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The high resolution infrared spectrum of the ν_4 band of 1,1,1- trifluoro - ethane

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► **To cite this version:**

Gianfranco Di Lonardo, Adriana Predoi-Cross, Michel Herman, Giandomenico Nivellini, Luciano Fusina, et al.. The high resolution infrared spectrum of the ν_4 band of 1,1,1- trifluoro - ethane. Molecular Physics, 2010, pp.1. 10.1080/00268971003720322 . hal-00595190

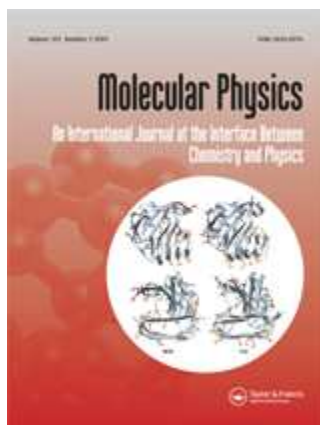
HAL Id: hal-00595190

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Submitted on 24 May 2011

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The high resolution infrared spectrum of the ν_4 band of 1,1,1-trifluoro-ethane

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2010-0019.R1
Manuscript Type:	Special Issue Paper -2 HRMS Stabia 09/ High Resolution Molecular Spectroscopy
Date Submitted by the Author:	17-Feb-2010
Complete List of Authors:	di Lonardo, Gianfranco; Università di Bologna, Dept. di Chimica Fisica e Inorganica Predoi-Cross, Adriana; University of Lethbridge, Department of Physics and Astronomy Herman, Michel; Université Libre de Bruxelles, Chimie quantique et Photophysique Nivellini, GianDomenico; Università di Bologna, Dipartimento di Chimica Fisica e Inorganica Fusina, Luciano; Università degli Studi di Bologna, Dipartimento di Chimica Fisica e Inorganica Ibrahim, Amr; University of Lethbridge, Department of Physics and Astronomy
Keywords:	CH ₃ CF ₃ , 1,1,1- trifluoroethane , high resolution, infrared spectrum, ν_4 fundamental



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4 **The high resolution infrared spectrum of the ν_4 band of 1,1,1- trifluoro –**
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31
32
33 Number of pages : 10
34

35 Number of figures : 3
36

37 Number of tables : 2
38
39
40
41

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10 Abstract

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12 The ν_4 band of 1,1,1- trifluoroethane (CH_3CF_3) has been studied using synchrotron radiation
13 at the far-infrared beamline, Canadian Light Source. The spectra were recorded at a
14 resolution of 0.00096 cm^{-1} in the spectral range 800 to 860 cm^{-1} using a Bruker IFS125 FT
15 spectrometer. Altogether 2785 lines were assigned to ${}^qP_K(J)$ and ${}^qR_K(J)$ transitions with J'' up
16 to 71 and K up to 45. The ${}^qQ_K(J)$ sub-branches are too congested and overlapped to other
17 hot-band Q branches to be analyzed. A Watson-type Hamiltonian containing the usual terms
18 up to the 6th power in the angular momentum operators was used in the analysis. The
19 spectroscopic parameters obtained from the fit reproduce 2636 transitions with a standard
20 deviation of about 0.00016 cm^{-1} .
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1. Introduction

