of the fundamental infrared bands of  $\text{H}^{13}\text{C}^{12}\text{CD}$  are  
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41 slightly more intense than the bands of the other species by  
42  
43 a factor from 5 to 10%. However, it is difficult to make  
44  
45 accurate considerations about the intensity of the bands,  
46  
47 because the transitions observed are very weak and the S/N  
48  
49 ratio generally is smaller than 10. A **probable** explanation  
50  
51 could be a small difference between the transition moments  
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53 of the two molecules. To confirm this hypothesis it would be  
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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  $\ell$ -doubling parameters  $q_v$  and  $q_v^J$  were included. The ro-vibrational energy term values are given by

$$T^0(v,J) = G_c^0(v) + B_v J(J+1) - D_v [J(J+1)]^2 \mp \frac{1}{2} \{ q_v [J(J+1)] + q_v^J [J(J+1)]^2 \} \quad (1)$$

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  $k = \ell_4 + \ell_5$ .

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

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50 An example of a ro-vibrational resonance is evident in the  
51 pattern of the  $\nu_3+\nu_4\leftarrow\nu_4$  band of  $\text{H}^{12}\text{C}^{13}\text{CD}$ . The upper state ( $\Pi$   
52 symmetry) is perturbed by a Coriolis interaction with the  
53  $\nu_2+\nu_4+\nu_5$  state ( $\Sigma^+$  symmetry). By using  $x_{24}$  and  $x_{25}$  from  $^{12}\text{C}_2\text{HD}$   
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[5], we calculated a vibrational term value of  $3024 \text{ cm}^{-1}$  for the  $\Sigma^+$  state of  $\text{H}^{12}\text{C}^{13}\text{CD}$  and  $3014 \text{ cm}^{-1}$  for the  $\Sigma^+$  state of  $\text{H}^{13}\text{C}^{12}\text{CD}$ . The energy separation between  $\Pi$  and  $\Sigma^+$  states is  $25 \text{ cm}^{-1}$  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  $\Pi$  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  $\Sigma^+$  states. Transitions involving the other  $\Delta$  component of the manifold, and also the  $\Sigma^-$  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,  $\ell$ -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

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3 transitions, except for the overlapped or very weak lines,  
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5 which were given zero weight.  
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8 Once the single fits were satisfactory, all the data of each  
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10 isotopomer were fitted together to provide a unique  
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12 determination of the ground state parameters. The analysis  
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14 consisted of the following steps. i) The combination  
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16 differences (GSCD) from all the bands in table 1 starting  
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18 from the ground state were fitted simultaneously to the best  
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20 values of  $B_0$  and  $D_0$ . A total of 231 and 210 GSCD were fitted  
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22 with a standard deviation of  $35 \times 10^{-5}$  and  $39 \times 10^{-5}$   $\text{cm}^{-1}$  for  
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24  $\text{H}^{12}\text{C}^{13}\text{CD}$  and  $\text{H}^{13}\text{C}^{12}\text{CD}$ , respectively. ii) The single band fits  
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26 (excluding the hot bands) were performed again constraining  
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28 the ground state parameters to the values determined in step  
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30 i). iii) For the hot bands,  $B_4$ ,  $D_4$ ,  $B_5$  and  $D_5$  were fixed to  
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32 the values obtained in step ii). In each fit all the  
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34 transition wavenumbers that differed from their calculated  
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36 values by more than  $0.001 \text{ cm}^{-1}$  were excluded from the data  
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38 set in the final cycle of the least-squares procedure.  
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45 The spectroscopic parameters obtained in the final fits are  
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47 listed in table 2.  
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52 [insert Table 2 about here]  
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3 The quality of the fits is very satisfactory, and the  
4 parameters show a remarkable improvement with respect to the  
5 previous work. They allow the calculation of the harmonic  
6 wavenumbers and the anharmonic constants listed in table 3  
7 for both molecules. These values are consistent with the  
8 corresponding ones calculated from the parameters reported  
9 for  $^{12}\text{C}_2\text{HD}$  [11] and  $^{13}\text{C}_2\text{HD}$  [7].  
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22 [insert Table 3 about here]  
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26 The assigned transitions for all the analyzed bands,  
27 together with the corresponding observed-calculated values  
28 obtained using the parameters in table 2, are available from  
29 the authors.  
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### 43 **Conclusions**

