

High-Resolution Infrared Spectrum of ν_5 , ν_4 , ν_3 , $\nu_4 + \nu_5$, and $2\nu_4$ Band Systems of Deuterobromoacetylene

Robert Brotherus,* Olavi Vaittinen,* Lauri Halonen,* Hans Bürger,† and Oliver Polanz†

*Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland; and †FB9-Anorganische Chemie, Universität Gesamthochschule, D-42097 Wuppertal, Germany

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High-resolution vibration–rotation spectra of gas-phase deuterobromoacetylene have been recorded in the 240–990 cm^{-1} infrared region. The analyzed band systems are rich in hot bands and have a high density of lines. Five band systems and a total of 124 vibration–rotation bands of the isotopic species DCC^{79}Br and DCC^{81}Br have been rotationally analyzed. Accurate rotational parameters and vibrational wavenumbers for 33 vibrational states of each species have been obtained from the rotational analysis. l doubling and rotational l resonance have been observed on some states and the respective resonance parameters have been obtained through nonlinear least-squares optimization. A Fermi resonance block model with perturbation terms has been used for the analysis of the vibrational states. With optimized parameters, the model produces root-mean-square deviations of observed – calculated wavenumbers of about 0.3 cm^{-1} for both isotopic species. © 1999 Academic Press

1. INTRODUCTION

High-resolution infrared spectra of acetylene (1–3) and its derivatives HCCF (4, 5), HCCCl (6), HCCBr (7–9), and HCCI (10, 11) have attracted interest in recent years. The aim of the research has been to obtain accurate vibrational term values from rotational analyses of the vibration–rotation bands and to develop models for explaining the vibrational energies in terms of anharmonic effects. Deuterated bromoacetylene (DCCBr) has not been previously analyzed with high resolution, but the nondeuterated counterpart HCCBr has been studied both in the fundamental (7, 12, 13) and overtone (8, 9) region.

DCCBr possesses five fundamental normal modes of vibration of which three are stretching modes and two are doubly degenerate bending modes. Table 1 shows the fundamental vibrational modes along with their approximate wavenumbers. The three lowest energy vibrational modes ν_5 , ν_4 , and ν_3 , and some of their combinations and overtones have been analyzed in the present work.

The high line density in all the band systems results from three factors: the high moment of inertia of DCCBr, the relatively large population of ν_5 , ν_4 , and ν_3 states at room temperature, and the two isotopic species (DCC^{79}Br and DCC^{81}Br) present. Although the high number of lines requires high resolution for the measurement and makes the rotational analysis more laborious, it also results in a large amount of information being obtainable from the spectrum. The large moment of inertia leads to detection of lines up to high values of the total angular momentum quantum number J and therefore, a high accuracy is obtained for the optimized rovibrational pa-

rameters. Multiple hot bands provide access to many otherwise unobservable vibrational states.

2. EXPERIMENTAL

DCCBr was prepared from *cis*-1,2-dibromoethane. A solution of 2.7 g KCN and 11.5 g KOD in 50 ml of D_2O was added to 4.0 ml of a commercial *cis/trans* mixture of $\text{C}_2\text{H}_2\text{Br}_2$ in an N_2 atmosphere. After an addition of a few ml of the solution, the pressure in the reactor was adjusted to 800 mbar and the temperature was slowly raised to 100°C. Volatile reaction products were passed through a -78°C trap and collected at -196°C . The by-product DCCD was separated by condensation of DCCBr in a -120°C trap. The yield was 13% with regard to the *cis/trans* dibromoethane mixture used.

All the spectra were recorded with Bruker IFS 120 HR FTIR spectrometers. The ν_5 and ν_4 band systems were recorded in Wuppertal and all the other band systems in Helsinki. The details of the three separate recordings are presented in Table 2. Line wavenumbers were deduced from the spectra with the Bruker Opus software automatic line detection routine. The wavenumber calibration was performed using H_2O and CO_2 lines, whose wavenumbers were taken from Ref. (14).

3. VIBRATIONAL STATES

Unsymmetrized vibrational states of DCCBr are denoted in the normal mode notation as $|v_1 v_2 v_3 v_4^l v_5^s\rangle$, where v_n is the number of vibrational quanta in the mode n , l_n is the vibrational angular momentum quantum number associated with the bending mode n .

TABLE 1
The Fundamental Vibrational Modes
of DCCBr

Name	Description	Wavenumber/cm ⁻¹	Degeneracy
$\nu_1(\Sigma^+)$	D-C stretch	2600 ^a	1
$\nu_2(\Sigma^+)$	C \equiv C stretch	1960 ^a	1
$\nu_3(\Sigma^+)$	Br-C stretch	603 ^b	1
$\nu_4(\Pi)$	D-C \equiv C bend	481 ^b	2
$\nu_5(\Pi)$	Br-C \equiv C bend	271 ^b	2

^a Estimated from a low-resolution infrared spectrum.

^b From the present work.

Second-order perturbation theory formula for the vibrational wavenumbers can be written as (15)

$$G_v = \sum_r \tilde{\nu}_r \nu_r + \sum_r x_{rr}(\nu_r^2 - \nu_r) + \sum_{r < r'} x_{rr'} \nu_r \nu_{r'} + \sum_t g_{tt}(l_t^2 - \nu_t) + \sum_{t < t'} g_{tt'} l_t l_{t'}, \quad [1]$$

where $\tilde{\nu}_r$ is the fundamental transition wavenumber of the vibrational mode r . The symbols x_{rr} , $x_{rr'}$, g_{tt} , and $g_{tt'}$ represent the vibrational anharmonicity parameters. The indices t and t' span the bending modes 4 and 5, whereas indices r and r' span all the vibrational modes 1–5. Note that the ground state energy has been subtracted from Eq. [1].

For vibrational states close to each other in energy, the perturbation theory formula in Eq. [1] fails to give the vibrational wavenumbers accurately. In these cases, variational theory with Hamiltonian matrix and off-diagonal matrix elements must be used in addition to the diagonal elements given by Eq. [1]. In the present analysis, there are two important vibrational resonances: Fermi resonance and vibrational l resonance. The Fermi resonance occurs between two quanta of C \equiv C—Br bending and one quantum of C—Br stretching and gives rise to matrix elements

$$\langle \nu_3, \nu_5^l | H/hc_0 | \nu_3 - 1, (\nu_5 + 2)^l \rangle = k_{355} \left[\frac{1}{8} \nu_3 (\nu_5 + l_5 + 2) \times (\nu_5 - l_5 + 2) \right]^{1/2}, \quad [2]$$

TABLE 2
The Experimental Details

Band system	ν_5	ν_4	ν_3	$\nu_4 + \nu_5, 2\nu_4$
Resolution /cm ⁻¹	0.0035	0.0035	0.0030	0.0020
Pressure /mbar	3	5	4	2
Path length /cm	120	28	80	200
Detector	Si bolometer	Si bolometer	MCT	MCT
Number of scans	75	140	350	120
Calibration	H ₂ O	CO ₂	CO ₂	CO ₂
Precision /cm ⁻¹	$\sim 10^{-4}$	$\sim 10^{-4}$	$\sim 10^{-4}$	$\sim 10^{-4}$

where k_{355} is a parameter describing the strength of the Fermi resonance.

The vibrational l resonance couples states with bending motion through their vibrational angular momentum. The off-diagonal elements are

$$\langle \nu_4^l, \nu_5^l | H/hc_0 | \nu_4^{l-2}, \nu_5^{l+2} \rangle = \frac{1}{4} r_{45} \{ [(\nu_4 + 1)^2 - (l_4 - 1)^2] \times [(\nu_5 + 1)^2 - (l_5 + 1)^2] \}^{1/2}. \quad [3]$$

A vibrational block diagonal model based on the Fermi resonance has been used to reduce the sizes of Hamiltonian matrices. In this model, each state is assigned a block quantum number V by

$$V = 2\nu_3 + 2\nu_4 + \nu_5. \quad [4]$$

The states with the same V form a resonance block. Because the fundamental wavenumbers of ν_4 or ν_3 are about twice that of ν_5 , V gives a rough approximation of the relative energy of the state. Hence, states with different block numbers are well separated from each other at least in the low-vibrational energy region and their interaction is adequately described by the perturbation parameters in Eq. [1]. The mixing of states within a resonance block is analyzed by diagonalization of a Hamiltonian matrix.

4. VIBRATION-ROTATION STATES

The total vibration-rotation energy of a linear molecule at a vibrational state ν and with a total angular momentum quantum number J and a vibrational angular momentum quantum number k_ν is given by

$$G = G_\nu + B_\nu [J(J+1) - k_\nu^2] - D_\nu [J(J+1) - k_\nu^2]^2, \quad [5]$$

where B_ν and D_ν are the rotational and centrifugal distortion

TABLE 3
A Summary of the Analyzed Band Systems

Band system	Wavenumber range / cm ⁻¹	Assignments	P and R branches	Q branches
ν_5	241 – 314	3107	24	12
ν_4	450 – 515	2523	24	8
ν_3	574 – 652	991	6	–
$\nu_4 + \nu_5$	720 – 800	2183	20	–
$2\nu_4$	925 – 990	3790	30	–
Total	241 – 990	12594	104	20