The 1,1,1- trifluoro – ethane, CH_3CF_3 , has been the subject of several spectroscopic investigations [1-7]. It attracted the interest of spectroscopists because of the presence of torsional splitting in the ground and excited vibrational states. Besides, the low energy torsional motion affects the whole infrared spectrum allowing the observation of many hot bands involving vibrationally excited torsional states. This molecule (HFC-143a) is also interesting from the environmental point of view since it could replace HCFC-22 (CHClF_2), eventually in mixture with other less flammable HFC [1]. The microwave and millimeter-wave rotational spectra in the ground and excited torsional states up to $\nu_6 = 3$ have been reported in the literature [2-4]. The high resolution infrared spectra of several fundamental and combination bands have been recorded and analyzed. In 1993 Fraser *et al.* [5] studied the molecular-beam spectrum of the Fermi triad $2\nu_6 + \nu_{11}$, $\nu_5 + \nu_{12}$ and ν_{10} located near 970 cm^{-1} . The ν_2 and ν_8 fundamentals and the combination bands $\nu_4 + \nu_5$ and $\nu_6 + \nu_9$ were analyzed by Duxbury *et al.* [6]. Later, Wang *et al.* [4] studied the high resolution infrared spectrum of the first overtone of the ν_6 at 423 cm^{-1} together with the millimeter-wave rotational spectra in the four lowest torsional states. Wang *et al.* [7] also recorded and analyzed the ν_5 band together with the $(\nu_5 + \nu_6) - \nu_6$ hot band. In this paper we report the analysis of the high resolution infrared spectrum of the ν_4 fundamental band, namely the C-C stretching, centred at 831 cm^{-1} , recorded using synchrotron radiation. This band was already reported by Nivellini *et al.* [8] at a resolution of 0.004 cm^{-1} , but no K structure was observed (see figure 7 in Ref. 8). It was obvious that a detailed information could have been obtained only using a high resolution spectrometer equipped with a very brilliant source. These experimental conditions can only be fulfilled by a synchrotron radiation facility equipped with a very high resolution infrared spectrometer.

2. Experimental

For this study we have recorded four absorption spectra at an unapodized resolution of 0.00096 cm^{-1} in the $510 - 1000\text{ cm}^{-1}$ spectral range using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Lightsource. A summary of the experimental conditions for each spectrum is given in Table 1. All the 1,1,1-trifluoroethane, CH_3CF_3 , spectra were recorded using a multipass coolable absorption cell with a 2 m base length. Figure 1 shows an overview of the vibrational band of interest. The cell was equipped with wedged KBr windows. The radiation generated by either the synchrotron source (SR) or an infrared globar (GB) was detected using a Ge:Cu detector fitted with a cold filter. The diameter of the iris was 1.15 mm. A 5 kHz electronic filter was used in the experiments. The CH_3CF_3 sample of 98% purity was supplied by the Cambridge Isotope Laboratories and was used without further purification. Besides the CH_3CF_3 lines, a few lines belonging to residual water vapour present in the evacuated spectrometer were identified in the spectra. The gas sample temperature and pressure were monitored continuously during the data recording. A T-type thermocouple mounted inside the cell was used to monitor the gas sample temperatures. The gas pressures ranged between 85 to 301 mTorr and were measured using a 0–1 Torr capacitance gauge (Baratron). The calibration of the wavenumber scale of each spectrum was performed relative to well determined positions of the ν_2 band carbon dioxide lines [9]. These lines appeared in the spectra due to residual amounts of carbon dioxide in the evacuated spectrometer tank. **The gain in S/N by adopting a SR instead of a GB source can be demonstrated by comparing spectra 3 and 4 (see Table 1). In fact, an increase of at least a factor of four in the S/N can be observed in the spectrum recorded with the SR source as shown in Figure 2.**

3. Description of the spectrum and analysis

The CH_3CF_3 molecule is a prolate symmetric top close to the spherical limit, $\gamma = (A - B) / \frac{1}{2}(A + B) = 0.06$. The $\nu_4 = 1$ state (C-C stretching) is of A_1 symmetry. As a consequence, the ν_4 band appears as a well behaved parallel band of medium-weak intensity, with a strong Q branch centred at about 830 cm^{-1} and a series of ${}^qP_K(J)$ branches in the lower wavenumber side, and the corresponding ${}^qR_K(J)$ branches in the higher wavenumber side, as can be seen in Figure 1. The P and R branches appear as a comb structure with a separation between successive J of about 0.345 cm^{-1} ($2B$) and could be analyzed up to $J'' = 69$ in the R side and up to $J'' = 71$ in the P side. Because of the small size ($0.0005726 \text{ cm}^{-1}$) and of the positive sign of the difference $[(A' - A'') - (B' - B'')]$ the K structure of all the R and P branches appears very congested and blue degraded. In fact, up to ${}^qP_K(12)$ on the low energy side, and up to ${}^qR_K(13)$ on the high energy one, the K structure cannot be resolved at all. Even at high J values, $K = 12$ is usually the lowest K resolved transition, and below $K = 9$ the branch generally appears as a strong unresolved band feature. For the same reason the central Q branch appears completely unresolved and overlapped with other Q branches belonging to many hot bands appearing in the spectrum. The only characteristic feature in this branch is the very sharp edge on the high wavenumber side at 831.177 cm^{-1} which denotes the band origin. Starting from this point, by measuring the average spacing between the qR branches, a tentative assignment of the J numbering of the ${}^qR_K(J)$ branches was attempted. Because of the presence of two groups of three identical fermions in the molecule an intensity alternation can be seen in the K structure of branches. The transitions with $K = 3n$ with $n = 0, 1, 2, \dots$ have twice the intensity of those with $K \neq 3n$ owing to the statistical weight of the corresponding K levels. Figure 3 illustrates the ${}^qR_K(46)$ in the region $846.70\text{-}846.83 \text{ cm}^{-1}$ where the intensity alternation is evident. Since K cannot be larger than J and because of the blue degradation of the branches, the line at higher wavenumber in a qR branch is the one with $J'' = K''$, which is a