44 The infrared spectrum of  $\text{H}^{12}\text{C}^{13}\text{CD}$  and  $\text{H}^{13}\text{C}^{12}\text{CD}$  has been  
45 detected in the 470–5200  $\text{cm}^{-1}$  spectral region. All the  
46 fundamental bands and some overtone, combination and hot  
47 bands have been analyzed. The spectroscopic parameters were  
48 determined with great accuracy from single band fits.  
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3 The transitions of the  $2\nu_1$  bands reported recently [3] were  
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5 fitted using our new ground state constants for  
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7 completeness. The values of the determined parameters for  
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9 the  $\nu_1=2$  states (see table 2) are, as expected, very close  
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11 to those given in table 2 of [3].  
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**Table Captions**

Table 1

Vibrational assignments and term values  $G_c^0$  (in  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$ ) of  $\text{H}^{12}\text{C}^{13}\text{CD}$  and  $\text{H}^{13}\text{C}^{12}\text{CD}$  <sup>a</sup>

Table 3

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

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3 **Captions for figures.**  
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10 Figure 1.

11  
12 The  $Q$ -branch of the  $\nu_4 \leftarrow GS$  band for  $H^{12}C^{13}CD$  and  $H^{13}C^{12}CD$ .  
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14 Experimental conditions:  $H^{13}C^{12}CH$  sample, pressure 1.33 kPa,  
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16 absorption path length 6.0 m, resolution  $0.005\text{ cm}^{-1}$ ,  
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18 acquisition time 110 h.  
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29 Figure 2.

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31 The  $Q$ -branch of the  $\nu_5 \leftarrow GS$  band for  $H^{13}C^{12}CD$ . Experimental  
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33 conditions:  $^{12}C_2HD$  sample, pressure 0.266 kPa, absorption  
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35 path length 0.18 m, resolution  $0.004\text{ cm}^{-1}$ , acquisition time  
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38 25 h.  
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Table 1

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

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

<sup>b</sup>  $\sigma$  (in  $\text{cm}^{-1}$ ) is the standard deviation of the fit.

<sup>c</sup> From Ref. [3].

Table 2

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

$\text{H}^{12}\text{C}^{13}\text{CD}$							
Transition	$\nu_c$	$B$	$D \times 10^6$	$H \times 10^9$	$L \times 10^{12}$	$q \times 10^3$	$q_J \times 10^8$
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	$\nu_c$	$B$	$D \times 10^6$	$H \times 10^9$	$L \times 10^{12}$	$q \times 10^3$	$q_J \times 10^8$
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)				

1	$2\nu_4 \leftarrow \text{GS}$	1030.332576 (176)	0.97245466 (424)	5.5820 (247)	2.1279 (497)	-0.2924 (320)		
2	$2\nu_5 \leftarrow \text{GS}$	1335.2350713 (762)	0.969930196 (644)	1.85600 (125)	0.049101 (641)			
3								
4	$\nu_4 + \nu_5 \leftarrow \text{GS}$	1194.400158 (202)	0.9707206 (210)	-7.202 (479)	-45.76 (256)			
5								
6	$\nu_3 + \nu_4 \leftarrow \text{GS}$	3080.559094 (211)	0.96331578 (211)	1.14531 (425)			4.27541 (253)	-7.823 (658)
7	$\nu_3 + \nu_4 \leftarrow \nu_4$	2564.067740 (101)	0.963313617 (887)	1.12730 (150)			4.26905 (104)	-5.605 (225)
8								
9	$\nu_3 + \nu_5 \leftarrow \nu_5$	2576.4035694 (866)	0.961842202 (680)	1.08482 (104)			3.348872 (802)	-1.874 (158)

<sup>a</sup>The standard deviation ( $1\sigma$ ) is indicated in parentheses in the unit of the last quoted digit.

