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Improved ground-state spectroscopic parameters of CH$_2$FI and assignment of the rotational spectrum of the v_6=1 state [1]

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Abstract

The rotational spectrum of fluoroiodomethane, CH$_2$FI, has been recorded in the 1.02-1.05 THz frequency range, allowing to extend the set of known spectroscopic parameters with respect to our previous work [*J. Chem. Phys.* **134**, 174312 (2011)]. In particular, three additional octic centrifugal-distortion constants and the K-dependence for all quadrupole-coupling constants have been determined. Furthermore, the rotational spectrum of the v_6=1 vibrational state has been recorded and assigned in the 171-184 and 534-536 GHz frequency ranges, spanning the quantum number J from 4 to 79. This allowed us to provide for the first time accurate rotational, quartic, sextic, and three octic centrifugal-distortion constants and the iodine hyperfine parameters.

Key words: fluoroiodomethane, rotational spectroscopy, THz frequency region, vibrational ground and ν_6 states

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1   Introduction

During the last decades, halogen-containing molecules have attracted a great deal of attention because of their connection with stratospheric ozone depletion and global warming [1]. However, reliable experimental data for many halocarbons are still unavailable, especially for those containing bromine and iodine. In particular, the investigation of iodine-containing asymmetric-top molecules using rotational spectroscopy has been hampered for a long time because of the difficulties related to the large iodine quadrupole coupling (see, for instance, Refs. [2,3]). As for fluoroiodomethane, CH_2FI, no spectroscopic study has been reported in the literature prior to our recent investigation of the vibrational ground state [2]. [2]

In Ref. [2], guided by theoretical predictions, the rotational spectrum of fluoroiodomethane has been investigated for the first time in the centimeter-, millimeter- and submillimeter-wave frequency regions leading to accurate values for the ground-state rotational constants, all quartic, sextic and two octic centrifugal-distortion constants. Furthermore, the hyperfine structure of the rotational spectrum has been resolved, thus allowing the accurate determination of the complete iodine quadrupole-coupling tensor and of the diagonal elements of the iodine spin-rotation tensor. In the present work, the investigation of the rotational spectrum of the vibrational ground state has been extended up to the THz frequency region thus enabling the determination of an increased set of spectroscopic parameters. Furthermore, in the present study the pure rotational spectrum of the lowest vibrational state ($v_6 = 1$ at ~ 270 cm^{-1} [4]) has been recorded and assigned in the millimeter-/submillimeter-wave regions, spanning the quantum numbers $4 \leq J \leq 79$, $0 \leq K_a \leq 12$ and $2 \leq K_c \leq 77$. A set of spectroscopic parameters up to octic centrifugal-distortion constants, also including the iodine hyperfine parameters, has been determined to a good accuracy.

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[2] As noted in Ref. [2], there was a brief mention of some spectroscopic work on CH_2FI by Sheridan in a conference proceedings [J. Sheridan, *Pure and Applied Chemistry* **11**, 455 (1965)], but no spectroscopic analysis and parameters were published.

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2 Experiment

2.1 Synthesis

Fluoroiodomethane was synthesized by Hunsdiecker chemistry through the precipitation reaction of sodium monofluoroacetate with silver nitrate followed by decarboxylation reaction of the produced silver monofluoroacetate with iodine as detailed in Ref. [2].