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3 strong line when $J'' = 3n$. In this way we were able to confirm the J numbering of the qR
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5 branch and assign the K structure. The J numbering was performed analogously in the ${}^qP_K(J)$
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7 region, but with less confidence for the first few J values because of the strong overlap with
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9 the qQ branches. In order to assist the assignments, the method of the ground state
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11 combination differences (GSCD) was adopted. Satellites branches accompany each P , Q and
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13 R branch of the ν_4 fundamental band. They arise from hot bands involving the first few
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15 vibrational states ν_6 , ν_{12} and $2\nu_6$ with origin at 223, 366 and 423.15 cm^{-1} , respectively [4,8].
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18 The large majority of the assignments were made in spectrum 4, (see Table 1) with a few
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20 exceptions for high J high K values where the spectrum 2 was used.
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25 Spectroscopic parameters for the ground state were already reported by Wang *et al.*
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27 [4, 7] in studies of the microwave and millimeter-wave rotational spectrum in the ground and
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29 in excited torsional states up to $\nu_6=4$ adopting an effective torsional-rotational Hamiltonian.
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32 No torsional splitting was ever observed in the ν_4 band and a torsional splitting of the
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34 order of 0.01 MHz was reported in the distortion moment-allowed Q branch transitions in the
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36 pure rotational spectrum [3]. The spectroscopic parameters for the ground state could thus be
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38 determined, by neglecting the splitting, from the fit of all the data available in the literature.
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40 The usual Hamiltonian for a prolate symmetric top with terms up to the 6th power in J , K was
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42 adopted. In addition, the $\Delta k = \pm 3$ interaction terms leading to the $K=3$ split transitions
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44 observed in the forbidden rotational Q branches [3] and, in a few cases, in the millimeter-
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46 wave spectrum at very high values of J [2] was taken into account.
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51 The diagonal matrix elements for a prolate rotor, including terms up to the sixth
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53 power in the angular momentum, are given by
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$$56$$

$$57 E(J,k)/hc = B [J(J+1) - k^2] + Ak^2 - D_J [J(J+1)]^2 - D_{JK} [J(J+1)]k^2 - D_K k^4 +$$

$$58$$

$$59 H_J [J(J+1)]^3 + H_{JK} [J(J+1)]^2 k^2 + H_{KJ} [J(J+1)]k^4 + H_K k^6, \quad (1)$$

$$60$$

and off-diagonal elements by

$$\langle J, k | H/hc | J, k \pm 3 \rangle = \{ [\varepsilon + \varepsilon_J J(J+1)](2k \pm 3) + \varepsilon_K[k^3 + (k \pm 3)^3] \} F_{\pm 3}(J, k),$$

(2)

where $F_{\pm 3}(J, k) = \{ [J(J+1)] - (k(k \pm 1)) [J(J+1) - (k \pm 1)(k \pm 2)] [J(J+1) - (k \pm 2)(k \pm 3)] \}^{1/2}$

and the signed quantum number $k = \pm K$.