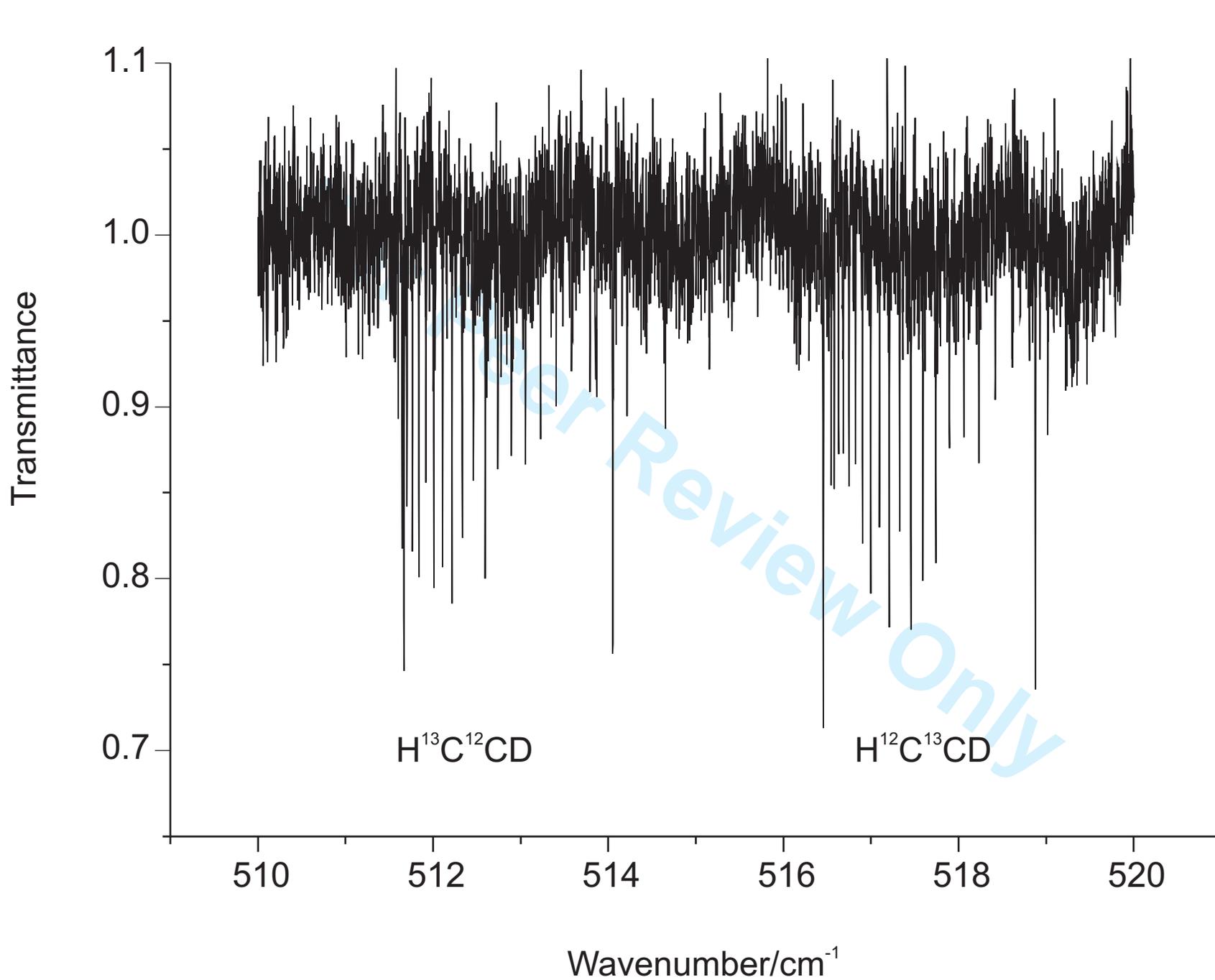
Rotational ground state constants were constrained during the fitting procedure.