2.2 Experimental details

For the $v_6 = 1$ state, the rotational spectrum was recorded in the 171-184 and 534-536 GHz frequency ranges. As a complete account of the measurements carried out for this species in the millimeter-/submillimeter-wave frequency regions can be found in Ref. [2], we refer interested readers to that reference for any information concerning the spectrometer and technique employed. For the vibrational ground state, in the present study THz measurements were performed in the 1.02-1.05 THz frequency range. While a description of our THz spectrometer can be found in Refs. [5,6], we briefly recall that the THz frequency source, phase-locked to a Rubidium frequency standard, is actually a tripler followed by another tripler (RPG GmbH), whose total radiation power ranges from 10 to 40 μW. To improve the Signal-to-Noise ratio, the frequency-modulation technique (with second harmonic detection) was employed, which was obtained by sine-wave modulating at 333 Hz the 80 MHz local oscillator of the synchronization loop. A liquid He-cooled Ge bolometer was employed as a detector. Measurements were performed at room temperature, employing gas pressures in the range 4-10 mTorr and 50-100 mTorr in the millimeter-/submillimeter-wave and THz frequency regions, respectively. The modulation depth was varied in the range 300-400 kHz for the former measurements and 1.8-2.7 MHz for the latter.

As already noted in Ref. [2], the resulting spectra show characteristic ΔJ=0, ΔK_a=+1, ΔK_c=-1 bands, denoted in the following as ^bQ bands, which are those mostly recorded. In addition, some ΔJ=+1, ΔK_a=+1, ΔK_c=+1 (b-type; ^bR), ΔJ=-1, ΔK_a=+1, ΔK_c=+1,-3 (b-type; ^bP), and ΔJ=+1, ΔK_a=0, ΔK_c=+1 (a-type; ^aR) transitions were also observed and assigned. Figure 1 provides an example of the THz measurements carried out; in particular, it shows one of the three ^bQ recorded bands, that with $K_a = 14$. Figure 2 shows the entire portion of spectrum recorded and assigned for the $v_6 = 1$ state in the millimeter-wave region. Transitions belonging to the vibrational ground state are also evident: as expected from the energy difference between the

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two states, they are ∼4 times more intense. Both figures 1 and 2 are example of the crowding that can take place in the recorded rotational spectra: the zooms in the insets make it evident. As usual, the assignment of such spectra was accomplished in iterative manner, supported by the use of graphical assignment techniques. In detail, the AABS package for Assignment and Analysis of Broadband Spectra [7–9] was employed, which allows direct graphical comparison of the spectrum with the prediction.

3   Results and discussion

For the ground state, the new recording in the THz region led to assignment of 321 additional distinct frequency lines (for a total of 1146 distinct frequencies). For the $v_6 = 1$ vibrational state, the recorded portions of spectrum led to assignment of a total of 685 distinct frequency lines. The corresponding transition frequencies have an estimated accuracy of 50 kHz and 25 kHz for the THz and millimeter-/submillimeter-wave measurements, respectively. Transitions for which the corresponding residuals exceed the applied cutoff criterion of 3.5 times the measurement error were excluded from fits. The latter are nonlinear least-squares fitting procedures in which each assigned transition is weighted proportionally to the inverse square of its experimental uncertainty and were carried with the SPFIT program of Pickett [10,11]. Watson's A-reduced Hamiltonian in the I^r representation [12] was employed. The results are reported in Table 1; for the vibrational ground state, those from our previous work are also given. From the comparison we note that, as expected, the present fit does not allow any improvement for the spectroscopic constants already determined in Ref. [2], but the new measurements enabled the determination of three additional octic centrifugal-distortion constants and the K-dependence for all quadrupole-coupling constants. As concerns the $v_6 = 1$ vibrational state, the assigned rotational transitions allowed us to determine, in addition to the rotational constants, all quartic, all sextic, and three octic centrifugal-distortion constants. One may notice that the spectroscopic parameters were derived with an accuracy comparable to that reached for the ground state: in the worst cases the difference in accuracy is largely smaller than one order of magnitude. Furthermore, we note that the rotational and centrifugal-distortion parameters obtained for the $v_6 = 1$ state are close to their ground-state counterparts, thus indicating that this vibrational excited state is essentially unperturbed. Concerning iodine hyperfine parameters, it was possible to determine the full quadrupole-coupling tensor as well as the J dependence of the diagonal elements. The diagonal elements of the iodine spin-rotation tensor were obtained as well. As sub-Doppler measurements were not carried out (as in Ref. [2]), the hyperfine parameters of the ν_6 state were obtained with uncertainties of 1-2 orders of magnitude larger than those for

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the vibrational ground state. As also noted for the rotational and centrifugal-distortion constants, the hyperfine parameters of the ν_6 are similar to those of the ground state.

