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High-Resolution Infrared Study of the Fundamental Bands of Deuteroiodoacetylene

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The high-resolution infrared spectrum of deuterated iodoacetylene has been measured in the region 200–2700 cm^{-1}. In addition to all five fundamentals, the bands $2\nu_4^0$ and $2\nu_5^0$ have been identified. The measurements were carried out by using a Fourier transform spectrometer at room temperature with instrumental resolution of about 0.0020 cm^{-1}. The ground state rotational constants $B_0 = 0.0970742961(72)\ \mathrm{cm}^{-1}$, $D_0 = 1.38482(20) \times 10^{-8}\ \mathrm{cm}^{-1}$, and $H_0 = -1.47(10) \times 10^{-15}\ \mathrm{cm}^{-1}$ have been determined by combining 462 ground state combination differences from the same bands mentioned above with accurate MW data from the literature. In addition, the molecular constants for all the fundamental levels have been obtained.

I. INTRODUCTION

Deuterated monoiodoacetylene, DCCI, is a linear molecule with five fundamental vibrations, three stretching modes of Σ^+ symmetry (C–D stretch at 2600 cm^{-1}, C–C stretch at 1930 cm^{-1}, and C–I stretch at 530 cm^{-1}), and two bending modes of Π symmetry (C–C–I bend at 250 cm^{-1} and C–C–D bend at 490 cm^{-1}). The IR studies of the DCCI molecule are almost entirely missing. Only the ν_1 band has previously been observed in our laboratory (*1*). The dipole moment of the molecule is very small and so there are problems when applying the microwave technics. Only recently the first observations have been made. Heineking and co-workers (*2–4*) have observed two rotational transitions $J = 1 \leftarrow 0$ and $J = 3 \leftarrow 2$ including eight and three hyperfine components, respectively. The accurate B and D rotational constants for the ground state have been reported (*2*).

The series of high-resolution infrared studies on the normal isotopic species of iodoacetylene has been going on in our laboratory during the past years (*5, 6*). As a natural continuation, we have started the measurements on the spectrum of deuterated species, DCCI. The present work reports the analysis of the fundamental bands of this molecule. Ground state rotational constants and molecular constants for all the fundamental levels have been obtained with high precision. In addition to the fundamentals, the $2\nu_4^0$ and $2\nu_5^0$ bands have been measured and applied in the ground state analysis. Our purpose is to continue the present studies with analyses of the numerous hot bands observed in the measured spectra and further to determine the harmonic force field of the HCCI molecule, in general.

II. EXPERIMENTAL DETAILS

The deuterated monoiodoacetylene sample was produced in our laboratory using the method of Brown and Tyler (*7*). In the process, in hypoiodite solution, the hydrogen of acetylene is replaced by iodine. At first, we made the weakly alkaline hypoiodite solution by adding iodine to potassium hydroxide. To obtain the other exchange reaction, too, the solution was prepared in deuterium oxide instead of normal water. Then acetylene was bubbled slowly through this solution and diiodoacetylene sedimented as a main product of the reaction. Deuteromonoiodoacetylene gas was collected in a trap at a temperature of −75°C and then distilled into the sample cell. The sample includes small amounts of acetylene and water as impurity, which can be seen in the spectrum. The spectrum shows that the species HCCI is present in the sample, too.

The measurements were performed with a Bruker IFS 120 HR FTIR spectrometer in Oulu. The components used in different spectral regions together with further experimental details are given in Table 1. All the measurements were performed at room temperature. The overview spectra of the fundamental bands are shown in Fig. 1 and a small part of the spectrum around the ν_5 Q branch in Fig. 2 illustrates the spectral overlap in the low wavenumber region. The spectra of the five fundamentals were measured in three different regions. The lowest one includes ν_3, ν_4, ν_5, and $2\nu_5^0$ bands between 230–550 cm^{-1}. The highest stretching, ν_1 at 2600 cm^{-1}, and the weakest of the fundamentals, ν_2 at 1930 cm^{-1}, were measured separately. In addition to the fundamentals and $2\nu_5^0$, the rather strong overtone band $2\nu_4^0$ at 1000 cm^{-1} was measured. In the calibration of the ν_1, ν_2, and $2\nu_4^0$ region spectra, the accurate N_2O and OCS lines were used (*8–10*).