The data in Table 2 of Ref. [2] were treated according to the suggestions of Ozier [3]. It was also decided not to consider the GSCD obtained from the data of the ν_4 band presently analyzed, since their accuracy is of the order of 5 MHz while that of microwave and millimetre-wave measurements is 0.2 MHz, in the worst case. The spectroscopic parameters for the vibrational ground state obtained from the fit are reported in column 2 of Table 2. They are in good agreement with those obtained taking into account the torsional splitting [7].

After completing the analysis of the ${}^qP_K(J)$ branches, all the ν_4 transitions were fitted using for the $\nu_4 = 1$ state the same Hamiltonian adopted for the ground state. Columns 3 and 4 in Table 2 list the spectroscopic parameters obtained from transition wavenumbers whose corresponding observed - calculated values do not exceed a chosen limit set to 0.0002 (fit I) and 0.0004 cm^{-1} (fit II), respectively. In the former case 694 out of 2785 fitted transitions (about 25%) exceeded the rejection limit and the obtained standard deviation of the fit was 0.00010 cm^{-1} . When a tolerance of 0.0004 cm^{-1} was adopted only 150 data (about 5%) were discarded but the standard deviation raised to 0.00016 cm^{-1} . It should be pointed out that the discarded transitions do not follow any specific trend but are scattered over all the assigned J and K values. Generally, in a spectrum taken at a resolution of 0.001 cm^{-1} with a $S/N \geq 50$ one would expect, with a well behaved Hamiltonian, to fit the large majority of the transitions

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3 ($\geq 90\%$) with a limit for rejection of 0.0001 cm^{-1} , obtaining a standard deviation of the fit of
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5 the order of $0.00006\text{-}0.00009 \text{ cm}^{-1}$ (*i.e.* 2-3 MHz). If this is not the case, **as in the present**
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7 **analysis**, it means that either in the Hamiltonian some important interaction terms are not
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9 considered or in the spectrum most of the transitions are overlapped, or both. The refinement
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11 of higher order coefficients (L_K and P_K) which could effectively account for the effect of
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13 perturbations, due to anharmonic or Coriolis interactions, did not improve significantly the
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15 quality of the fit. In fact, by adopting a rejection limit of 0.0002 cm^{-1} , the number of fitted
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17 transitions increased from 2091 to 2256 and the standard deviation of the fit remained almost
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19 unchanged. Moreover, the additional 165 transitions which were retained in the fit are
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21 randomly distributed over all J and K quantum numbers. This observation suggests that the
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23 high density of the lines, which leads to a large number of overlapping features in the spectra,
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25 is responsible of the quality of the fit. Although perturbations cannot be excluded a priori,
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27 they should be extremely small. All the diagonal parameters for the $v_4 = 1$ state have been
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29 determined, with the exception of H_{JK} which has been set equal to the corresponding value of
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31 the ground state. Also the $\Delta k = \pm 3$ interaction constants, ε and ε_J , have been fixed to the
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33 corresponding ground state values, since no $K = 3$ transition has been identified in the
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35 spectrum due to the congestion of the low K lines.
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44 The spectroscopic parameters in columns 3 and 4 of Table 2 are very similar, most of
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46 their values being within 3σ or less. Moreover, their values are close to the corresponding
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48 ones in the ground state, further supporting the hypothesis that the $v_4 = 1$ state is practically
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50 unperturbed. All line wavenumbers from the ro-vibrational analyses can be made available
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52 from the Bologna author.
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4. Conclusions

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3 The $\nu_4 = 1$ vibrational state (C-C stretching) of CH_3CF_3 has been spectroscopically
4 characterized through the observation and the analysis of the $\nu_4 - \text{GS}$ band at 831 cm^{-1} . An
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6 improved set of ground state spectroscopic parameters, however neglecting torsional
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8 splitting, was obtained from the analysis of all the data available in the literature. Two sets of
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10 spectroscopic parameters for the excited state have been evaluated. They differ for the chosen
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12 rejection limit (0.0002 or 0.0004 cm^{-1}), for the number of data excluded in the final fit (694 or
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14 150), leading to a standard deviation of the fit of 0.00010 and 0.00016 cm^{-1} , respectively.
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27 Acknowledgments

28
29 L.Fusina, G.Nivellini and G. Di Lonardo acknowledge the Università di Bologna and the
30
31 Ministero della Ricerca e dell'Università (PRIN "Trasferimento di energia e di carica: dalle
32
33 collisioni ai processi dissipativi") for financial support. A. Predoi-Cross acknowledges the
34
35 support she received from the National Sciences and Engineering Research Council of
36
37 Canada. In Brussels this work was supported by the Fonds National de la Recherche
38
39 Scientifique (F.R.S.-FNRS, contracts FRFC and IISN) and the « Action de Recherches
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41 Concertées de la Communauté française de Belgique ».
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Table captions

Table 1. Summary of experimental conditions of CH₃CF₃ spectra.