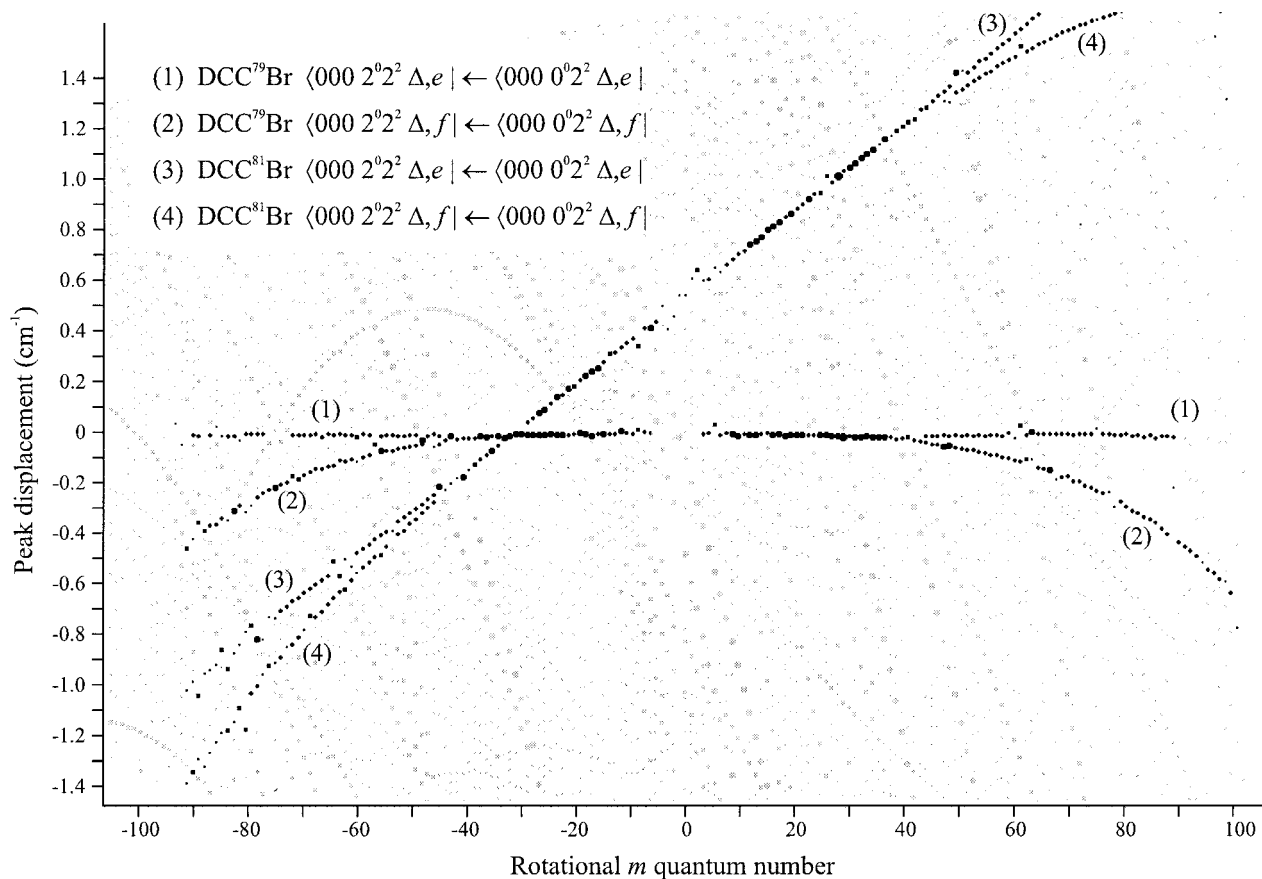


FIG. 1. A Loomis-Wood view of the $2\nu_4$ band system as shown by the analysis software. The m quantum numbers on the x axis are for the band (1). The y axis is defined by the wavenumber displacement of a peak from the predicted wavenumber of band (1). See text for additional information.

constants of the state v . With some vibrational states, it is necessary to add a sixth-order rotational term $H_v[J(J+1) - k_v^2]^3$ to Eq. [5] to obtain an accurate fit of rotational energies for high J values.

Rotational l resonance couples the vibrational and rotational motions of the molecule. These elements have the form (4)

$$\begin{aligned} \langle v_t^{J+1}, J, k+1 | H/hc_0 | v_t^{J-1}, J, k-1 \rangle \\ = \frac{1}{4} q_l [(v_t+1)^2 - l_t^2]^{1/2} [J(J+1) - k(k+1)]^{1/2} \\ \times [J(J+1) - k(k-1)]^{1/2}, \end{aligned} \quad [6]$$

where q_l is a resonance parameter consisting of a constant and a J -dependent part and is given by $q_l = q_{l0} + q_{lJ} J(J+1)$. Because the value of the resonance element depends on J , the calculation of energy levels requires a separate Hamiltonian matrix to be set up and diagonalized for each value of J .

Vibration-rotation states $|v_1 v_2 v_3 v_4^{l_4} v_5^{l_5}, Jk\rangle$ with $k = l_4 + l_5$ and $l_4 \neq 0$ or $l_5 \neq 0$ do not transform as an irreducible representation of the molecular point group. It is more convenient to use properly

symmetrized linear combinations of these states because matrix elements coupling states with different symmetry are necessarily zero. This reduces the resonance blocks further into uncoupled subblocks according to their symmetry.

The symmetric linear combinations are obtained with the formulas

$$\begin{aligned} |v_1 v_2 v_3 v_4^{l_4} v_5^{l_5}, \Gamma, J, e\rangle &= \frac{1}{\sqrt{2}} |v_1 v_2 v_3 v_4^{+l_4} v_5^{+l_5}, Jk\rangle \\ &+ (-1)^k \frac{1}{\sqrt{2}} |v_1 v_2 v_3 v_4^{-l_4} v_5^{-l_5}, Jk\rangle, \\ |v_1 v_2 v_3 v_4^{l_4} v_5^{l_5}, \Gamma, J, f\rangle &= \frac{1}{\sqrt{2}} |v_1 v_2 v_3 v_4^{+l_4} v_5^{+l_5}, Jk\rangle \\ &- (-1)^k \frac{1}{\sqrt{2}} |v_1 v_2 v_3 v_4^{-l_4} v_5^{-l_5}, Jk\rangle, \end{aligned} \quad [7]$$

where Γ is the symmetry symbol of the state and e or f is the parity of the symmetrized state. Γ is defined by the total

TABLE 4
The Analyzed Vibration–Rotation Bands of DCC⁷⁹Br

#	Sys-tem	Upper state	Lower state	Ty-pe	Pks	$10^3 \Delta$ /cm ⁻¹	ΔG_v /cm ⁻¹	Δ_B	Δ_D	B'/cm^{-1}	$D' \times 10^8$ /cm ⁻¹	$H' \times 10^{14}$ /cm ⁻¹	Note
1	v ₅	000 1 ¹ 0 ⁰ Πe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	180	0.26	278.775143(27)			0.12218374(32)	2.0589(27)	0	
2	v ₅	000 1 ¹ 0 ⁰ Πf	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	79	0.19	278.775441(82)			0.12230589(32)	2.0752(27)	0	
3	v ₅	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	109	0.30	262.821301(56)			0.12235036(69)	2.4793(83)	0	
4	v ₅	000 2 ⁰ 0 ⁰ Δe	000 0 ⁰ 1 ¹ Πe	PR	135	0.30	279.356553(52)			0.12256788(69)	2.0856(83)	0	
5	v ₅	000 2 ⁰ 0 ⁰ Δf	000 0 ⁰ 1 ¹ Πf	PR	139	0.26	279.356628(45)			0.12256619(48)	2.1128(49)	0	
6	v ₅	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	131	0.34	324.538211(62)			0.12174519(69)	1.7426(83)	0	
7	v ₅	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πf	Q	69	0.37	324.538047(89)			0.12174400(48)	1.7240(49)	0	
8	v ₅	001 1 ¹ 0 ⁰ Πe	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	80	0.35	288.302688(84)			0.12202310(160)	1.8232(230)	0	
9	v ₅	001 1 ¹ 0 ⁰ Πf	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	42	0.38	288.303070(110)			0.12218139(160)	1.7704(520)	0	
10	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	PR	101	0.26	269.119273(51)			0.12252224(89)	2.4031(120)	0	
11	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	Q	52	0.26	269.119580(78)			0.12273238(89)	2.5016(120)	0	
12	v ₅	000 0 ⁰ 3 ³ Φe	000 0 ⁰ 2 ² Δe	PR	139	0.30	279.935022(69)			0.12288621(97)	2.1702(160)	0	
13	v ₅	000 0 ⁰ 3 ³ Φf	000 0 ⁰ 2 ² Δf	PR	104	0.26	279.934702(64)			0.12288684(66)	2.1523(98)	0	
14	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ² Δe	PR	59	0.35	252.583750(110)			0.12252185(99)	2.4202(180)	0	
15	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ² Δf	Q	12	0.19	252.584120(580)			0.12250732(85)	2.1795(130)	0	
16	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ² Δf	PR	58	0.30	252.584010(110)			0.12273269(66)	2.5009(98)	0	
17	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ² Δe	Q	46	0.20	252.584305(74)			0.12273157(97)	2.5034(160)	0	
18	v ₅	000 0 ⁰ 4 ⁰ $\Sigma^+ e$	000 0 ⁰ 3 ¹ Πe	PR	54	0.31	258.746360(110)			0.12279101(200)	2.9118(520)	0	
37	v ₄	000 1 ¹ 0 ⁰ Πe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	202	0.09	480.659357(14)			0.12202033(14)	2.0257(10)	0	
38	v ₄	000 1 ¹ 0 ⁰ Πf	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	52	0.19	480.659240(129)			0.12209232(18)	2.0260(19)	0	
39	v ₄	000 1 ¹ 1 ¹ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	32	0.12	481.990547(79)			0.12237162(20)	2.0327(1012)	0	α
40	v ₄	000 1 ¹ 1 ¹ Δe	000 0 ⁰ 1 ¹ Πe	PR	120		482.192144(86)			0.12237767(26)	2.1099(1037)	0	
41	v ₄	000 1 ¹ 1 ¹ $\Sigma^- f$	000 0 ⁰ 1 ¹ Πf	PR	108	0.21	479.700959(67)	-1.4	-1.6	0.12238188(19)	2.1100(19)	0	
42	v ₄	000 1 ¹ 1 ¹ $\Sigma^- f$	000 0 ⁰ 1 ¹ Πe	Q	30	0.22	479.701527(148)	0	0	0.12237849(38)	1.8972(173)	0	
43	v ₄	000 1 ¹ 1 ¹ Δf	000 0 ⁰ 1 ¹ Πf	PR	123	0.23	482.191853(51)	-1.7	-1.4	0.12237782(19)	2.0479(19)	0	
44	v ₄	000 1 ¹ 1 ¹ Δf	000 0 ⁰ 1 ¹ Πe	Q	31	0.33	482.192802(225)	0	0	0.12237868(42)	2.1342(141)	0	
45	v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 1 ¹ 0 ⁰ Πe	PR	121	0.30	474.345120(71)	0.9	0.5	0.12219018(15)	2.0976(14)	0	
46	v ₄	000 2 ⁰ 0 ⁰ Δe	000 1 ¹ 0 ⁰ Πe	PR	117	0.22	484.144329(71)	0.5	0.3	0.12218531(15)	1.9860(13)	0	
47	v ₄	000 2 ⁰ 0 ⁰ Δf	000 1 ¹ 0 ⁰ Πf	PR	99	0.21	484.144262(71)	-0.1	-0.2	0.12218566(18)	2.0437(18)	0	
48	v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 1 ¹ 0 ⁰ Πf	Q	27	0.23	474.343957(273)	0	0	0.12219361(41)	2.2007(126)	0	
49	v ₄	000 1 ¹ 2 ⁰ Πe	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	PR	65	0.21	481.669039(99)	0.1	-0.4	0.12244686(50)	2.5324(48)	0	
50	v ₄	000 1 ¹ 2 ² Φe	000 0 ⁰ 2 ² Δe	PR	54	0.28	483.735333(93)	0.2	-0.4	0.12269763(69)	2.0210(93)	0	
51	v ₄	000 1 ¹ 2 ² Πf	000 0 ⁰ 2 ² Δf	PR	38	0.32	481.161415(196)	1.3	0.7	0.12270528(52)	2.2684(67)	0	
52	v ₄	000 2 ² 1 ¹ Φf	000 1 ¹ 1 ¹ Δf	PR	48	0.39	485.716181(151)	0.8	0.8	0.12250475(25)	1.7569(38)	0	
69	v ₃	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	185	0.11	603.313225(19)	1.8	1.2	0.12174414(14)	1.7468(12)	2.95(4)	

angular momentum so that symmetry symbols Σ^+ , Π , Δ ... correspond to the k values 0, ± 1 , ± 2 , ..., respectively. The symmetrization is done separately for each J manifold of vibration–rotation states.

