March, 1981] *Bull. Chem. Soc. Jpn.*, *54*, *897—900 (1981)*

Measurement and Analysis of the ν_4 Band of Fluoroform and Its Molecular Constants

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(Received August 30, 1980)

The ν_4 fundamental of fluoroform has been measured with a tunable diode-laser source spectrometer. The following molecular constants were determined: $\nu_0=1377.8458\ \mathrm{cm}^{-1}$, $B_4=0.344788\ \mathrm{cm}^{-1}$, $C_4=0.189134\ \mathrm{cm}^{-1}$ $(C\zeta)_4=0.18619\ \mathrm{cm}^{-1}$, $D_4^J=3.78\times10^{-7}\ \mathrm{cm}^{-1}$, $D_4^{JK}=-5.73\times10^{-7}\ \mathrm{cm}^{-1}$, $D_4^K=2.94\times10^{-7}\ \mathrm{cm}^{-1}$, $\eta_4^J=1.44\times10^{-6}\ \mathrm{cm}^{-1}$, and $\eta_4^K=-8.2\times10^{-7}\ \mathrm{cm}^{-1}$. Using the molecular constants of the $2\nu_3$, the Coriolis x-y interaction constant between the ν_4 fundamental and $2\nu_3$, $|\zeta_{334}|$, was estimated to be 0.065.

Although fluoroform is one of the most simple molecules belonging to the point group C_{3v}, only a few studies of its rotation-vibration spectra have been reported.$^{1-4)}$ This is largely due to the deficiency in the resolving power of the spectrometers. Graner *et al.*$^{1)}$ have observed the infrared spectra for the ν_6 and ν_3 fundamentals with an approximate resolution of 0.03 cm^{-1}. As for the ν_4 fundamental, the observations have been done under rather poor resolution. The molecular constants have been obtained from the analyses of the heads of the successive Q's in these works,$^{2-4)}$ because the resolving power was not quite enough to resolve the successive Q branches into their fine structures. The present report concerns itself with the measurement of the rotation-vibration spectra for the ν_4 fundamental of fluoroform by the use of a tunable diode laser-source spectrometer and with the analysis of the rotation-vibration spectra.

Experimental

The sample used in this study was a commercial product and was used without further purification. The survey spectrum of the ν_4 band of fluoroform was recorded from 1350 to 1410 cm^{-1} using a Nicolet 7199A Fourier transform infrared spectrometer at a resolution of 0.06 cm^{-1}. The observation was made at room temperature using a 10 cm gas cell. The sample pressure was about 9 Torr.

The high resolution spectra were recorded from 1361 to 1385 cm^{-1} by the use of a tunable diode laser-source spectrometer (Laser Analytics, model LS 3). The sample pressure was 0.5—1.5 Torr. As the resolution of the instrument was estimated to be 10^{-4}—10^{-3} cm^{-1}, the line-width of the observed spectrum was governed by the Doppler broadening. About ten modes could be oscillated in the region cited above. In order to determine an accurate frequency value, the wavelengths of a few lines for each mode were measured by the use of a Michelson interferometer-type wavelength meter which was designed and constructed by Nagai *et al.*$^{5)}$ The wavelengths of the other lines were determined relative to these frequencies by observing the interference fringes arising from a confocal germanium etalon. The free spectral range was calibrated to be 0.009929± 0.000008 cm^{-1} by the use of the OCS lines in the 870 cm^{-1} region. The precision of the wavelength measurement was about 0.0015 cm^{-1}. The accuracy of the wavelength measurement was restricted by the incomplete alignment of the reference He–Ne laser beam in parallel with the diode laser source.$^{5)}$ It is believed to be better than 0.001 cm^{-1}.