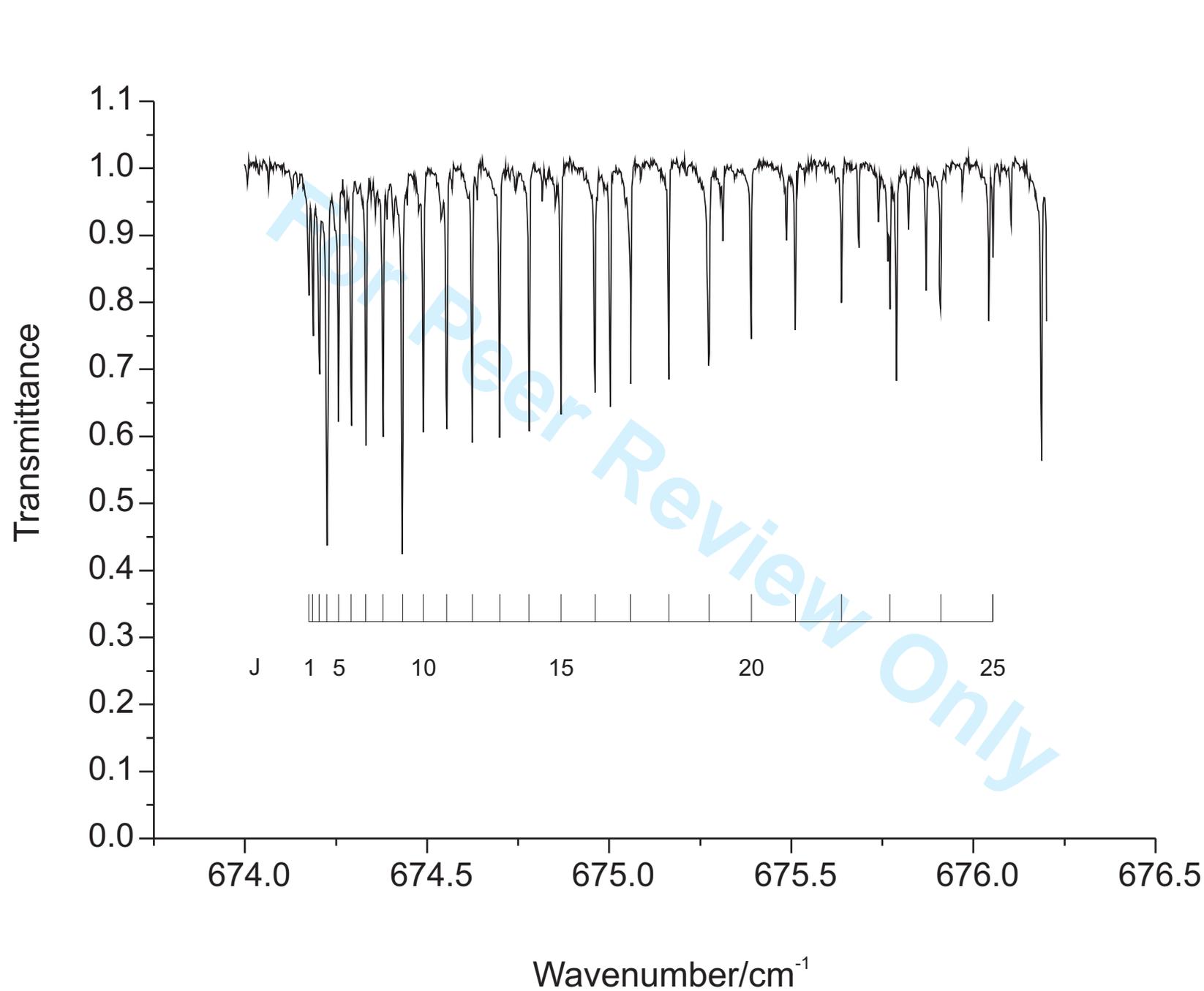
Table 3

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

	$\text{H}^{12}\text{C}^{13}\text{CD}$	$\text{H}^{13}\text{C}^{12}\text{CD}$
$\tilde{\omega}_1^0$	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)