The present results allow to complete the picture concerning how the rotational constants for the vibrational ground and lowest-lying states of difluoromethane, CH_2F_2, change by replacing one fluorine with another halogen. The vibrational mode of interest is the CFX scissoring motion which is labeled as ν_4 in CH_2F_2. Moving to the CH_2FX species, with X = Cl, Br and I, the symmetry point group changes from C_{2v} to C_s, thus leading to the ν_6 labeling for the CFX scissor. The comparison is summarized in Table 2; from this table it is noted that for all molecules when going from the ground to the excited state the A constant increases, while B and C decrease. The extent of such variations decreases a little from F to I; in fact, ΔA varies from 0.7% for CH_2F_2 to less than 0.5% for CH_2FI, ΔB from -0.2% to -0.07%, and ΔC from -0.4% to -0.15%.

4 Conclusion

In the present work a spectroscopic investigation of CH_2FI has been carried out: the rotational spectra of the ground and $v_6 = 1$ states have been observed by means of THz spectroscopy for the former and by millimeter-/submillimeter-wave spectroscopy for the latter. Concerning the vibrational ground state, this study provides an enlargement of the set of the spectroscopic constants available in the literature, with the determination of three additional octic centrifugal-distortion constants and the K-dependence for all quadrupole-coupling constants. With respect to the vibrational $v_6 = 1$ excited state, a set of spectroscopic parameters up to octic distortion terms together with the relevant iodine hyperfine parameters have been accurately evaluated for the first time.

Complete results files and source files for the fitting program as well as the list of measured transition frequencies (for both ground and $v_6 = 1$ states) can be obtained by the authors upon request.

5 Acknowledgments

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Captions of the Tables

Table 1. Ground state and $v_6{=}1$ spectroscopic parameters of CH_2FI.

Table 2. Rotational constants of the vibrational ground and lowest-lying states for the CH_2FX series, with X=F,Cl,Br and I.

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Captions of the Figures

Figure 1. The complete recording of the ^bQ band with $K_a = 14$ at 1.03 THz.

Figure 2. The complete recording carried out for the $v_6 = 1$ state in the millimeter-wave region: among a few transitions belonging to the vibrational ground state and a number of ^aR, ^bP, and ^bR lines of ν_6, the ^bQ band with $K_a = 2$ is evident.

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Table 1
Ground state and v_6=1 spectroscopic parameters of CH$_2$FI.