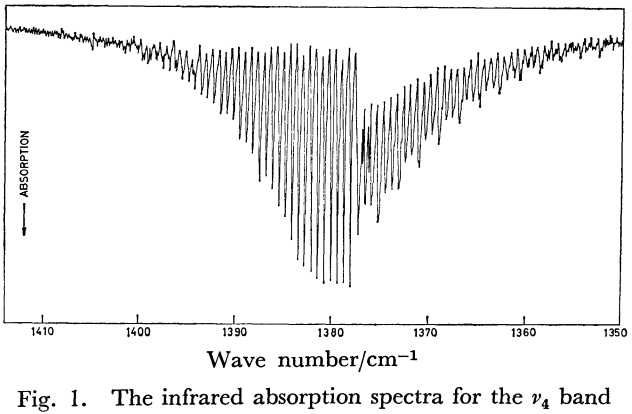

Fig. 1. The infrared absorption spectra for the ν_4 band of fluoroform recorded by the Fourier transform spectrometer.

Results and Discussion

Observed Spectra. The spectra for the ν_4 band recorded by the Fourier transform spectrometer is shown in Fig. 1. We can see the usual intensity alternation due to the three-fold symmetry for the sub-bands on the low frequency side (the 1377—1350 cm^{-1} region). These sub-bands may therefore be assigned to the successive ^{R}Q lines. In the high frequency region (the 1377—1400 cm^{-1} region), on the other hand, we cannot recognize any clear intensity alternations. This happens because these sub-bands on the high frequency side are mainly composed from

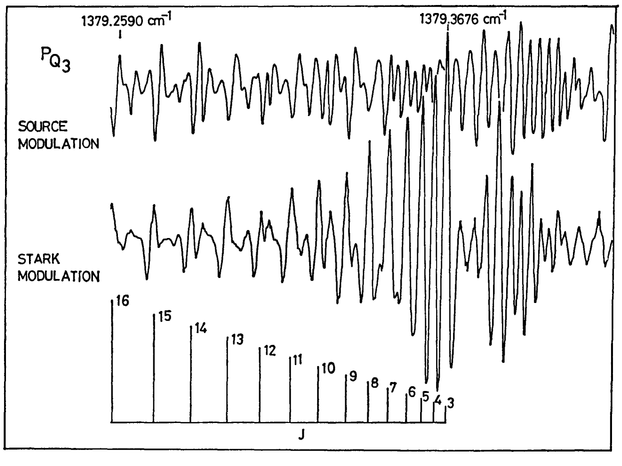

Fig. 2. The high resolution spectra observed by the diode laser-source spectrometer (upper: source modulation, lower: Stark modulation).

the ^RR lines instead of ^PQ lines. The ^PQ lines form only a background of the high frequency side.

Figure 2 shows the part of the high resolution spectra observed by the diode laser-source spectrometer which may be assigned to the $^PQ_3$ line series. The upper spectra were recorded by modulating the source diode by a sine wave of 5 kHz and detecting the absorption signal at 10 kHz by the use of a phase-sensitive detection method. The lower spectra were recorded by the use of the usual Stark modulation method. The modulation frequency and the electric field were 100 kHz and 200 V_{p-p}/cm (being superposed on the 200 V/cm DC field), respectively. The lower spectra were used for the J-number assignment.

The observed frequency values are summarized in Table 2, together with the assignments.

Assignment of the Observed Spectra. First, we calculated the synthetic spectra corresponding to the ν_4 fundamental by using the approximate molecular constants given in the references.[1,4)] The spectral simulation showed that a group of lines having the same K value forms a localized sub-band, ^PQ or ^RQ, and that a group of lines having the same $(J-K)$ value form a localized sub-band, ^PP or ^RR. The comparison between the observed and the calculated frequencies leads to the rigorous assignments of K and $(J-K)$ numbers to the sub-bands ^PQ, ^RQ, ^PP, and ^RR. The sub-bands ^PP and ^RR can be identified from the sub-bands ^PQ and ^RQ, because the component lines of ^PP and ^RR show the intensity alternation due to the three-fold symmetry. The assignments of K numbers to the ^PQ and ^RQ sub-bands are confirmed by the low-resolution spectra of Fig. 1.