The rotational constants for vibrationally excited levels are given in the present model by

$$B(|v_1 v_2 v_3 v_4^{[u_4]} v_5^{[u_5]} \Gamma\rangle) = B_0 - \sum_{i=1}^N c_i^2 \left(\sum_{r=1}^5 \alpha_r v_r \right)_i, \quad [8]$$

where B_0 is the rotational constant for the ground state, N is the number of basis states in the resonance block, i is the index of

the basis state, and c_i is the coefficient of the basis state i in the linear combination of the resonance state. v_r is the number of quanta on the vibrational mode r in the basis vector i and α_r is the parameter describing the effect of different vibrational modes to B .

5. ANALYSIS METHODS

Formulas for allowed vibration–rotation transition wave-numbers can be deduced from Eq. [5] with the appropriate selection rules. For example, for P -branch transitions, one obtains

TABLE 4—Continued

#	Sys- tem	Upper state	Lower state	Ty- pe	Pks	$10^3 \Delta$ /cm ⁻¹	ΔG_v /cm ⁻¹	Δ_B	Δ_D	B'/cm^{-1}	$D' \times 10^8$ /cm ⁻¹	$H' \times 10^{14}$ /cm ⁻¹	Note
70	v ₃	001 0 ⁰ 1 ¹ Πe	000 0 ⁰ 1 ¹ Πe	PR	148	0.14	612.840785(38)	-0.2	-0.4	0.12202500(19)	1.8528(24)	0.86(17)	
71	v ₃	001 0 ⁰ 1 ¹ Πf	000 0 ⁰ 1 ¹ Πf	PR	164	0.19	612.840762(47)	0.4	0.6	0.12218371(19)	1.8120(23)	1.41(11)	
75	v ₄ +v ₅	000 1 ¹ 1 ¹ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	169	0.13	760.766005(30)			0.12237157(9)	1.9991(191)	0	b
76	v ₄ +v ₅	000 1 ¹ 1 ¹ Δe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	118		760.967474(61)			0.12237778(9)	2.1542(191)	0	
77	v ₄ +v ₅	000 1 ¹ 2 ² Πe	000 0 ⁰ 1 ¹ Πe	PR	139	0.13	760.518169(23)	-0.4	-0.2	0.12267677(18)	2.1410(16)	0	
78	v ₄ +v ₅	000 1 ¹ 2 ² Πf	000 0 ⁰ 1 ¹ Πf	PR	135	0.12	760.517968(22)	-0.3	-0.7	0.12270419(19)	2.2558(18)	0	
79	v ₄ +v ₅	000 2 ² 1 ¹ Πe	000 1 ¹ 0 ⁰ Πe	PR	108	0.17	763.468716(37)	0.1	-2.6	0.12247890(15)	2.2876(16)	0	
80	v ₄ +v ₅	000 2 ² 1 ¹ Πf	000 1 ¹ 0 ⁰ Πf	PR	112	0.16	763.468354(33)	-1.8	-1.9	0.12252224(18)	2.3777(18)	0	
81	v ₄ +v ₅	000 1 ¹ 3 ³ Δe	000 0 ⁰ 2 ² Δe	PR	82	0.21	761.253251(57)	-0.2	0.1	0.12300779(68)	2.2106(88)	0	
82	v ₄ +v ₅	000 1 ¹ 3 ³ Δf	000 0 ⁰ 2 ² Δf	PR	87	0.16	761.253287(41)	0.0	-0.6	0.12300919(49)	2.2320(62)	0	
83	v ₄ +v ₅	000 2 ² 2 ² $\Sigma^- f$	000 1 ¹ 1 ¹ $\Sigma^- f$	PR	64	0.19	764.929367(63)	-0.8	-1.1	0.12281944(21)	2.0858(31)	0	
84	v ₄ +v ₅	000 1 ¹ 4 ⁴ Φf	000 0 ⁰ 3 ³ Φf	PR	77	0.21	761.989775(58)	-0.1	0.4	0.12332829(90)	2.2929(153)	0	
95	2v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	195	0.11	955.005022(17)	-1.4	-0.9	0.12219011(14)	2.0970(10)	0	
96	2v ₄	000 2 ⁰ 1 ¹ Πe	000 0 ⁰ 1 ¹ Πe	PR	175	0.11	956.553976(17)	0	0	0.12247071(18)	2.1478(15)	0	
97	2v ₄	000 2 ⁰ 1 ¹ Πf	000 0 ⁰ 1 ¹ Πf	PR	173	0.10	956.553995(16)	0	0	0.12255103(19)	2.1404(18)	0	
98	2v ₄	000 3 ¹ 0 ⁰ Πe	000 1 ¹ 0 ⁰ Πe	PR	176	0.11	952.556649(18)	-1.1	-1.7	0.12224488(14)	2.0690(10)	0	
99	2v ₄	000 3 ¹ 0 ⁰ Πf	000 1 ¹ 0 ⁰ Πf	PR	167	0.09	952.556707(17)	0	0	0.12239151(18)	2.0870(16)	0	
100	2v ₄	000 2 ⁰ 2 ² $\Sigma^+ e$	000 0 ⁰ 2 ² $\Sigma^+ e$	PR	124	0.23	957.063945(45)	0	0	0.12258412(50)	2.5602(47)	0	
101	2v ₄	000 2 ⁰ 2 ² Δe	000 0 ⁰ 2 ² Δe	PR	130	0.24	959.205711(49)	0	0	0.12280184(68)	2.1559(87)	0	
102	2v ₄	000 2 ⁰ 2 ² Δf	000 0 ⁰ 2 ² Δf	PR	146	0.18	959.205218(33)	0	0	0.12280460(49)	2.1855(61)	0	
103	2v ₄	001 2 ⁰ 0 ⁰ $\Sigma^+ e$	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	114	0.16	954.075116(40)	-0.4	-0.7	0.12205299(16)	1.8114(37)	7.68(43)	
104	2v ₄	000 3 ¹ 1 ¹ $\Sigma^- f$	000 1 ¹ 1 ¹ $\Sigma^- f$	PR	120	0.19	953.320829(37)	-1.7	-2.3	0.12264396(20)	2.1392(20)	0	
105	2v ₄	000 3 ¹ 1 ¹ Δf	000 1 ¹ 1 ¹ Δf	PR	126	0.17	954.345753(38)	1.7	2.3	0.12263606(19)	2.1048(20)	0	
106	2v ₄	000 2 ⁰ 3 ³ Φf	000 0 ⁰ 3 ³ Φf	PR	53	0.18	960.904580(90)	-0.2	0.1	0.12313113(92)	2.3727(164)	0	
107	2v ₄	000 4 ⁰ 0 ⁰ $\Sigma^+ e$	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	PR	110	0.15	950.804950(37)	-0.1	1.6	0.12244461(14)	2.2428(11)	0	
108	2v ₄	000 4 ² 0 ⁰ Δe	000 2 ² 0 ⁰ Δe	PR	92	0.17	950.614492(41)	3.5	5.1	0.12243968(16)	1.9116(16)	0	
109	2v ₄	000 4 ² 0 ⁰ Δf	000 2 ² 0 ⁰ Δf	PR	84	0.18	950.614763(43)	-0.6	-2.0	0.12243992(19)	2.0869(23)	0	

Note. See text for the definition of $10^3 \Delta$, Δ_B , and Δ_D .

^a The upper states of these bands form a rotational l -resonance pair. The optimized resonance parameters obtained are $q_4 + q_5 = 19.381(265) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -1.47(171) \times 10^{-10} \text{ cm}^{-1}$ (compare to note b).

^b The upper states of these bands form a rotational l -resonance pair. The optimized resonance parameters obtained are $q_4 + q_5 = 19.285(41) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -2.34(29) \times 10^{-10} \text{ cm}^{-1}$ (compare to note a).

$$\begin{aligned}
 \tilde{\nu}_p &= \Delta G_v + B'[J'(J' + 1) - k'^2] \\
 &- D'[J'(J' + 1) - k'^2]^2 \\
 &- B''[(J' + 1)(J' + 2) - k''^2] \\
 &+ D''[(J' + 1)(J' + 2) - k''^2]^2,
 \end{aligned}
 \tag{9}$$

where B' and D' are the rotational constants of the upper state, B'' and D'' are the rotational constants of the lower state, and ΔG_v is the vibrational band origin. The transition wavenumber formulas for P and R branches can be combined by defining an auxiliary quantum number m by $m = -J' - 1$ in P branch and $m = J'$ in R branch. This leads to a single formula for both branches

$$\begin{aligned}
 \tilde{\nu}_{PR} &= \Delta G_v + B'[m(m + 1) - k'^2] \\
 &- D'[m(m + 1) - k'^2]^2 \\
 &- B''[m(m - 1) - k''^2] \\
 &+ D''[m(m - 1) - k''^2]^2,
 \end{aligned}
 \tag{10}$$

allowing the lines in both branches of a band to be fitted with a single polynomial.

Rotational parameters for both the lower and upper vibrational states of a band can be determined with a linear least-squares fit when no rotational resonances are present. A fourth-order polynomial (sixth order if H terms are included) in m fits the transition wavenumbers according to Eq. [10], and the rotational parameters are calculated from the resulting polynomial coefficients.

However, if the lower state parameters are known with high accuracy from the analysis of other bands, they can be held fixed and only the upper state parameters are optimized. With such a reduced wavenumber fit (4), one can usually obtain the upper state parameters with higher accuracy (as measured by the standard error of the parameters) than with a free optimization. Hence it is the default method used in this study. A free optimization has been used to determine final state parameters only for the ground state, and in some rare cases, where it has resulted in higher accuracy.