Parameter		Ground state		v_6=1 state
		Ref. [2]	This work	
A_0	(MHz)	38418.85846(14)	38418.85975(11)	38597.27108(68)
B_0	(MHz)	2875.248173(42)	2875.248265(35)	2871.90013(17)
C_0	(MHz)	2721.043224(41)	2721.043299(34)	2716.63028(16)
Δ_J	(kHz)	1.135127(31)	1.135201(21)	1.13945(12)
Δ_{JK}	(kHz)	-20.73612(20)	-20.73474(17)	-20.83488(82)
Δ_K	(kHz)	557.2573(47)	557.3208(29)	575.235(41)
δ_J	(kHz)	0.0956780(16)	0.0956836(29)	0.0966497(55)
δ_K	(kHz)	5.9673(15)	5.9675(12)	6.5088(29)
Φ_J	(Hz)	0.0004040(88)	0.0004295(40)	0.000685(33)
Φ_{JK}	(Hz)	0.01684(93)	0.01665(58)	0.0189(20)
Φ_{KJ}	(Hz)	-1.8337(47)	-1.8077(31)	-1.994(23)
Φ_K	(Hz)	29.778(28)	30.526(14)	30.59(43)
ϕ_J	(Hz)	0.00012432(62)	0.00012622(97)	0.0001226(17)
ϕ_{JK}	(Hz)	0.00593(67)	0.00619(50)	0.0060(20)
ϕ_K	(Hz)	2.52(30)	2.35(17)	3.19(66)
L_J	(mHz)	0.00000296(75)	0.00000033(19)	-0.0000301(28)
L_{JK}	(mHz)	–	-0.00419(15)	
L_{KKJ}	(mHz)	0.220(10)	0.1697(51)	1.33(20)
L_K	(mHz)	–	-2.553(32)	
l_J	(mHz)	–	-0.000000192(52)	
$1.5\chi_{aa}$	(MHz)	-2372.4213(40)	-2372.4210(47)	-2375.42(12)
$(\chi_{bb}\text{-}\chi_{cc})/4$	(MHz)	-103.3207(13)	-103.3490(53)	-103.163(24)
$|\chi_{ab}|$	(MHz)	857.209(70)	857.216(51)	850.89(24)
$1.5\chi_{aa}^{J}$ [a]	(kHz)	-2.166(43)	-2.186(50)	-2.82(38)
$1.5\chi_{aa}^{K}$ [b]	(kHz)	6.65(62)	12.94(74)	
$(\chi_{bb}\text{-}\chi_{cc})^{J}/4$ [a]	(kHz)	0.2338(28)	0.2326(32)	0.249(10)
$(\chi_{bb}\text{-}\chi_{cc})^{K}/4$ [b]	(kHz)	–	27.3(50)	
$|\chi_{ab}|^{J}$ [a]	(kHz)	0.69(14)	1.285(52)	
$|\chi_{ab}|^{K}$ [b]	(kHz)	–	-77.0(31)	
C_{aa}	(kHz)	18.25(33)	18.82(39)	21.4(19)
C_{bb}	(kHz)	7.087(79)	7.146(91)	9.0(13)
C_{cc}	(kHz)	10.644(70)	10.673(80)	12.4(13)
RMS error[c]	(kHz)	19.6	35.7	24.67
$\overline{\chi^2}$ [d]		0.90	1.08	0.99

[a] J dependence of nuclear quadrupole-coupling constants.

[b] K dependence of nuclear quadrupole-coupling constants.

[c] Standard deviation of the fit.

[d] Dimensionless (weighted) standard deviation.

Table 2

Rotational constants of the vibrational ground and lowest-lying states for the CH_2FX series, with X=F,Cl,Br and I.

	CH_2F_2	$CH_2{}^{35}ClF$	$CH_2{}^{79}BrF$	CH_2FI
Ground state				
A_0 (MHz)	49142.82[a]	41811.22[b]	39852.97[c]	38418.86[d]
B_0 (MHz)	10604.71[a]	5715.98[b]	3772.96[c]	2874.25[d]
C_0 (MHz)	9249.84[a]	5194.89[b]	3523.95[c]	2721.04[d]
Vibrational state	$v_4=1$	$v_6=1$	$v_6=1$	$v_6=1$
Frequency (cm^{-1})	528.[e]	384.[f]	311.[g]	$\sim$270.[h]
A (MHz)	49480.53[e]	42059.58[b]	40053.30[c]	38597.28[d]
B (MHz)	10582.94[e]	5708.45[b]	3767.94[c]	2871.90[d]
C (MHz)	9216.50[e]	5182.99[b]	3517.27[c]	2716.63[d]

[a] Ref. [13].

[b] Ref. [14].

[c] Ref. [15].

[d] This work.

[e] Ref. [16].

[f] Ref. [17].