The assignment of J numbers to the component fine structure lines of each sub-bands can be done without ambiguity by using the Stark modulated spectra and the missing lines rule ($J \geq K$). As the apparent intensity of a Stark modulated spectrum is observed to be stronger for lower J, the lines of the smallest J number in a sub-band is easily found. Therefore, the J number is rigorously assigned to the individual component lines in consideration of the missing lines rule and the already determined K and $(J-K)$ values. In this way we could identify about 100 lines and make a rigorous assignment of J and K numbers. Using these lines, trial molecular constants were obtained by least-squares method; these in turn were used in the spectral simulation to make further assignments.

Determination of the Molecular Constants. The vibration-rotation energy of a symmetric top in an E-vibrational state can be written in the form (for $v_4=1$):

$$\begin{aligned}E(J,k,l) = {} & \nu_0 + (C_4-B_4)k^2 + B_4J(J+1) - 2(C\zeta)_4kl \\ & - D_4^JJ^2(J+1)^2 - D_4^{JK}J(J+1)k^2 \\ & - D_4^Kk^4 + \eta_4^JJ(J+1)kl + \eta_4^Kk^3l, \qquad (1)\end{aligned}$$

where ν_0 is the vibrational energy, C_4 and B_4 are the rotational constants, ζ is the Coriolis coupling constant, D_4^J, D_4^{JK}, and D_4^K are the centrifugal distortion constants, and η_4^J and η_4^K express the dependence of the Coriolis coupling on J and K.

Table 1. Molecular constants of the ν_4 band of CHF_3 (cm^{-1})

ν_0	1377.84576(33)	η_4^J	$1.436(35)\times10^{-6}$
B_4	0.3447884(12)	η_4^K	$-8.20(28)\times10^{-7}$
C_4	0.18913390(54)		Ground State
$(C\zeta)_4$	0.186195(10)	B_0	0.34520105(7)
D_4^J	$3.7774(85)\times10^{-7}$	C_0	0.18925(10)
D_4^{JK}	$-5.735(18)\times10^{-7}$	D_0^J	3.779×10^{-7}
D_4^K	$2.941(12)\times10^{-7}$	D_0^{JK}	$-6.0375(134)\times10^{-7}$
q_4	$-1.115(12)\times10^{-4}$	D_0^K	3.72×10^{-7}

Numbers in parentheses denote the standard deviation σ.

From the selection rules for a perpendicular band ($\Delta k=+1$, $\Delta l=+1$, and $\Delta J=0$, ±1; or $\Delta k=-1$, $\Delta l=-1$, and $\Delta J=0$, ±1), the transition frequencies can be calculated as the differences between the energy levels of the upper and lower states. The energy of the ground state can be given by this formula:

$$\begin{aligned}E(J,k) = {} & (C_0-B_0)k^2 + B_0J(J+1) \\ & - D_0^JJ^2(J+1)^2 - D_0^{JK}J(J+1)k^2 - D_0^Kk^4. \qquad (2)\end{aligned}$$

The B_0, D_0^J, D_0^{JK}, and C_0 values were obtained by the microwave studies[6,7)] and/or by the analysis of the infrared spectra.[3,4,8)] The D_0^K value was calculated from the harmonic force field.[7)] After fixing all these molecular constants related with the ground state, the molecular constants of the excited state were determined by the least-squares method. The constants thus obtained are listed in Table 1 together with the fixed ground state values. The observed frequencies are listed in Table 2 with their assignments and the calculated frequencies.

l-type Doubling. In the case of the ν_4 fundamental, the effect of the l-type resonance is not so drastic as was observed for the ν_6 fundamental.[1)] This is because the Coriolis coupling constant ζ_4 takes a positive value, which produces a repulsive effect on the interacting pair. As the precision of the frequency measurement exceeds the order of 10^{-3} cm^{-1}, it is possible to determine the l-type doubling constant, q_4. In our analysis, we take l-type resonace into account as well as l-type doubling.