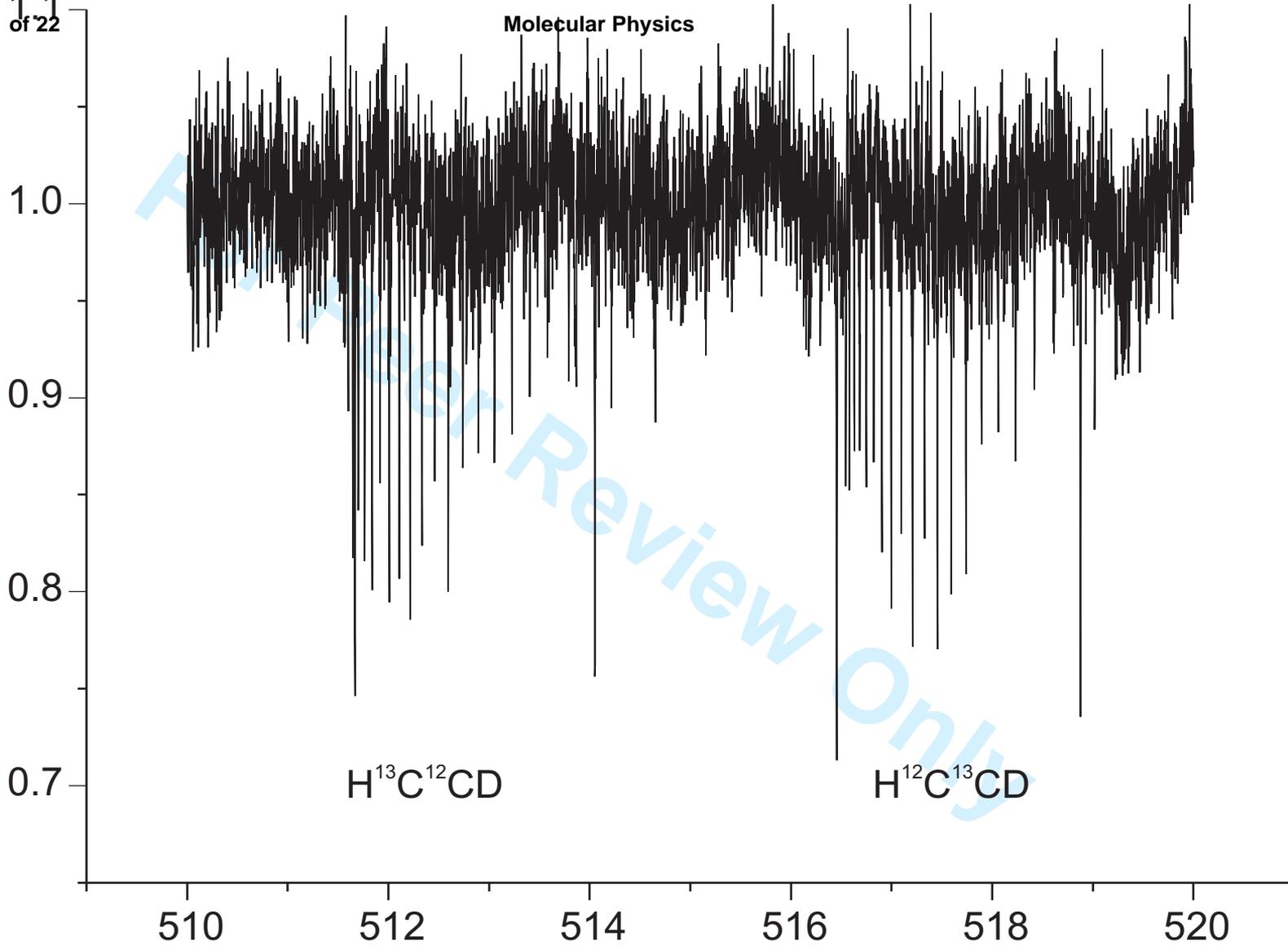
<sup>a</sup> The standard deviation ( $1\sigma$ ) is indicated in parentheses in the unit of the last quoted digit.