TABLE 5
The Analyzed Vibration–Rotation Bands of DCC⁸¹Br

#	Sys- tem	Upper state	Lower state	Ty- pe	Pks	$10^3 \Delta$ /cm ⁻¹	ΔG_v /cm ⁻¹	Δ_B	Δ_D	B'/cm^{-1}	$D' \times 10^8$ /cm ⁻¹	$H' \times 10^{14}$ /cm ⁻¹	Note
19	v ₅	000 1 ¹ 0 ⁰ Πe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	180	0.18	278.692696(26)			0.12151073(24)	2.0295(24)	0	
20	v ₅	000 1 ¹ 0 ⁰ Πf	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	69	0.40	278.692835(90)			0.12163155(24)	2.0444(24)	0	
21	v ₅	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	108	0.28	262.327580(54)			0.12166593(61)	2.4501(64)	0	
22	v ₅	000 2 ² 0 ⁰ Δe	000 0 ⁰ 1 ¹ Πe	PR	133	0.31	279.274273(57)			0.12189160(61)	2.0546(64)	0	
23	v ₅	000 2 ² 0 ⁰ Δf	000 0 ⁰ 1 ¹ Πf	PR	147	0.29	279.274477(52)			0.12189081(53)	2.0869(53)	0	
24	v ₅	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	130	0.33	323.262009(59)			0.12108391(61)	1.7003(64)	0	
25	v ₅	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πf	Q	71	0.30	323.262017(75)			0.12108343(53)	1.6875(53)	0	
26	v ₅	001 1 ¹ 0 ⁰ Πe	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	79	0.40	288.320990(110)			0.12136165(180)	1.8094(280)	0	
27	v ₅	001 1 ¹ 0 ⁰ Πf	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	41	0.21	288.321115(93)			0.12151961(180)	1.7615(280)	0	
28	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	PR	100	0.24	268.941355(49)			0.12183916(61)	2.3623(64)	0	
29	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	Q	52	0.25	268.941503(72)			0.12204614(53)	2.4625(53)	0	
30	v ₅	000 0 ⁰ 3 ³ Φe	000 0 ⁰ 2 ² Δe	PR	82	0.38	279.853245(93)			0.12220729(130)	2.0848(220)	0	
31	v ₅	000 0 ⁰ 3 ³ Φf	000 0 ⁰ 2 ² Δf	PR	86	0.48	279.852800(120)			0.12220929(140)	2.1244(190)	0	
32	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ² Δe	PR	62	0.39	251.994320(120)			0.12183821(130)	2.3378(220)	0	
33	v ₅	000 0 ⁰ 3 ¹ Πe	000 0 ⁰ 2 ² Δf	Q	19	0.20	251.994440(440)			0.12183983(140)	2.3652(190)	0	
34	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ² Δf	PR	54	0.39	251.994702(130)			0.12204651(140)	2.4530(250)	0	
35	v ₅	000 0 ⁰ 3 ¹ Πf	000 0 ⁰ 2 ² Δe	Q	39	0.27	251.994800(110)			0.12204453(130)	2.4174(220)	0	
36	v ₅	000 0 ⁰ 4 ⁰ $\Sigma^+ e$	000 0 ⁰ 3 ¹ Πe	PR	66	0.35	258.352684(95)			0.12209953(210)	2.7742(420)	0	
53	v ₄	000 1 ¹ 0 ⁰ Πe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	185	0.10	480.659285(17)	0	0	0.12134831(17)	2.0033(14)	0	
54	v ₄	000 1 ¹ 0 ⁰ Πf	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	Q	56	0.20	480.659510(102)	0	0	0.12142000(19)	2.0143(19)	0	
55	v ₄	000 1 ¹ 1 ¹ $\Sigma^+ e$	000 0 ⁰ 1 ¹ Πe	PR	38	0.12	481.986423(55)			0.12169717(17)	1.9366(212)	0	a
56	v ₄	000 1 ¹ 1 ¹ Δe	000 0 ⁰ 1 ¹ Πe	PR	139		482.192371(80)			0.12170403(23)	2.1425(218)	0	
57	v ₄	000 1 ¹ 1 ¹ Σf	000 0 ⁰ 1 ¹ Πf	PR	81	0.14	479.701145(54)	-0.5	-1.0	0.12170770(22)	2.0867(19)	0	
58	v ₄	000 1 ¹ 1 ¹ Σf	000 0 ⁰ 1 ¹ Πe	Q	26	0.22	479.701334(155)	0	0	0.12171012(42)	2.2479(200)	0	
59	v ₄	000 1 ¹ 1 ¹ Δf	000 0 ⁰ 1 ¹ Πf	PR	125	0.23	482.192605(55)	1.5	1.5	0.12170368(22)	2.0258(19)	0	
60	v ₄	000 1 ¹ 1 ¹ Δf	000 0 ⁰ 1 ¹ Πe	Q	25	0.32	482.191792(298)	0	0	0.12170314(69)	1.9501(324)	0	
61	v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 1 ¹ 0 ⁰ Πe	PR	121	0.21	474.341917(51)	2.0	1.0	0.12151693(17)	2.0748(15)	0	
62	v ₄	000 2 ² 0 ⁰ Δe	000 1 ¹ 0 ⁰ Πe	PR	122	0.27	484.144387(72)	-1.4	-1.9	0.12151198(18)	1.9639(16)	0	
63	v ₄	000 2 ² 0 ⁰ Δf	000 1 ¹ 0 ⁰ Πf	PR	97	0.28	484.144160(87)	1.8	1.1	0.12151190(26)	2.0170(23)	0	
64	v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 1 ¹ 0 ⁰ Πf	Q	27	0.21	474.345008(197)	0	0	0.12151951(36)	2.1455(80)	0	
65	v ₄	000 1 ¹ 2 ⁰ Πe	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	PR	71	0.25	481.648060(111)	1.5	1.4	0.12176143(35)	2.5064(57)	0	
66	v ₄	000 1 ¹ 2 ² Πf	000 0 ⁰ 2 ² Δf	PR	49	0.47	483.736691(174)	0.5	0.9	0.12202052(64)	1.9206(165)	0	
67	v ₄	000 1 ¹ 2 ² Φe	000 0 ⁰ 2 ² Δe	PR	45	0.29	481.150453(280)	-0.3	-0.2	0.12202754(49)	2.2237(69)	0	
68	v ₄	000 2 ² 1 ¹ Φf	000 1 ¹ 1 ¹ Δf	PR	49	0.46	485.716883(220)	0.3	0.5	0.12182941(28)	1.7336(40)	0	

In the case of bands that experience rotational l -resonance in their upper states, a nonlinear least-squares optimization must be used. Assignments of two or more bands are analyzed together and Hamiltonian matrices with off-diagonal elements given by Eq. [6] are diagonalized for each J manifold. Note that none of the analyzed bands possess a resonance on their lower states.

The combination difference formula (16)

$$\tilde{\nu}_R - \tilde{\nu}_P = (2B'' - 6D'')(J' + \frac{1}{2}) - 8D''(J' + \frac{1}{2})^3 \quad [11]$$

has been used for the line assignment. The formula gives the wavenumber separation of P - and R -branch lines having the same

upper state J . When lines from some branch (P or R) have been assigned with trial J values and a trial vibrational lower state, Eq. [11] can be used to predict line positions in the other branch. Comparison of these predicted wavenumbers and actual line positions allows one to confirm or discard the assumed assignments. A computer program has been used to automatically try several J values and lower state assignments and find the combination that produces the most accurate predictions.

In addition to a regular view of the spectrum, a Loomis–Wood (17) type image has been used to aid in line assignment and in finding weak bands. An example of such an image is shown in Fig. 1. The image shows the spectrum lines as dots on a two-dimensional display. The x axis is defined by the rota-

TABLE 5—Continued

#	Sys- tem	Upper state	Lower state	Ty- pe	Pks	$10^3 \Delta$ /cm ⁻¹	ΔG_v /cm ⁻¹	Δ_B	Δ_D	B'/cm^{-1}	$D' \times 10^8$ /cm ⁻¹	$H' \times 10^{14}$ /cm ⁻¹	Note
72	v ₃	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	186	0.11	601.954668(19)	-0.5	-1.0	0.12108392(17)	1.7153(16)	2.90(5)	
73	v ₃	001 0 ⁰ 1 ¹ Πe	000 0 ⁰ 1 ¹ Πe	PR	154	0.16	611.583167(41)	0.1	-0.1	0.12136173(23)	1.8337(26)	1.19(17)	
74	v ₃	001 0 ⁰ 1 ¹ Πf	000 0 ⁰ 1 ¹ Πf	PR	154	0.17	611.583093(40)	-0.2	-0.2	0.12152003(22)	1.7941(23)	1.95(11)	
85	v ₄ +v ₅	000 1 ¹ 1 ¹ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	165	0.15	760.679449(32)			0.12169736(9)	1.9541(154)	0	b
86	v ₄ +v ₅	000 1 ¹ 1 ¹ Δe	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	104		760.885728(78)			0.12170358(11)	2.1538(154)	0	
87	v ₄ +v ₅	000 1 ² 2 ² Πe	000 0 ⁰ 1 ¹ Πe	PR	135	0.12	760.425414(21)	-0.7	-1.6	0.12200175(22)	2.1220(19)	0	
88	v ₄ +v ₅	000 1 ² 2 ² Πf	000 0 ⁰ 1 ¹ Πf	PR	132	0.11	760.425230(22)	1.5	2.8	0.12202766(22)	2.2299(19)	0	
89	v ₄ +v ₅	000 2 ² 1 ¹ Πe	000 1 ¹ 0 ⁰ Πe	PR	91	0.14	763.381663(39)	-1.4	-2.1	0.12180415(17)	2.2581(18)	0	
90	v ₄ +v ₅	000 2 ² 1 ¹ Πf	000 1 ¹ 0 ⁰ Πf	PR	107	0.15	763.381299(34)	1.9	2.6	0.12184637(25)	2.3411(22)	0	
91	v ₄ +v ₅	000 1 ¹ 3 ³ Δe	000 0 ⁰ 2 ² Δe	PR	99	0.15	761.160006(32)	-0.8	0.1	0.12232971(54)	2.1697(76)	0	
92	v ₄ +v ₅	000 1 ¹ 3 ³ Δf	000 0 ⁰ 2 ² Δf	PR	98	0.21	761.159925(43)	-0.4	0.5	0.12233039(44)	2.1925(59)	0	
93	v ₄ +v ₅	000 2 ² 2 ² $\Sigma^- f$	000 1 ¹ 1 ¹ $\Sigma^- f$	PR	74	0.24	764.839728(62)	2.1	1.2	0.12214281(24)	2.0624(31)	0	
94	v ₄ +v ₅	000 1 ¹ 4 ⁴ Φf	000 0 ⁰ 3 ³ Φf	PR	87	0.20	761.895083(65)	-0.2	-0.5	0.12264522(80)	2.2307(82)	0	
110	2v ₄	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	000 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	199	0.11	955.001756(18)	2.0	2.2	0.12151682(17)	2.0735(14)	0	
111	2v ₄	000 2 ⁰ 1 ¹ Πe	000 0 ⁰ 1 ¹ Πe	PR	146	0.10	956.550153(18)	0	0	0.12179605(22)	2.1267(18)	0	
112	2v ₄	000 2 ⁰ 1 ¹ Πf	000 0 ⁰ 1 ¹ Πf	PR	183	0.12	956.550234(20)	0	0	0.12187577(22)	2.1188(18)	0	
113	2v ₄	000 3 ¹ 0 ⁰ Πe	000 1 ¹ 0 ⁰ Πe	PR	170	0.12	952.550396(20)	0.2	-0.1	0.12157150(17)	2.0455(14)	0	
114	2v ₄	000 3 ¹ 0 ⁰ Πf	000 1 ¹ 0 ⁰ Πf	PR	162	0.13	952.550364(23)	0	0	0.12171592(25)	2.0563(21)	0	
115	2v ₄	000 2 ⁰ 2 ⁰ $\Sigma^+ e$	000 0 ⁰ 2 ⁰ $\Sigma^+ e$	PR	129	0.12	957.012703(24)	0	0	0.12189733(32)	2.5298(41)	0	
116	2v ₄	000 2 ⁰ 2 ² Δe	000 0 ⁰ 2 ² Δe	PR	97	0.15	959.167155(37)	0	0	0.12212613(53)	2.1250(76)	0	
117	2v ₄	000 2 ⁰ 2 ² Δf	000 0 ⁰ 2 ² Δf	PR	97	0.13	959.166777(28)	0	0	0.12212751(44)	2.1398(57)	0	
118	2v ₄	001 2 ⁰ 0 ⁰ $\Sigma^+ e$	001 0 ⁰ 0 ⁰ $\Sigma^+ e$	PR	97	0.13	954.142405(33)	-1.1	-1.1	0.12139187(18)	1.7610(35)	5.34(38)	
119	2v ₄	000 3 ¹ 1 ¹ $\Sigma^- f$	000 1 ¹ 1 ¹ $\Sigma^- f$	PR	81	0.16	953.315277(39)	0.2	0.4	0.12196798(22)	2.1150(20)	0	
120	2v ₄	000 3 ¹ 1 ¹ Δf	000 1 ¹ 1 ¹ Δf	PR	96	0.12	954.338519(36)	0.8	-0.3	0.12196001(22)	2.0748(22)	0	
121	2v ₄	000 2 ⁰ 3 ³ Φf	000 0 ⁰ 3 ³ Φf	PR	87	0.14	960.881238(49)	0.4	0.3	0.12245060(80)	2.2238(80)	0	
122	2v ₄	000 4 ⁰ 0 ⁰ $\Sigma^+ e$	000 2 ⁰ 0 ⁰ $\Sigma^+ e$	PR	79	0.17	950.790857(48)	1.7	2.3	0.12177028(18)	2.2769(24)	0	
123	2v ₄	000 4 ² 0 ⁰ Δe	000 2 ² 0 ⁰ Δe	PR	86	0.17	950.605251(42)	1.0	0.4	0.12176437(19)	1.8810(27)	0	
124	2v ₄	000 4 ² 0 ⁰ Δf	000 2 ² 0 ⁰ Δf	PR	96	0.18	950.605358(40)	1.0	1.9	0.12176459(26)	2.0618(26)	0	