The perturbed energies can be obtained from the diagonalization of a 2×2 matrix of this form:

$$\begin{bmatrix} E(K-1,\ l=-1) & W \\ W & E(K+1,\ l=+1) \end{bmatrix}, \qquad (3)$$

where K is the absolute value of k. The off-diagonal element, W, has this form:

$$W = -\frac{q_4}{2}[J(J+1)-K(K+1)]^{1/2}[J(J+1)-K(K-1)]^{1/2}. \qquad (4)$$

The explicit expression for the perturbed energy level can be written as

$$\begin{aligned}2E_\pm(J,K\pm1,\pm1) = {} & E(J,K-1,-1) + E(J,K+1,+1) \\ & \pm\{E[(J,K-1,-1)-E(J,K+1,1)]^2 \\ & +q_4^2[J(J+1)-K(K+1)][J(J+1) \\ & -K(K-1)]\}^{1/2}, \qquad (5)\end{aligned}$$

where E_+ and E_- correspond to the perturbed states of the upper and lower levels of the interacting pair, respectively. In order to determine the sign of q_4, the twelve lines which are definitely assigned to the

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES OF THE ν_4 BAND

Assignment[a) K (J)	Observed frequency (cm^{-1})	Obsd−Calcd (cm^{-1})
PQ 3 (3)	1379.3676	0.0011
PQ 3 (4)	1379.3637	0.0006
PQ 3 (5)	1379.3596	0.0006
PQ 3 (6)	1379.3547	0.0008
PQ 3 (7)	1379.3487	0.0006
PQ 3 (8)	1379.3421	0.0007
PQ 3 (9)	1379.3350	0.0012
PQ 3(10)	1379.3267	0.0012
PQ 3(11)	1379.3172	0.0010
PQ 3(12)	1379.3074	0.0012
PQ 3(13)	1379.2967	0.0014
PQ 3(14)	1379.2851	0.0015
PQ 3(15)	1379.2724	0.0014
PQ 3(16)	1379.2590	0.0014
PQ 3(17)	1379.2449	0.0015
PQ 3(18)	1379.2299	0.0015
PQ 3(19)	1379.2139	0.0014
PQ 3(20)	1379.1968	0.0011
PQ 3(21)	1379.1793	0.0011
PQ 3(22)	1379.1609	0.0011
PQ 3(23)	1379.1414	0.0008
PQ 3(24)	1379.1214	0.0009
PQ 3(25)	1379.1005	0.0009
PQ 3(26)	1379.0788	0.0009
PQ 3(27)	1379.0563	0.0009
PQ 3(28)	1379.0321	0.0001
PQ 3(29)	1379.0078	0.0000
PQ 3(30)	1378.9831	0.0003
PQ 3(31)	1378.9573	0.0004
PQ 3(32)	1378.9305	0.0002
PQ 3(33)	1378.9031	0.0003
PQ 3(34)	1378.8747	0.0003
PQ 3(35)	1378.8452	-0.0001
PQ 9(23)	1383.2575	0.0019
PQ 9(24)	1383.2357	0.0011
PQ 9(25)	1383.2142	0.0013
PQ 9(26)	1383.1922	0.0020
PQ 9(27)	1383.1682	0.0015
PQ 9(28)	1383.1436	0.0013
PQ 9(29)	1383.1182	0.0012
PQ 9(30)	1383.0922	0.0013
PQ 9(31)	1383.0655	0.0016
PQ 9(32)	1383.0379	0.0019
PQ 9(33)	1383.0088	0.0015
PQ 9(34)	1382.9794	0.0017
PQ 9(35)	1382.9489	0.0017
PQ 9(36)	1382.9181	0.0022
PQ 9(37)	1382.8871	0.0034
PQ 9(38)	1382.8541	0.0035