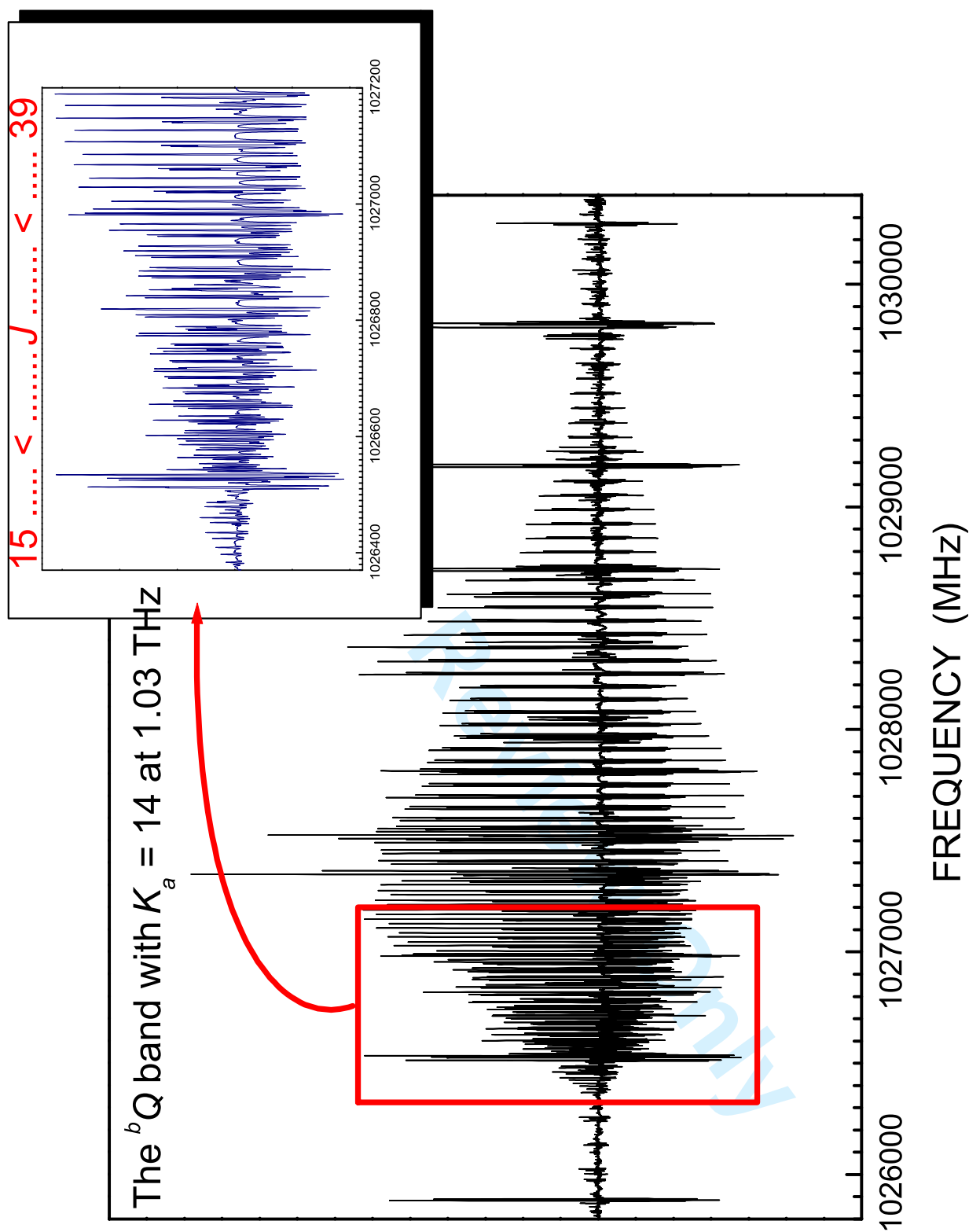[g] Ref. [18].

[h] Ref. [4].