Table 2. Spectroscopic parameters (in cm⁻¹) for the ground state and the $\nu_4 = 1$ state of CH₃CF₃.

Figure captions

Figure 1.

The infrared spectrum of CH₃CF₃ in the region between 800 and 860 cm⁻¹ showing the ν_4 fundamental band centered at 831 cm⁻¹. The J numbering of the ${}^qP_K(J)$ and ${}^qR_K(J)$ branches is indicated. Experimental conditions, see Table 1, spectrum 4.

Figure 2 .

A portion of the CF₃CH₃ ν_4 band recorded at the far-infrared beamline using the (A) global source and (B) the synchrotron. See Table 1, spectra 3 and 4, for more detailed experimental conditions.

Figure 3.

Section of the infrared spectrum of CH₃CF₃ in the region between 846.70 and 846.83 cm⁻¹ showing the K structure of the ${}^qR_K(46)$ branch. Experimental conditions, see Table 1, spectrum 4.

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Table 1. Summary of experimental conditions of CH₃CF₃ spectra.

	Source	Pressure (mTorr)	Temperature (K)	Pathlength (m)	Scanning speed (KHz)	Resolution (cm ⁻¹)	Optical Filter (cm ⁻¹)	Detector Filter (cm ⁻¹)	Detector Gain	No. Scans
1	SR ^a	85	298.25	24.15	40	0.00096	510-1000	490-1190	64	104
2	SR ^a	200	298.25	72.15	60	0.00096	510-1000	490-1190	64	142
3	GB ^b	200	298.45	24.15	40	0.00096	none	490-1190	64	350
4	SR ^a	301	216.75	24.15	40	0.00096	300-1250	300-1200	16	374

^a synchrotron source.

^b global source.

Table 2. Spectroscopic parameters (in cm^{-1}) for the ground state and the $\nu_4 = 1$ state of CH_3CF_3 .

	ground state	$\nu_4 = 1$ fit I ^a	$\nu_4 = 1$ fit II ^b
V_0	–	831.1769618 (191)	831.1769049 (147)
A	0.18342224765 (679)	0.1831688643 (668)	0.1831692008 (482)
B	0.172957554120 (378)	0.1726383363 (289)	0.1726383572 (217)
$D_J \times 10^9$	42.184614 (487)	42.2685 (130)	42.27015 (962)
$D_{JK} \times 10^9$	66.78631 (169)	66.8795 (194)	66.9199 (138)
$D_K \times 10^9$	-65.783 (114)	-65.6094 (688)	-65.3255 (485)
$H_J \times 10^{15}$	18.336 (682)	17.38 (162)	17.32 (119)
$H_{JK} \times 10^{15}$	-0.866 (282)	-0.866 ^c	-0.866 ^c
$H_{KJ} \times 10^{12}$	0.148304 (820)	0.1350 (115)	0.15254 (810)
$H_K \times 10^{12}$	2.480 (615)	2.3751 (234)	2.4458 (165)
$\mathcal{E} \times 10^9$	8.32004 (442)	8.32004 ^c	8.32004 ^c
$\mathcal{E}_J \times 10^{15}$	-14.782 (868)	-14.782 ^c	-14.782 ^c
total number of data	478	2785	2785
number of data retained in the fit	447	2635	2091
weighted standard deviation	$1.42 \times 10^{-7} \text{ cm}^{-1}$	$1.56 \times 10^{-4} \text{ cm}^{-1}$	$1.00 \times 10^{-4} \text{ cm}^{-1}$

a) Tolerance for rejection = 0.0004 cm^{-1} .

b) Tolerance for rejection = 0.0002 cm^{-1} .

c) Fixed to the ground state value.