PQ 9(39)	1382.8195	0.0028
PQ11(13)	1384.7970	0.0007
PQ11(14)	1384.7843	0.0004
PQ11(15)	1384.7716	0.0009
PQ11(16)	1384.7575	0.0010
PQ11(17)	1384.7422	0.0008
PQ11(18)	1384.7264	0.0009
PQ11(19)	1384.7098	0.0011
PQ11(20)	1384.6922	0.0012
PQ11(21)	1384.6745	0.0021
PQ11(22)	1384.6551	0.0021
PQ11(23)	1384.6348	0.0022
PQ11(24)	1384.6141	0.0027
PQ11(25)	1384.5917	0.0024
RQ 0(27)	1377.0493	-0.0002
RQ 0(28)	1377.0290	-0.0006
RQ 0(29)	1377.0092	0.0001
RQ 0(30)	1376.9873	-0.0005
RQ 0(31)	1376.9655	-0.0003
RQ 0(32)	1376.9431	-0.0000
RQ 0(34)	1376.8954	-0.0002
RQ 0(35)	1376.8708	-0.0000
RQ 0(36)	1376.8453	0.0000
RQ 0(37)	1376.8195	0.0004
RQ 0(38)	1376.7925	0.0004
RQ 0(39)	1376.7642	-0.0003
RQ 6 (7)	1373.2028	-0.0007
RQ 6 (8)	1373.1964	-0.0008
RQ 6 (9)	1373.1892	-0.0008
RQ 6(10)	1373.1813	-0.0008
RQ 6(11)	1373.1725	-0.0009
RQ 6(12)	1373.1630	-0.0009
RQ 6(13)	1373.1530	-0.0006
RQ 6(14)	1373.1414	-0.0011
RQ 6(15)	1373.1296	-0.0010
RQ 6(16)	1373.1164	-0.0015
RQ 6(17)	1373.1030	-0.0014
RQ 6(18)	1373.0904	0.0003
RQ 6(19)	1373.0734	-0.0016
RQ 6(20)	1373.0579	-0.0013
RQ 6(21)	1373.0400	-0.0025
RQ 6(22)	1373.0234	-0.0016
RQ 6(23)	1373.0043	-0.0025
RQ 6(24)	1372.9856	-0.0022
RQ 6(25)	1372.9656	-0.0023
RQ 6(26)	1372.9451	-0.0022
RQ 6(27)	1372.9242	-0.0017
RQ 6(28)	1372.9022	-0.0015
RQ 6(29)	1372.8792	-0.0014
RQ 6(30)	1372.8552	-0.0016
RQ 6(31)	1372.8314	-0.0008
RQ 6(32)	1372.8053	-0.0015
RQ 6(33)	1372.7799	-0.0007
RQ 6(34)	1372.7520	-0.0017
RQ 6(35)	1372.7238	-0.0021
RQ 6(36)	1372.6949	-0.0024
RQ 6(37)	1372.6659	-0.0020
RQ 6(38)	1372.6352	-0.0026
RQ 6(39)	1372.6060	-0.0008
RQ 7 (8)	1372.5157	-0.0015
RQ 7 (9)	1372.5088	-0.0013
RQ 7(10)	1372.5009	-0.0013
RQ 7(11)	1372.4920	-0.0016
RQ 7(12)	1372.4827	-0.0014
RQ 7(13)	1372.4727	-0.0011
RQ 7(14)	1372.4608	-0.0020
RQ 7(15)	1372.4489	-0.0021
RQ 7(16)	1372.4364	-0.0020
RQ 7(17)	1372.4232	-0.0017
RQ 7(18)	1372.4087	-0.0020
RQ 7(19)	1372.3943	-0.0015
RQ18(19)	1364.9547	-0.0009
RQ18(20)	1364.9396	-0.0010
RQ18(21)	1364.9241	-0.0008
RQ18(22)	1364.9068	-0.0017
RQ18(23)	1364.8897	-0.0016
RQ18(24)	1364.8717	-0.0016
RQ18(25)	1364.8537	-0.0009
RQ18(26)	1364.8337	-0.0015
RQ18(27)	1364.8143	-0.0007
RQ18(28)	1364.7932	-0.0009
RQ18(29)	1364.7715	-0.0009
RQ18(30)	1364.7491	-0.0008
RQ18(31)	1364.7254	-0.0014