Note. See text for the definition of $10^3 \Delta$, Δ_B , and Δ_D .

^a The upper states of these bands form a rotational l -resonance pair. The optimized resonance parameters obtained are $q_4 + q_5 = 19.077(42) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -0.03(172) \times 10^{-10} \text{ cm}^{-1}$ (compare to note b).

^b The upper states of these bands form a rotational l -resonance pair. The optimized resonance parameters obtained are $q_4 + q_5 = 19.040(28) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -2.84(34) \times 10^{-10} \text{ cm}^{-1}$ (compare to note a).

tional m quantum number of the selected band and y axis by the wavenumber deviation of the line from the calculated line wavenumber of the selected band. Therefore the selected band is straightened to the x axis, and other bands that have similar rotational constants are seen as strings of dots with different slopes and curvatures. In regular Loomis–Wood implementations (18, 19), polynomials are used for the calculation of wavenumber origins on the x axis. The use of general calculated wavenumbers in the present method also makes it possible to employ Loomis–Wood view for bands that experience rotational resonances.

With as dense spectra as in the present work, rigorous criteria had to be established to ensure correct assignment of the lines. The danger of misassignment is small for strong bands originating from the ground vibrational states but becomes larger for weak hot bands. With very weak bands, most of the lines are totally overlapped by lines of stronger bands

and the reliability of assignment lowers to a point where the analysis must be discontinued.

Criteria for accepting a band as correctly assigned include the following requirements. When using the combination difference formula in Eq. [11], there has to be a single choice of m values and a lower state that produces outstanding predictions as compared to all the other possibilities. Final deviations of calculated – observed wavenumbers for the band must be small and random, both for the free optimization and for the optimization with lower state constants fixed. When two or more bands have a common lower state, their analysis must yield equal values (within reasonable error limits) for the lower state rotational parameters. Finally, for perpendicular bands there must be a corresponding Q branch found at the band center ($m = 0$).

The effects of l doubling and isotopic shifts have also helped to confirm the assignments. The Loomis–Wood image in Fig. 1 shows an example of an isotopic band pair where bands of

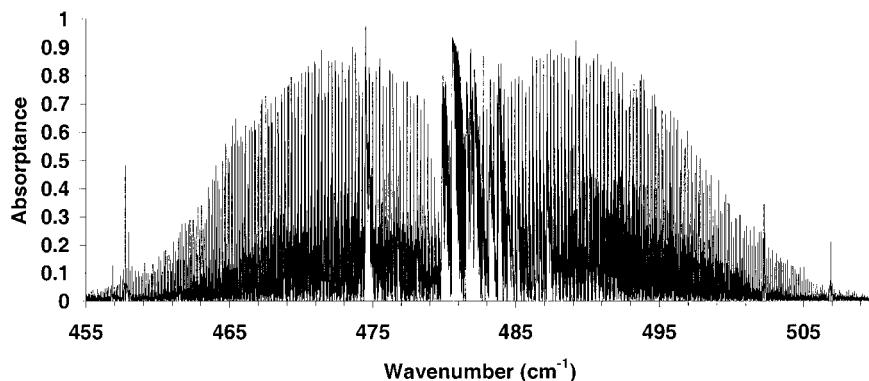


FIG. 2. The ν_4 band system of DCCBr. ν_4 is a perpendicular band system corresponding to the $\text{C}\equiv\text{C}-\text{D}$ bending motion and thus contains strong Q branches in addition to P and R branches.

both isotopic species are further split into e and f subbands. A common and predictable pattern in such band groups increases the probability of their correct assignment.

Final confirmation of the correct assignment is provided by the vibrational analysis. Only small deviations of calculated and observed values have been required both for the vibrational wavenumbers and for the rotational constants.

6. ROTATIONAL ANALYSIS

Figure 2 shows a typical band system, the ν_4 band system. Figure 3 presents a narrow range of the spectrum in the $2\nu_4$

band system showing the high density of lines. A total of five band systems were analyzed in the study, summarized in Table 3. The analysis included all the vibration-rotation band systems below 1000 cm^{-1} , except the $2\nu_5$, $3\nu_5$, and $\nu_3 + \nu_5$ systems. The $\nu_3 + \nu_5$ band system is expected to be extremely weak and was not observed in any of the measured spectra. $2\nu_5$ and $3\nu_5$ were only barely visible with long absorption path lengths and were not analyzed due to small signal-to-noise ratios. Instead, the $2\nu_5$ and $3\nu_5$ overtone states have been analyzed from hot bands in the ν_5 band system.

ν_5 and ν_4 are perpendicular band systems with strong Q branches. The other studied band systems are parallel and

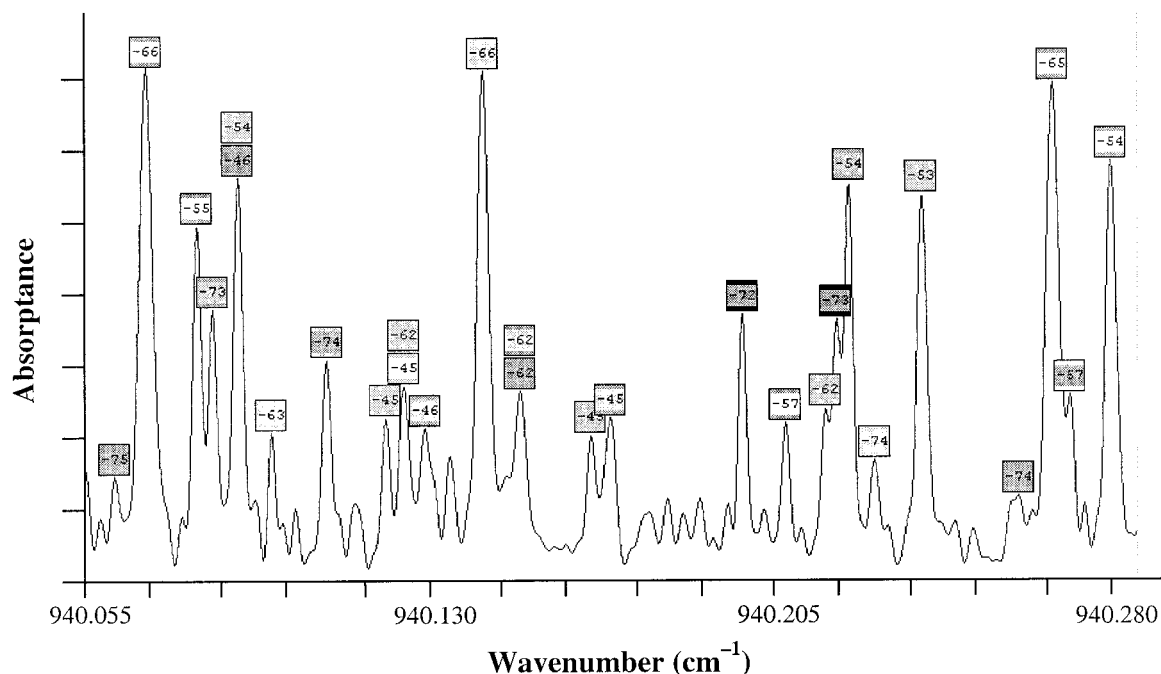


FIG. 3. A small range of the $2\nu_4$ band system and some peak assignments as presented by the analysis software. The numbers show the rotational m assignments. (The assignment labels are actually color-coded according to the band.)