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TABLE 1
Experimental Details of the Measurements of DCCI

Band	ν_1	ν_2	ν_3	ν_4	ν_5	$2\nu_4^0$	$2\nu_5^0$
Region [cm^{-1}]	2573-2621	1916-1951	511-542	468-519	228-275	956-1003	455-492
Source	Globar	Globar	Globar	Globar	Globar	Globar	Globar
Detector	InSb (77 K)	InSb (77 K)	Bolometer (1.8 K)	Bolometer (1.8 K)	Bolometer (1.8 K)	MCT (77 K)	Bolometer (1.8 K)
Beamsplitter	Ge on KBr	Ge on KBr	Mylar 3.5μm	Mylar 3.5μm	Mylar 3.5μm	Ge on KBr	Mylar 3.5μm
Windows	KBr	KBr	KRS5	KRS5	KRS5	KBr	KRS5
Doppler width [cm^{-1}]	0.0026	0.0019	0.0005	0.0005	0.0003	0.0010	0.0005
Instrumental resolution	0.0020	0.0020	0.00185	0.00185	0.00185	0.0020	0.00185
Experimental linewidth	0.0045	0.0035	0.0020	0.0020	0.0020	0.0025	0.0020
Sample pressure [Pa]	52	52	40	40	40	52	40
Path length [m]	3.2	19.2	6.4	6.4	6.4	19.2	6.4
Calibration	N_2O (8)	OCS (9)	H_2O (11)	H_2O (11)	H_2O (11)	OCS (10)	H_2O (11)

The calibration of the crowded lower region spectra (ν_3, ν_4, ν_5, and $2\nu_5^0$) was performed with 42 water lines (*11*) observed in the spectrum as impurity.

III. ANALYSIS AND RESULTS

1. *Ground State Constants*

In the assignment work the Loomis–Wood program (*12*) was used. The number of assigned lines with the highest observed J values are shown in Table 2. As a first step of the analysis the ground state rotational constants were determined. The differences $\delta(J, \Delta J = 2) = \nu_R(J) - \nu_P(J + 2)$ between the observed P and R lines, with the same upper state, were first calculated. Then the polynomial

$$\begin{aligned}\delta(J, \Delta J) = {} & B_0[(J + \Delta J)(J + \Delta J + 1) - J(J + 1)] \\ & - D_0[(J + \Delta J)^2(J + \Delta J + 1)^2 - J^2(J + 1)^2] \qquad [1] \\ & + H_0[(J + \Delta J)^3(J + \Delta J + 1)^3 - J^3(J + 1)^3],\end{aligned}$$

where $\Delta J = 2$ in the case of IR data, was fitted to these differences. The ground state rotational constants were obtained from each observed band separately. The fits agree well with each other, and because the standard deviations of the separate fits are nearly equal, the differences of all the bands were put into the same final IR fit with equal weights. The results are seen in the upper part of Table 3. The constant H is not well determined in the separate fits but the statistical accuracy is clearly improved in the combined IR analysis. The present values are in good agreement with the results of MW analysis (*2*) shown in Table 3, too.

The next step was to add the rotational transitions from Ref. (*2*) to the fit. Since the rotational lines exhibit hyperfine structure, the unsplit line positions were first calculated using the same hyperfine model and constants as in Ref. (*2*). Then for these corrected lines Eq. [1] was used with $\Delta J = 1$. Estimated from the standard deviations, 1.2 kHz (Ref. (*2*)) and 4.7×10^{-5} cm^{-1} (Table 3), the relative weights of 10^6 were given to the rotational lines.