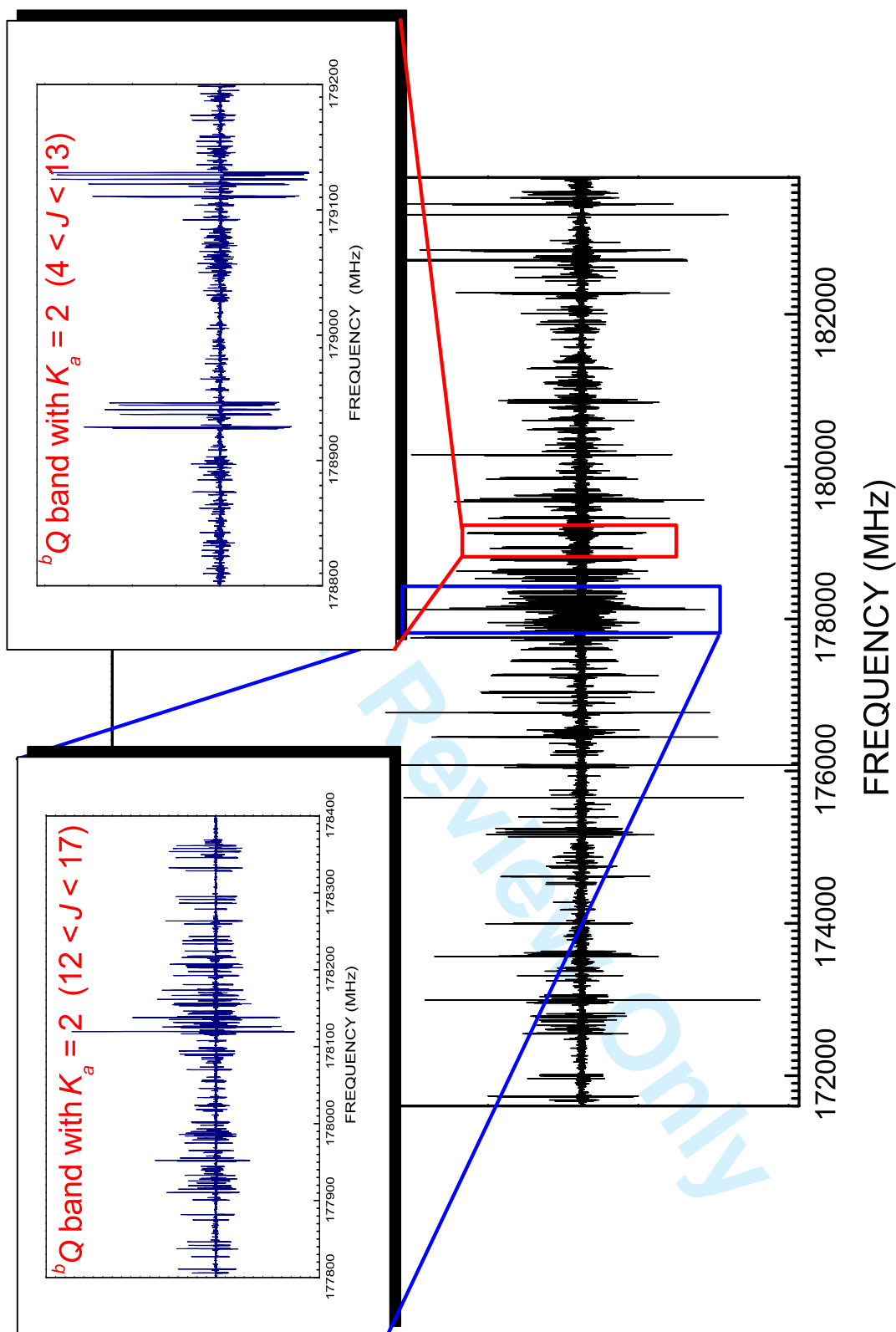Fig. 1. The complete recording of the ${}^bQ$ band with $K_a = 14$ at 1.03 THz.

Fig. 2. The complete recording carried out for the $v_6 = 1$ state in the millimeter-wave region: among a few transitions belonging to the vibrational ground state and a number of ^aR, ^bP, and ^bR lines of ν_6, the ^bQ band with $K_a = 2$ is evident.