TABLE 6
The Vibrational State Parameters for DCC⁷⁹Br

State	G_v/cm^{-1}		B/cm^{-1}	$D \times 10^8/\text{cm}^{-1}$	$H \times 10^{14}/\text{cm}^{-1}$	Band	Note	State	G_v/cm^{-1}		B/cm^{-1}	$D \times 10^8/\text{cm}^{-1}$	$H \times 10^{14}/\text{cm}^{-1}$	Band	Note
000 0 ⁰ 0 ⁰ Σ^+	0.0	<i>e</i>	0.12192165(14)	2.0154(10)	0	37				<i>f</i>	0.12270419(19)	2.2558(18)	0	78	
000 0 ⁰ 1 ¹ Π	278.775290(80)	<i>e</i>	0.12218360(18)	2.0550(15)	0	96	<i>c, e</i>	000 1 ¹ 2 ² Φ	1041.867234(134)	<i>e</i>	0.12269763(69)	2.0210(93)	0	50	
		<i>f</i>	0.12230572(19)	2.0718(18)	0	97	<i>c, e</i>	000 0 ⁰ 4 ⁰ Σ^+	1069.462223(150)	<i>e</i>	0.12209950(210)	2.7742(420)	0	18	
000 1 ¹ 0 ⁰ Π	480.659357(14)	<i>e</i>	0.12202033(14)	2.0257(10)	0	37	<i>d, e</i>	000 2 ⁰ 1 ¹ Π	1235.329275(57)	<i>e</i>	0.12247071(18)	2.1478(15)	0	96	
		<i>f</i>	0.12209302(18)	2.0352(16)	0	99	<i>d, e</i>			<i>f</i>	0.12255103(19)	2.1404(18)	0	97	
000 0 ⁰ 2 ⁰ Σ^+	541.596590(100)	<i>e</i>	0.12234911(50)	2.4692(47)	0	100		000 2 ² 1 ¹ Π	1244.127986(46)	<i>e</i>	0.12247890(15)	2.2876(16)	0	79	
000 0 ⁰ 2 ² Δ	558.131880(100)	<i>e</i>	0.12256539(68)	2.0519(87)	0	101				<i>f</i>	0.12252224(18)	2.3777(18)	0	80	
		<i>f</i>	0.12256744(49)	2.1346(61)	0	102		000 2 ² 1 ¹ Φf	1246.683333(176)	<i>f</i>	0.12250475(25)	1.7569(38)	0	52	
001 0 ⁰ 0 ⁰ Σ^+	603.313221(20)	<i>e</i>	0.12174414(14)	1.7468(12)	2.95(4)	69	<i>b</i>	000 1 ¹ 3 ³ Δ	1319.385147(78)	<i>e</i>	0.12300779(68)	2.2106(88)	0	81	
000 1 ¹ 1 ¹ Σ^-	758.476243(105)	<i>f</i>	0.12238188(19)	2.1100(19)	0	41				<i>f</i>	0.12300919(49)	2.2320(62)	0	82	
000 1 ¹ 1 ¹ Σ^+	760.766005(29)	<i>e</i>	0.12237157(8)	1.9991(186)	0	75	<i>a, e</i>	000 3 ¹ 0 ⁰ Π	1433.216010(25)	<i>e</i>	0.12224488(14)	2.0690(10)	0	98	
000 1 ¹ 1 ¹ Δe	760.967410(50)	<i>e</i>	0.12237778(9)	2.1542(186)	0	76	<i>a, e</i>			<i>f</i>	0.12239151(18)	2.0870(16)	0	99	
000 1 ¹ 1 ¹ Δf		<i>f</i>	0.12237782(19)	2.0479(19)	0	43		000 2 ² 0 ⁰ Σ^+	1498.660535(109)	<i>e</i>	0.12258412(50)	2.5602(47)	0	100	
000 0 ⁰ 3 ¹ Π	810.715863(110)	<i>e</i>	0.12250732(90)	2.1795(150)	0	10		000 2 ² 2 ² Δ	1517.337343(100)	<i>e</i>	0.12280184(68)	2.1559(87)	0	101	
		<i>f</i>	0.12273269(90)	2.5009(150)	0	16				<i>f</i>	0.12280460(49)	2.1855(61)	0	102	
000 0 ⁰ 3 ³ Φ	838.066582(120)	<i>e</i>	0.12288620(90)	2.1702(150)	0	12		000 2 ² 2 ² Σ^-	1523.405618(123)	<i>f</i>	0.12281944(21)	2.0858(31)	0	83	
		<i>f</i>	0.12288683(90)	2.1523(150)	0	13		001 2 ⁰ 0 ⁰ Σ^+	1557.388339(40)	<i>e</i>	0.12205299(16)	1.8114(37)	7.68(43)	103	<i>b</i>
001 0 ⁰ 1 ¹ Π	891.616067(64)	<i>e</i>	0.12202500(19)	1.8528(24)	0.86(17)	70	<i>b</i>	000 1 ¹ 4 ⁴ Φ	1600.056347(133)	<i>f</i>	0.12332829(90)	2.2929(153)	0	84	
		<i>f</i>	0.12218371(19)	1.8120(23)	1.41(11)	71	<i>b</i>	000 3 ¹ 1 ¹ Σ^-	1711.797074(89)	<i>f</i>	0.12264396(20)	2.1392(20)	0	104	
000 2 ⁰ 0 ⁰ Σ^+	955.005022(17)	<i>e</i>	0.12219011(14)	2.0970(10)	0	95		000 3 ¹ 1 ¹ Δ	1715.312906(89)	<i>f</i>	0.12263606(19)	2.1048(20)	0	105	
000 2 ⁰ 0 ⁰ Δ	964.803652(72)	<i>e</i>	0.12218531(15)	1.9860(13)	0	46		000 2 ² 3 ³ Φ	1798.971163(150)	<i>f</i>	0.12313113(92)	2.3727(164)	0	106	
		<i>f</i>	0.12218566(18)	2.0437(18)	0	47		000 4 ⁰ 0 ⁰ Σ^+	1905.809949(44)	<i>e</i>	0.12244461(14)	2.2428(11)	0	107	
000 1 ¹ 2 ⁰ Π	1023.265602(141)	<i>e</i>	0.12244686(50)	2.5324(48)	0	49		000 4 ² 0 ⁰ Δ	1915.418215(53)	<i>e</i>	0.12243968(16)	1.9116(16)	0	108	
000 1 ¹ 2 ² Π	1039.293359(80)	<i>e</i>	0.12267677(18)	2.1410(16)	0	77				<i>f</i>	0.12243992(19)	2.0869(23)	0	109	

^a The states $\langle 000\ 1^1 1^1\ \Sigma^+, e \rangle$ and $\langle 000\ 1^1 1^1\ \Delta, e \rangle$ are in rotational l -resonance. The resonance parameters: $q_4 + q_5 = 19.285(41) \times 10^{-5}\ \text{cm}^{-1}$, $q_{4J} + q_{5J} = -2.34(29) \times 10^{-10}\ \text{cm}^{-1}$.

^b The state requires an additional H parameter for an accurate fit due to Fermi resonance between ν_3 and $2\nu_5$.

^c These e and f states form an l -doubling pair with parameters (see note e): $q = \Delta B = 12.212(30) \times 10^{-5}\ \text{cm}^{-1}$, $q_{5J} = -\Delta D = -1.68(25) \times 10^{-10}\ \text{cm}^{-1}$.

^d These e and f states form an l -doubling pair with parameters (see note e): $q_4 = \Delta B = 7.269(25) \times 10^{-5}\ \text{cm}^{-1}$, $q_{4J} = -\Delta D = -0.95(20) \times 10^{-10}\ \text{cm}^{-1}$.

^e Calculating $q_4 + q_5$ from values in notes c and d yields (compare to note a): $q_4 + q_5 = 19.482(40) \times 10^{-5}\ \text{cm}^{-1}$, $q_{4J} + q_{5J} = -2.63(35) \times 10^{-10}\ \text{cm}^{-1}$.

hence lack discernible Q branches. The low number of bands that could be analyzed in the ν_3 band system results from the presence of small amounts of HCC⁷⁹Br and HCC⁸¹Br in the sample. The strong ν_4 band systems of these isotopomers are in the same wavenumber region as ν_3 band system of DCCBr resulting in a problematic overlap.

Tables 4 and 5 list the results for the analyzed bands of DCC⁷⁹Br and DCC⁸¹Br, respectively. The $10^3\Delta$ column shows the root mean square residual of the observed – calculated line wavenumbers. The upper state rotational parameters B' , D' , and H' have been calculated by keeping the lower state parameters fixed to values shown in Tables 6 and 7. In those cases where H' is exactly zero in the table, it has been fixed to zero in the calculation. The standard errors in the last decimal places of the parameters are shown in parentheses. The reported standard errors reflect the total uncertainty in the upper state parameter values. The same number of decimal places is given for each parameter of the same type. Note that it is necessary to use at least the present number of decimals in order to achieve adequate prediction accuracy.

The Δ_B values following the lower state B parameters are

important indicators of reliability of the assignment and they have been calculated with

$$\Delta_B = \frac{B''_{\text{free}} - B''_{\text{fixed}}}{\sigma_B}, \quad [12]$$

where B''_{free} is the value of the lower state B parameter from the free optimization of the band, B''_{fixed} is the value of the parameter in the state of Tables 6 and 7, and σ_B is the standard deviation of the parameter. Δ_D is calculated in a similar way using the respective D parameters. For the band assignment to be reliable, the rotational parameter values for a certain state obtained from different bands must be close to each other. Therefore, a Δ value of about 3 or less, meaning that the parameters from different sources differ from each other by less than 3 standard deviations, has been considered acceptable. The absence of Δ values in the ν_5 band system is due to the fact that only calculations with lower state parameters fixed were performed for them. A Δ value of exactly 0 indicates that

TABLE 7
The Vibrational State Parameters for DCC⁸¹Br

State	G_v / cm^{-1}		B / cm^{-1}	$D \times 10^8 / \text{cm}^{-1}$	$H \times 10^{14} / \text{cm}^{-1}$	Band	Note
000 0 ⁰ 0 ⁰ Σ^+	0.0	<i>e</i>	0.12125016(17)	1.9934(14)	0	53	
000 0 ⁰ 1 ¹ Π	278.692770(90)	<i>e</i>	0.12151095(22)	2.0354(18)	0	111	<i>c, e</i>
		<i>f</i>	0.12163196(22)	2.0513(18)	0	112	<i>c, e</i>
000 1 ¹ 0 ⁰ Π	480.659285(17)	<i>e</i>	0.12134831(17)	2.0033(14)	0	53	<i>d, e</i>
		<i>f</i>	0.12141954(25)	2.0050(21)	0	114	<i>d, e</i>
000 0 ⁰ 2 ⁰ Σ^+	541.020340(110)	<i>e</i>	0.12166522(31)	2.4378(41)	0	115	
000 0 ⁰ 2 ² Δ	557.967140(110)	<i>e</i>	0.12189007(53)	2.0221(75)	0	116	
		<i>f</i>	0.12189086(44)	2.0868(57)	0	117	
001 0 ⁰ 0 ⁰ Σ^+	601.954662(19)	<i>e</i>	0.12108392(17)	1.7153(16)	2.90(5)	72	<i>b</i>
000 1 ¹ 1 ¹ Σ^-	758.393935(104)	<i>f</i>	0.12170770(22)	2.0867(19)	0	57	
000 1 ¹ 1 ¹ Σ^+	760.679449(32)	<i>e</i>	0.12169736(9)	1.9541(154)	0	85	<i>a, e</i>
000 1 ¹ 1 ¹ Δe	760.885545(105)	<i>e</i>	0.12170358(11)	2.1538(154)	0	86	<i>a, e</i>
000 1 ¹ 1 ¹ Δf		<i>f</i>	0.12170368(22)	2.0258(19)	0	59	
000 0 ⁰ 3 ¹ Π	809.96186(150)	<i>e</i>	0.12183916(89)	2.3378(120)	0	28	
		<i>f</i>	0.12204614(66)	2.4625(98)	0	34	
000 0 ⁰ 3 ³ Φ	837.820385(130)	<i>e</i>	0.12220729(80)	2.0848(80)	0	30	
		<i>f</i>	0.12220929(80)	2.1244(80)	0	31	
001 0 ⁰ 1 ¹ Π	890.275900(71)	<i>e</i>	0.12136173(23)	1.8337(26)	1.19(17)	73	<i>b</i>
		<i>f</i>	0.12152003(22)	1.7941(23)	1.95(11)	74	<i>b</i>
000 2 ⁰ 0 ⁰ Σ^+	955.001743(18)	<i>e</i>	0.12151682(17)	2.0735(14)	0	110	
000 2 ² 0 ⁰ Δ	964.803632(57)	<i>e</i>	0.12151198(18)	1.9639(16)	0	62	
		<i>f</i>	0.12151190(26)	2.0170(23)	0	63	
000 1 ¹ 2 ⁰ Π	1022.668391(158)	<i>e</i>	0.12176143(35)	2.5064(57)	0	65	
000 1 ¹ 2 ² Π	1039.118090(64)	<i>e</i>	0.12200175(22)	2.1220(19)	0	87	
		<i>f</i>	0.12202766(22)	2.2299(19)	0	88	
000 1 ¹ 2 ² Φ	1041.703842(200)	<i>e</i>	0.12202052(64)	1.9206(165)	0	66	
000 0 ⁰ 4 ⁰ Σ^+	1068.314544(160)	<i>e</i>	0.12209953(200)	2.7742(520)	0	36	
000 2 ⁰ 1 ¹ Π	1235.242962(64)	<i>e</i>	0.12179605(22)	2.1267(18)	0	111	
		<i>f</i>	0.12187577(22)	2.1188(18)	0	112	
000 2 ² 1 ¹ Π	1244.040878(43)	<i>e</i>	0.12180415(17)	2.2581(18)	0	89	
		<i>f</i>	0.12184637(25)	2.3411(22)	0	90	
000 2 ² 1 ¹ Φf	1246.602292(220)	<i>f</i>	0.12182941(28)	1.7336(40)	0	68	
000 1 ¹ 3 ³ Δ	1319.127112(78)	<i>e</i>	0.12232971(54)	2.1697(76)	0	91	
		<i>f</i>	0.12233039(44)	2.1925(59)	0	92	
000 3 ¹ 0 ⁰ Π	1433.209777(50)	<i>e</i>	0.12157150(17)	2.0455(14)	0	113	
		<i>f</i>	0.12171592(25)	2.0563(21)	0	114	
000 2 ⁰ 2 ⁰ Σ^+	1498.033043(113)	<i>e</i>	0.12189733(32)	2.5298(41)	0	115	
000 2 ⁰ 2 ² Δ	1517.134104(110)	<i>e</i>	0.12212613(53)	2.1250(76)	0	116	
		<i>f</i>	0.12212751(44)	2.1398(57)	0	117	
000 2 ² 2 ² Σ^-	1523.233632(122)	<i>f</i>	0.12214281(24)	2.0624(31)	0	93	
001 2 ⁰ 0 ⁰ Σ^+	1556.097067(33)	<i>e</i>	0.12139187(18)	1.7610(35)	5.34(38)	118	<i>b</i>