RQ18(32)	1364.7012	-0.0017
RQ18(33)	1364.6765	-0.0017
RQ18(34)	1364.6512	-0.0016
RQ18(35)	1364.6251	-0.0015
RQ18(36)	1364.5978	-0.0019
RQ18(37)	1364.5698	-0.0022
RQ18(38)	1364.5423	-0.0013
RQ18(39)	1364.5134	-0.0011
RQ18(40)	1364.4832	-0.0014
RQ18(41)	1364.4523	-0.0017
RQ18(42)	1364.4215	-0.0011
RQ18(43)	1364.3889	-0.0016
RQ18(44)	1364.3554	-0.0022
PP28(28)	1377.0457	-0.0013
PP29(29)	1377.0328	-0.0009
PP31(31)	1377.0062	-0.0003
PP32(32)	1376.9924	-0.0001
PP33(33)	1376.9775	-0.0008
PP34(34)	1376.9628	-0.0010
PP35(35)	1376.9489	-0.0002
PP36(36)	1376.9343	0.0001
PP37(37)	1376.9193	0.0003
PP38(38)	1376.9035	-0.0000
PP39(39)	1376.8880	0.0001
PP40(40)	1376.8727	0.0008
PP41(41)	1376.8571	0.0013
PP42(42)	1376.8404	0.0010
PP43(43)	1376.8239	0.0012
PP44(44)	1376.8069	0.0010
PP45(45)	1376.7891	0.0003
PP46(46)	1376.7729	0.0015
PP47(47)	1376.7551	0.0012
PP48(48)	1376.7375	0.0014
PP49(49)	1376.7190	0.0009
PP50(50)	1376.7003	0.0005
PP51(51)	1376.6809	-0.0004
PP 1 (8)	1372.4545	-0.0016
PP 2 (9)	1372.4414	-0.0024
PP 3(10)	1372.4296	-0.0016
PP 4(11)	1372.4169	-0.0014
PP 5(12)	1372.4032	-0.0020
PP 6(13)	1372.3894	-0.0024
PP 7(14)	1372.3768	-0.0013
PP 8(15)	1372.3626	-0.0015
PP 9(16)	1372.3480	-0.0018
PP10(17)	1372.3345	-0.0008
PP11(18)	1372.3193	-0.0011
PP12(19)	1372.3051	-0.0001
PP 5(13)	1371.7069	0.0016
PP 6(14)	1371.6932	0.0021
PP 7(15)	1371.6779	0.0014
PP 8(16)	1371.6633	0.0016
PP 9(17)	1371.6482	0.0016
PP10(18)	1371.6321	0.0009
PP11(19)	1371.6175	0.0020
PP12(20)	1371.6012	0.0017
PP13(21)	1371.5845	0.0014
PP14(22)	1371.5683	0.0018
PP15(23)	1371.5514	0.0019
PP16(24)	1371.5345	0.0023
PP17(25)	1371.5162	0.0016
PP18(26)	1371.4983	0.0016
PP19(27)	1371.4798	0.0013
PP20(28)	1371.4607	0.0008
PP21(29)	1371.4411	0.0001
PP22(30)	1371.4204	-0.0013
PP23(31)	1371.3993	-0.0028
PP24(32)	1371.3768	-0.0053
PP25(33)	1371.3531	-0.0088
PP26(34)	1371.3270	-0.0142
PP27(35)	1371.2982	-0.0220
PP 1(18)	1365.4570	0.0000
PP 2(19)	1365.4369	0.0001
PP 3(20)	1365.4162	-0.0001
PP 4(21)	1365.3956	0.0001
PP 5(22)	1365.3746	0.0002
PP 6(23)	1365.3531	0.0002
PP 7(24)	1365.3316	0.0005
PP 8(25)	1365.3100	0.0010
PP 9(26)	1365.2872	0.0008
PP10(27)	1365.2645	0.0010
RP 1(16)	1365.4963	0.0003
RP 2(15)	1365.5162	0.0010
RP 3(14)	1365.5358	0.0016
PP 1(19)	1364.7534	0.0001