The obtained constants with some statistical information from both the separate and final fits are seen in Table 3. The values obtained seem to be reasonable when compared with those of HCCI, which are listed at the end of Table 3.

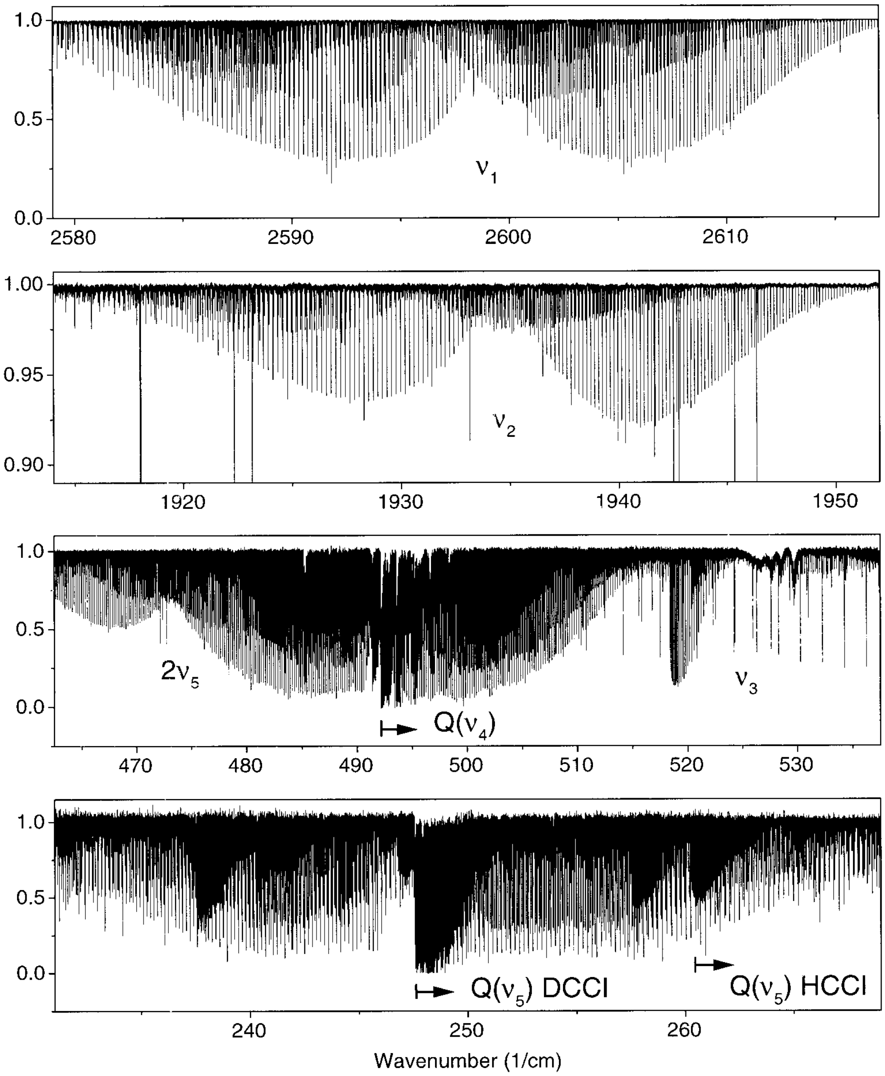

FIG. 1. Overview spectra of the fundamental bands of DCCI. Experimental conditions are given in Table 1. Note the transmittance scale in the case of the very weak ν_2 band. The *P* branch of the ν_3 band is seen just under the *Q* branch at 520 cm^{-1} and the *R* branch is the weak series above 530 cm^{-1}. A strong Fermi resonance mixes the upper states of the bands $2\nu_5^0$ and ν_3 badly. The assignments given here are based on the mixing ratios obtained from the preliminary analysis of this resonance.