TABLE 7—Continued

State	G_v / cm^{-1}		B / cm^{-1}	$D \times 10^8 / \text{cm}^{-1}$	$H \times 10^{14} / \text{cm}^{-1}$	Band	Note
000 1 ¹ 4 ⁴ Φ	1599.715468(145)	<i>f</i>	0.12264522(80)	2.2307(82)	0	94	
000 3 ¹ 1 ¹ Σ^-	1711.709211(98)	<i>f</i>	0.12196798(22)	2.1150(20)	0	119	
000 3 ¹ 1 ¹ Δ	1715.223876(97)	<i>f</i>	0.12196001(22)	2.0748(22)	0	120	
000 2 ⁰ 3 ³ Φ	1798.701621(138)	<i>f</i>	0.12245060(80)	2.2238(80)	0	121	
000 4 ⁰ 0 ⁰ Σ^+	1905.792596(53)	<i>e</i>	0.12177028(18)	2.2769(24)	0	122	
000 4 ² 0 ⁰ Δ	1915.408946(35)	<i>e</i>	0.12176437(19)	1.8810(27)	0	123	
		<i>f</i>	0.12176459(26)	2.0618(26)	0	124	

^a The states $\langle 000\ 1^1 1^1 \Sigma^+, e |$ and $\langle 000\ 1^1 1^1 \Delta j e |$ are in rotational l -resonance. The resonance parameters: $q_4 + q_5 = 19.040(28) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -2.84(34) \times 10^{-10} \text{ cm}^{-1}$.

^b The state requires an additional H parameter for an accurate fit due to Fermi resonance between ν_3 and $2\nu_5$.

^c These e and f states form an l -doubling pair with parameters (see Note e) $q_5 = \Delta B = 12.101(32) \times 10^{-5} \text{ cm}^{-1}$, $q_{5J} = -\Delta D = -1.59(25) \times 10^{-10} \text{ cm}^{-1}$.

^d These e and f states form an l -doubling pair with parameters (see Note e) $q_4 = \Delta B = 7.123(32) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} = -\Delta D = -0.17(25) \times 10^{-10} \text{ cm}^{-1}$.

^e Calculating $q_4 + q_5$ from the values in Notes c and d yields (compare to Note a) $q_4 + q_5 = 19.224(45) \times 10^{-5} \text{ cm}^{-1}$, $q_{4J} + q_{5J} = -1.76(35) \times 10^{-10} \text{ cm}^{-1}$.

the band in question has been used to calculate the final values of the parameters in Tables 6 and 7.

Tables 6 and 7 summarize the final parameters for all the analyzed vibrational states. Since many bands share a common lower or upper state, these parameters have many potential sources. The parameters in Tables 6 and 7 have been selected as the best possible parameters as measured by the magnitude of their standard deviation. The “band” column shows the number of the band (as listed in Tables 4 and 5) used for the parameter source. The vibrational term values for the states with l doubling have been calculated from the average of the respective term values of e and f subbands.

The parameters α_3 , α_4 , and α_5 in Eq. [8] describing the vibrational dependence of the rotational constant B have been calculated from the obtained state parameters. α_4 and α_5 have been calculated directly with $\alpha_r = B_0 - B_r$. This is not possible for α_3 due to the Fermi resonance between states $|001\ 0^0 0^0 \Sigma\rangle$ and $|000\ 0^0 2^0 \Sigma\rangle$. Instead, the formula $B_{\nu_3} + B_{2\nu_5} = B_{\nu_3}^0 + B_{2\nu_5}^0$ has been used where $B_{\nu_3}^0$ and $B_{2\nu_5}^0$ are the unperturbed rotational constants. This leads to the formula $\alpha_3 = 2B_{\nu_5} - B_{2\nu_5} - B_{\nu_3}$. The calculated α parameters are displayed in Table 8.

7. VIBRATIONAL ANALYSIS

Tables 9 and 10 show the results of the vibrational calculation for DCC⁷⁹Br and DCC⁸¹Br, respectively. For the states with l doubling, the B constant has been calculated as the average of the respective e and f substate B constants. Deviations of observed – calculated values are shown both for the vibrational wavenumbers and for the rotational constants. Only

the vibrational wavenumber deviations have been used for the least-squares optimization.

The standard error of the fits of DCC⁷⁹Br and DCC⁸¹Br are 0.310 and 0.308 cm^{-1} , respectively. We consider both the vibrational wavenumbers and the rotational constants to be well calculated by the present resonance block model.

Table 11 lists the values for the optimized vibrational parameters and their respective standard errors. An optimization with all the parameters free was first attempted, but it resulted in parameters x_{55} and x_{35} being poorly defined. In the final optimization, these parameters were fixed to their optimized values in HCCBr from Ref. (7). These parameters are expected to have similar values in both HCCBr and DCCBr since they do not involve significantly the hydrogen or deuterium motion.

8. DISCUSSION

The energy region analyzed in the present study has been sufficiently low in order to make unambiguous vibrational

TABLE 8
The α Parameters

Parameter	DCC ⁸¹ Br	DCC ⁷⁹ Br
$\alpha_5 \times 10^4 / \text{cm}^{-1}$	– 3.230(2)	– 3.213(2)
$\alpha_4 \times 10^4 / \text{cm}^{-1}$	– 1.350(2)	– 1.338(2)
$\alpha_3 \times 10^4 / \text{cm}^{-1}$	3.961(3)	3.938(3)

Note. The uncertainties in parentheses represent 1 standard error in the last decimal place of the parameter.

TABLE 9
The Vibrational Fit for DCC⁷⁹Br

State	G_e Obs ^c /cm ⁻¹	Obs - Calc /cm ⁻¹	B / cm ⁻¹	$(B-B_0) \times 10^4$ /cm ⁻¹	$B-B_0$ Calc /cm ⁻¹	Obs - Calc /cm ⁻¹	Note
000 0 ⁰ 0 ⁺ Σ^+	0.0		0.12192165(14)	0.0	0.00	0.00	
000 0 ⁰ 1 ⁻ Π	278.7752	-0.041	0.12224466(12)	3.2301(12)	3.23	0.00	
000 1 ⁰ 0 ⁻ Π	480.6593	0.250	0.12205668(11)	1.3503(11)	1.35	0.00	
000 0 ⁰ 2 ⁺ Σ^+	541.5965	-0.040	0.12234911(50)	4.2746(50)	4.14	0.13	
000 0 ⁰ 2 ⁻ Δ	558.1319	-0.101	0.12256642(42)	6.4477(42)	6.46	-0.01	
001 0 ⁰ 0 ⁺ Σ^+	603.3132	0.984	0.12174414(14)	-1.7751(18)	-1.64	-0.14	
000 1 ¹ 1 ⁻ Σ^-	758.4762	0.231	0.12238188(19)	4.6023(19)	4.58	0.02	
000 1 ¹ 1 ⁺ Σ^+	760.7660	0.200	0.12237157(8)	4.4992(8)	4.58	-0.08	
000 1 ¹ 1 ⁻ Δ	760.9674	0.117	0.12237779(8)	4.5614(8)	4.58	-0.02	
000 0 ⁰ 3 ⁻ Π	810.7159	-0.027	0.12262001(64)	6.9836(64)	6.94	0.04	
000 0 ⁰ 3 ⁺ Φ	838.0666	-0.181	0.12288651(64)	9.6486(64)	9.69	-0.04	
001 0 ⁰ 1 ⁻ Π	891.6161	-0.207	0.12210436(14)	1.8271(14)	2.02	-0.19	
000 2 ⁰ 0 ⁺ Σ^+	955.0050	0.110	0.12219011(14)	2.6846(14)	2.70	-0.02	
000 2 ⁰ 0 ⁻ Δ	964.8037	0.116	0.12218531(15)	2.6366(15)	2.70	-0.06	
000 1 ² 2 ⁻ Π	1023.2656	-0.041	0.12244686(50)	5.2521(50)	5.41	-0.16 a	
000 1 ² 2 ⁺ Π	1039.2934	0.175	0.12269048(14)	7.6883(14)	7.77	-0.08	
000 1 ² 2 ⁺ Φ	1041.8672	-0.024	0.12269763(69)	7.7598(69)	7.81	-0.05 b	
000 0 ⁰ 4 ⁺ Σ^+	1069.4622	0.119	0.12279101(210)	8.6936(210)	8.61	0.08	
000 2 ⁰ 1 ⁻ Π	1235.3293	0.125	0.12251087(14)	5.8922(14)	5.93	-0.04	
000 2 ⁰ 1 ⁺ Π	1244.1280	-0.046	0.12250057(12)	5.7892(12)	5.93	-0.14	
000 2 ⁰ 1 ⁺ Φf	1246.6833	-0.069	0.12250475(25)	5.8310(25)	5.93	-0.10 b	
000 1 ³ 3 ⁻ Δ	1319.3851	0.093	0.12300849(45)	10.8684(45)	11.01	-0.14	
000 3 ⁰ 0 ⁻ Π	1433.2160	-0.032	0.12231820(11)	3.9655(11)	4.05	-0.08	
000 2 ⁰ 2 ⁺ Σ^+	1498.6605	-0.304	0.12258412(50)	6.6247(50)	6.67	-0.05	
000 2 ² 2 ⁻ Δ	1517.3373	0.128	0.12280322(45)	8.8157(45)	8.96	-0.14	
000 2 ² 2 ⁻ Σ^-	1523.4056	-0.231	0.12281944(21)	8.9779(21)	9.16	-0.18	
001 2 ⁰ 0 ⁺ Σ^+	1557.3883	-0.756	0.12205299(16)	1.3134(16)	1.33	-0.02	
000 1 ⁴ 4 ⁻ Φ	1600.0563	-0.027	0.12332829(90)	14.0664(90)	14.25	-0.18 b	
000 3 ¹ 1 ⁻ Σ^-	1711.7971	0.071	0.12264396(20)	7.2231(20)	7.28	-0.06	
000 3 ¹ 1 ⁻ Δ	1715.3129	0.059	0.12263606(19)	7.1441(19)	7.28	-0.14 a	
000 2 ⁰ 3 ⁻ Φ	1798.9712	0.123	0.12313113(92)	12.0948(92)	12.30	-0.21 b	
000 4 ⁰ 0 ⁺ Σ^+	1905.8099	0.134	0.12244461(14)	5.2296(14)	5.40	-0.17	
000 4 ⁰ 0 ⁻ Δ	1915.4182	-0.050	0.12243980(13)	5.1815(13)	5.40	-0.22	