PP 2(20)	1364.7330	0.0007
PP 3(21)	1364.7113	0.0002
PP 4(22)	1364.6896	0.0001
PP 5(23)	1364.6674	-0.0002
PP 6(24)	1364.6453	-0.0001
PP 7(25)	1364.6228	0.0000
PP 8(26)	1364.6000	0.0002
PP 9(27)	1364.5771	0.0007
PP10(28)	1364.5538	0.0011
PP11(29)	1364.5296	0.0010
PP12(30)	1364.5050	0.0009
PP13(31)	1364.4808	0.0016
PP14(32)	1364.4558	0.0019
PP15(33)	1364.4298	0.0016
PP16(34)	1364.4032	0.0012
PP17(35)	1364.3765	0.0010
PP18(36)	1364.3486	0.0001
RR30(33)	1380.0676	0.0027
RR31(34)	1380.0639	0.0023
RR32(35)	1380.0610	0.0030
RR33(36)	1380.0573	0.0030
RR34(37)	1380.0532	0.0028
RR35(38)	1380.0494	0.0031
RR36(39)	1380.0450	0.0029
RR37(40)	1380.0404	0.0027
RR38(41)	1380.0359	0.0028
RR39(42)	1380.0308	0.0025
RR40(43)	1380.0251	0.0018
RR41(44)	1380.0200	0.0018
RR42(45)	1380.0146	0.0016
RR43(46)	1380.0084	0.0009
RR44(47)	1380.0026	0.0006
RR45(48)	1379.9960	-0.0002
RR46(49)	1379.9894	-0.0009
RR47(50)	1379.9831	-0.0012
RR48(51)	1379.9763	-0.0018
RR49(52)	1379.9661	-0.0057
RR50(53)	1379.9538	-0.0115
RR18(23)	1381.4325	0.0010
RR19(24)	1381.4297	0.0009
RR20(25)	1381.4268	0.0009
RR21(26)	1381.4239	0.0010
RR22(27)	1381.4202	0.0006
RR23(28)	1381.4167	0.0006
RR24(29)	1381.4128	0.0005
RR25(30)	1381.4089	0.0005
RR26(31)	1381.4040	-0.0003
RR27(32)	1381.3995	-0.0005
RR28(33)	1381.3948	-0.0006
RR29(34)	1381.3894	-0.0013
RR30(35)	1381.3835	-0.0022
RR42(50)	1383.2488	-0.0004
RR44(52)	1383.2269	-0.0008
RR46(54)	1383.2058	0.0003
RR48(56)	1383.1820	-0.0003
RR50(48)	1383.1590	0.0006
RR52(60)	1383.1335	-0.0001
RR54(62)	1383.1082	0.0003
RR56(64)	1383.0817	0.0002
RR57(65)	1383.0688	0.0008
RR58(66)	1383.0546	0.0003
RR60(68)	1383.0267	0.0005
RR 1(11)	1384.8550	0.0022
RR 2(12)	1384.8518	0.0022
RR 3(13)	1384.8476	0.0015
RR 4(14)	1384.8439	0.0014
RR 5(15)	1384.8397	0.0011
RR 6(16)	1384.8353	0.0008
RR 7(17)	1384.8310	0.0008
RR 8(18)	1384.8266	0.0009
RR 9(19)	1384.8216	0.0006
RR10(20)	1384.8167	0.0006
RR11(21)	1384.8109	-0.0000
RR12(22)	1384.8058	0.0003
RR13(23)	1384.7994	-0.0005
RR14(24)	1384.7934	-0.0007
RR15(25)	1384.7879	-0.0001
RR16(26)	1384.7814	-0.0004
RR17(27)	1384.7749	-0.0004
RR18(28)	1384.7682	-0.0003
RR19(29)	1384.7611	-0.0004
RR20(30)	1384.7541	-0.0002
RR21(31)	1384.7462	-0.0007
RR22(32)	1384.7386	-0.0006
RR23(33)	1384.7304	-0.0009