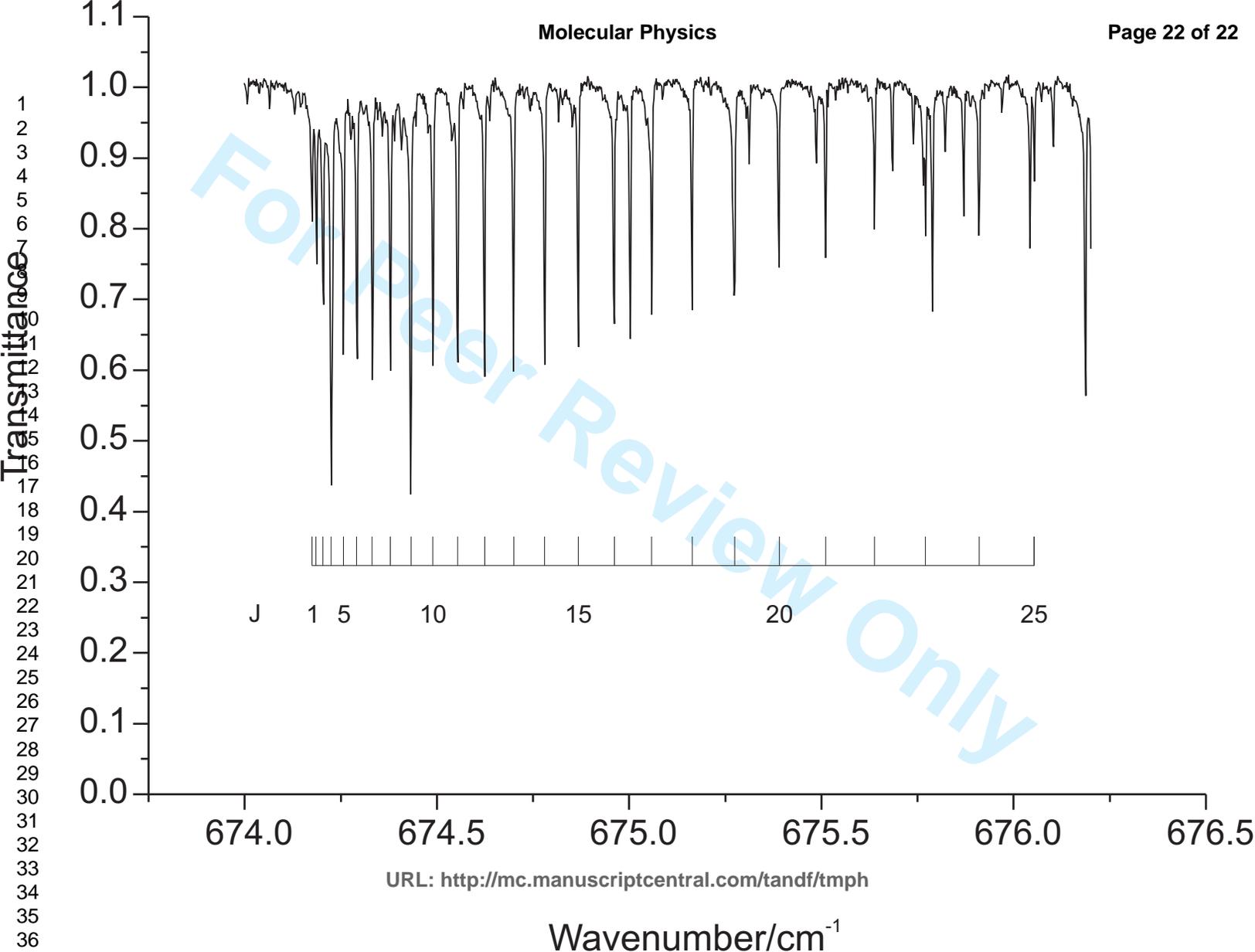


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