^a Only e or f substate parameters could be determined for these states and the reported B values are hence for $B(e)$ or $B(f)$. However, in these levels the $B(e)$ and $B(f)$ constants have similar values and either of them is a good approximation for the average.

^b The l doubling of these states was too small to be observed. The observed parameters hence represent both parities.

^c The uncertainty in the last decimal place of the vibrational wavenumbers is less than 2.

assignments. Only in the higher overtone region mixing of the vibrational states is expected to be so prominent and complex that the normal mode notation loses its meaning and the vibrational assignment becomes problematic (4, 9).

The present work has demonstrated the importance of using as high a resolution as possible in the analysis of dense spectra. Even a small improvement in the measurement resolution will significantly add to the information obtained from the spectrum. This improvement can be noted by comparing the results obtained for the ν_4 and $2\nu_4$ band system, where a resolution increase from 0.003 to 0.002 cm⁻¹ increased the number of analyzable bands from 24 to 30 and decreased the average standard error from 0.26 to 0.15 cm⁻¹.

One should note the rotational l resonance between the states $|000 1^1 1^1 \Delta, e\rangle$ and $|000 1^1 1^1 \Sigma^+, e\rangle$. These states have been analyzed both from the ν_4 band system hot bands with the $|000 0^0 1^1 \Pi, e\rangle$ lower state and the $\nu_4 + \nu_5$ band system bands originating from the ground state. In the latter case, the $|000 1^1 1^1 \Delta, e\rangle \leftarrow |000 0^0 0^0 \Sigma^+, e\rangle$ transitions are allowed by the resonance although they are formally forbidden due to $\Delta k = 2$. Their presence allows a simultaneous analysis of the bands to both resonant states and therefore accurate determination of the resonance parameters. The same resonance parameters obtained from the ν_4 band system have similar values but are less accurate due to the relative

TABLE 10
The Vibrational Fit for DCC⁸¹Br

State	G_e Obs ^c /cm ⁻¹	Obs - Calc /cm ⁻¹	B / cm ⁻¹	$(B-B_0) \times 10^4$ /cm ⁻¹	$B-B_0$ Calc /cm ⁻¹	Obs - Calc /cm ⁻¹	Note
000 0 ⁰ 0 ⁺ Σ^+	0.0		0.12125016(17)	0.0	0.00	0.00	
000 0 ⁰ 1 ⁻ Π	278.6928	-0.041	0.12157146(16)	3.2130(16)	3.21	0.00	
000 1 ⁰ 0 ⁻ Π	480.6593	0.246	0.12138393(15)	1.3377(15)	1.34	0.00	
000 0 ⁰ 2 ⁺ Σ^+	541.0203	-0.041	0.12166522(31)	4.1506(31)	4.04	0.11	
000 0 ⁰ 2 ⁻ Δ	557.9671	-0.102	0.12189047(40)	6.4031(40)	6.43	-0.03	
001 0 ⁰ 0 ⁺ Σ^+	601.9546	0.980	0.12108392(17)	-1.6624(17)	-1.56	-0.10	
000 1 ¹ 1 ⁻ Σ^-	758.3939	0.230	0.12170770(22)	4.5754(22)	4.55	0.03	
000 1 ¹ 1 ⁺ Σ^+	760.6794	0.199	0.12169736(9)	4.4720(9)	4.55	-0.08	
000 1 ¹ 1 ⁻ Δ	760.8855	0.116	0.12170363(11)	4.5347(11)	4.55	-0.02	
000 0 ⁰ 3 ⁻ Π	809.9619	-0.021	0.12194265(60)	6.9249(60)	6.87	0.05	
000 0 ⁰ 3 ⁺ Φ	837.8204	-0.185	0.12220829(60)	9.5813(60)	9.64	-0.06	
001 0 ⁰ 1 ⁻ Π	890.2759	-0.231	0.12144088(16)	1.9072(16)	2.05	-0.14	
000 2 ⁰ 0 ⁺ Σ^+	955.0017	0.105	0.12151682(17)	2.6666(17)	2.68	-0.01	
000 2 ⁰ 0 ⁻ Δ	964.8036	0.112	0.12151194(18)	2.6178(18)	2.68	-0.06	
000 1 ² 2 ⁻ Π	1022.6684	-0.054	0.12176143(35)	5.1127(35)	5.30	-0.19 a	
000 1 ² 2 ⁺ Π	1039.1181	0.175	0.12201471(17)	7.6455(17)	7.73	-0.08	
000 1 ² 2 ⁺ Φ	1041.7038	-0.022	0.12202052(64)	7.7036(64)	7.76	-0.06 b	
000 0 ⁰ 4 ⁺ Σ^+	1068.3145	0.134	0.12209953(200)	8.4937(200)	8.52	-0.03	
000 2 ⁰ 1 ⁻ Π	1235.2430	0.125	0.12183591(17)	5.8575(17)	5.89	-0.03	
000 2 ⁰ 1 ⁺ Π	1244.0409	-0.044	0.12182526(17)	5.7510(17)	5.89	-0.14	
000 2 ⁰ 1 ⁺ Φf	1246.6023	-0.067	0.12182941(28)	5.7925(28)	5.89	-0.10 b	
000 1 ³ 3 ⁻ Δ	1319.1271	0.092	0.12233005(40)	10.7989(40)	10.95	-0.15	
000 3 ⁰ 0 ⁻ Π	1433.2098	-0.035	0.12164371(17)	3.9355(17)	4.01	-0.07	
000 2 ⁰ 2 ⁺ Σ^+	1498.0330	-0.334	0.12189733(32)	6.4717(32)	6.55	-0.08	
000 2 ² 2 ⁻ Δ	1517.1341	0.131	0.12212682(40)	8.7666(40)	8.91	-0.14	
000 2 ² 2 ⁻ Σ^-	1523.2336	-0.226	0.12214281(24)	8.9265(24)	9.10	-0.17	
001 2 ⁰ 0 ⁺ Σ^+	1556.0971	-0.721	0.12139187(18)	1.4171(18)	1.39	0.03	
000 1 ⁴ 4 ⁻ Φ	1599.7155	-0.030	0.12264522(80)	13.9506(80)	14.17	-0.22 b	
000 3 ¹ 1 ⁻ Σ^-	1711.7092	0.075	0.12196798(22)	7.1782(22)	7.23	-0.05	
000 3 ¹ 1 ⁻ Δ	1715.2239	0.064	0.12196001(22)	7.0985(22)	7.23	-0.13 a	
000 2 ⁰ 3 ⁻ Φ	1798.7016	0.129	0.12245060(80)	12.0044(80)	12.23	-0.23 b	
000 4 ⁰ 0 ⁺ Σ^+	1905.7926	0.129	0.12177028(18)	5.2012(18)	5.35	-0.15	
000 4 ⁰ 0 ⁻ Δ	1915.4089	-0.049	0.12176447(13)	5.1431(13)	5.35	-0.21	

^a Only e or f substate parameters could be determined for these states and the reported B values are hence for $B(e)$ or $B(f)$. However, in these levels the $B(e)$ and $B(f)$ constants have similar values and either of them is a good approximation for the average.

^b The l doubling of these states was too small to be observed. The observed parameters hence represent both parities.

^c The uncertainty in the last decimal place of the vibrational wavenumbers is less than 2.

TABLE 11
The Optimized Spectroscopic Parameters
for the Vibrational Model

Constant	DCC ⁷⁹ Br /cm ⁻¹	DCC ⁸¹ Br /cm ⁻¹
$\tilde{\nu}_3$	588.788(361) ^b	587.206(361)
$\tilde{\nu}_4$	480.410(107)	480.414(107)
$\tilde{\nu}_5$	278.816(95)	278.734(94)
x_{44}	-0.514(44)	-0.516(43)
x_{55}	-0.464 ^a	-0.509 ^a
x_{35}	2.823 ^a	3.022 ^a
x_{45}	0.902(59)	0.898(58)
g_{44}	2.448(50)	2.449(50)
g_{45}	0.723(51)	0.724(51)
g_{55}	0.764(43)	0.810(43)
k_{355}	-35.735(223)	-35.647(223)
r_{45}	1.161(112)	1.158(117)

^a Fixed to the respective values for HCC⁷⁹Br and HCC⁸¹Br due to limited amount of data.

^b The uncertainties in parenthesis represent 1 standard error in the last decimal place of the parameter.

weakness of the hot bands as compared to bands originating from the ground vibrational state.

Also notable is the weakening of the l doubling of the e and f parity states as the coupling becomes more and more indirect. In the direct doubling case, for example, between $|000\ 0^0 1^1 \Pi, e\rangle$ and $|000\ 0^0 1^1 \Pi, f\rangle$, the rotational constants of the states differ from each other considerably and two clearly separate bands are observed. The doubling of states $|000\ 0^0 2^2 \Pi, e\rangle$ and $|000\ 0^0 2^2 \Pi, f\rangle$ is, on the other hand, indirect in the first order, and the difference of the B constants is therefore smaller. This causes the bands to merge together and they separate only at high J values, as seen in the Loomis–Wood image of Fig. 1. The doubling of $|000\ 0^0 3^3 \Pi, e\rangle$ and $|000\ 0^0 3^3 \Pi, f\rangle$ is even weaker and hot bands with these lower states are completely merged at the present resolution.

Whereas most rotational levels can be accurately calculated with only B and D parameters, the vibrational states involving ν_3 (C–Br stretching) need additional H parameters due to a Fermi resonance between the ν_3 and $2\nu_5$ states. The effect of this resonance is incorporated into the effective H parameters in the rotational fit, whereas the vibrational fit includes the resonance explicitly.

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