TABLE 2. Continued

Assignment[a] $K(J)$	Observed frequency (cm^{-1})	Obsd−Calcd (cm^{-1})
RR24(34)	1384.7233	0.0001
RR25(35)	1384.7144	−0.0004
RR26(36)	1384.7062	−0.0000
RR27(37)	1384.6977	0.0004
RR28(38)	1384.6882	−0.0000
RR29(39)	1384.6800	0.0011
RR30(40)	1384.6706	0.0013
RR31(41)	1384.6604	0.0009
RR32(42)	1384.6510	0.0015
RR33(43)	1384.6403	0.0011
RR34(44)	1384.6309	0.0023
RR35(45)	1384.6203	0.0025
RR36(46)	1384.6101	0.0033
RR37(47)	1384.5987	0.0032
RR38(48)	1384.5877	0.0037

The standard deviation of the residuals
$\sigma = 0.0023\ cm^{-1}$.

[a] For example, PQ 3(3) denotes $^{P}Q_3(3)$.

$^{R}Q_0$ were carefully observed. The standard deviation arising in the least-squares fitting has shown that the negative sign was definitely preferable to the positive sign. The final result for q_4 is included in Table 1.[9]

x-y Type Coriolis Interaction. The standard deviation of $0.0023\ cm^{-1}$ for the overall least-squares fit is somewhat too large if we consider the precision of the wavelength measurement. This may hint at the existence of an x-y type Coriolis interaction between ν_4 and $2\nu_3$, because the band origin of $2\nu_3$ is expected to be about $1400\ cm^{-1}$. The intensity of the $2\nu_3$ band is so weak, in comparison with the ν_4 band, that we failed to pick up the lines of $2\nu_3$ in the $1400\ cm^{-1}$ region. Therefore, we attempted to consider the effect of such an x-y type Coriolis interaction by using the frequencies calculated for $2\nu_3$. The molecular constants were estimated from the results obtained for the $2\nu_3-\nu_3$.[1] The details are:

$$\nu = 700.1009 + 699.310 = 1399.411\ cm^{-1}$$

$$B = B_0 - 0.641\times10^{-3} - 0.6463\times10^{-3} = 0.343914\ cm^{-1}$$

$$C \simeq C_0 - 2\times1.700\times10^{-4} = 0.18852\ cm^{-1}$$

$$D^J = 3.52\times10^{-7}\ cm^{-1}$$

$$D^{JK} \simeq D_0^{JK} - 2\times(0.28\times10^{-8}) = -6.0935\times10^{-7}\ cm^{-1}$$

and

$$D^K \simeq D_0^K = 3.27\times10^{-7}\ cm^{-1}.$$

The matrix elements of the Hamiltonian for the Coriolis interaction between ν_4 and $2\nu_3$ are expressed as

$$\langle v_3 = 2, J, K|H_c|\ v_4 = 1,\ l = \pm1,\ J, K\pm1\rangle = \pm\xi_{334}[J(J+1)-K(K\pm1)]^{1/2}.$$

The ζ_{334} value is obtained from the ξ_{334} value by this relation:[10]

$$\xi_{334} = \left(\frac{1}{\sqrt{2}}\right)[(\nu_4/\nu_{33})^{1/2} + (\nu_{33}/\nu_4)^{1/2}]B\zeta_{334}.$$

By considering the x-y Coriolis interaction, the standard deviation value was reduced from $0.0024\ cm^{-1}$ to $0.0012\ cm^{-1}$. The final interaction parameters obtained are: $|\xi_{334}|=0.03185\pm0.00054\ cm^{-1}$ and $|\zeta_{334}|=0.065$. Other molecular constants did not change their magnitude very much, except for η_4^J and η_4^K. These values were obtained to be $(6.94\pm0.32)\times10^{-7}\ cm^{-1}$ and $(-1.30\pm0.24)\times10^{-7}\ cm^{-1}$, respectively. As this treatment of the x-y type Coriolis interaction is not complete, we have listed the molecular constant values which were obtained without considering this interaction in Table 1. However it must be concluded that the interaction parameter $|\zeta_{334}|$ takes the value of about 0.065 and that the molecular constants given in Table 1 are not affected much by the neglect of this type of interaction.

The authors are grateful to Dr. Jun Nakagawa of Hiroshima University for his helpful suggestions about the computer program.

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