2. *Upper State Constants*

In each vibrational level, the unperturbed vibration–rotation term values are the diagonal elements of the conventional energy matrix. For a linear molecule they are expressed as

$$T_{v,l,J} = G_v + B_v[J(J+1) - l^2] - D_v[J(J+1) - l^2]^2 + H_v[J(J+1) - l^2]^3. \qquad [2]$$

For a stretching mode with Σ^+ symmetry the term values are calculated from this expression with $l = 0$. In the case of a bending fundamental with Π symmetry, the term values are obtained by substituting $l = \pm 1$ and by using an auxiliary term $\pm\frac{1}{2}[q_t + q_t^J J(J+1)]J(J+1)$ resulting from the *l* doubling. Equation [2] is applied for the ground state with G_v, v, and l set to zero.

In the analysis of the bands, the ground state constants were constrained according to the values from the final fit (DCCI) given in Table 3. The summary of the experimental data with the range of rotational levels is given in Table 2 and the results from the fits are collected in Table 4. Furthermore, by using the results from Tables 3 and 4, the rotational constants B_v and the centrifugal

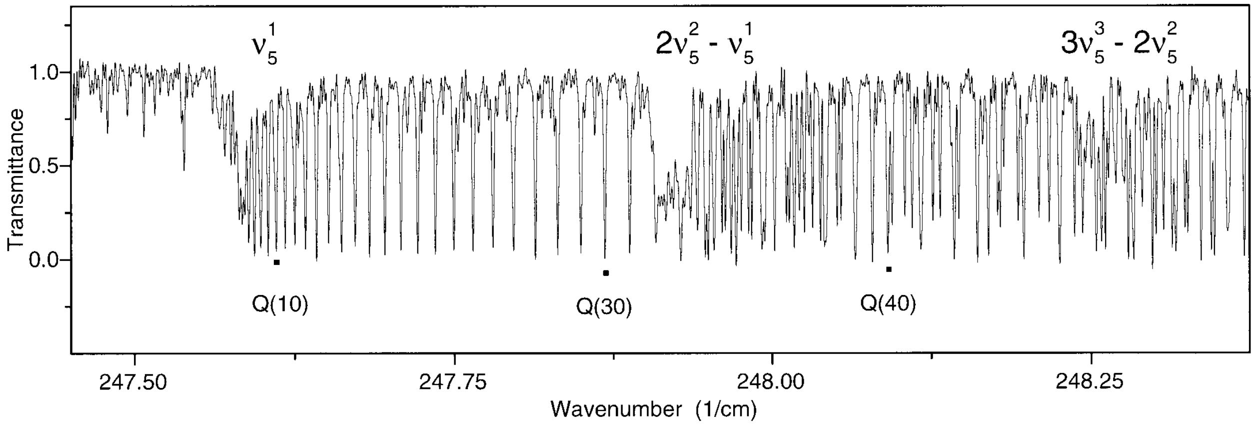

FIG. 2. Part of the spectrum in the region of the ν_5 *Q* branch to illustrate the density of the spectra. The bending CCI is very low in wavenumbers and so many hot bands starting from the level $v_5 = 1$ and from its overtones can be seen in the spectra.

distortion constants D_v and H_v have been calculated and listed in Table 5.

IV. DISCUSSION

Mainly because of the large quadrupole moment and spin of iodine nucleus, the two-nuclei (D and I) hyperfine splittings are quite conspicuous in the DCCI molecule; see again the rotational transitions in Ref. (*2*). The effects are so large that they can be seen in the low *J* infrared lines, too. These lines appear slightly broadened and are, unfortunately in our point of view, clearly shifted from their unperturbed positions. Our model did not include the hyperfine effects and so we had to exclude the lines with $J \leqslant 5$ in all the bands from the analysis. Another reason for rather large line omission, see Table 2, is the growdiness of the spectra. Especially in low wavenumber region, see Figures 1 and 2, lots of lines were extracted. Furthermore, in the case of ν_1 band there seems to be a local resonance. The *P* and *R* lines up to $J = 15$ are symmetrically shifted and had to be left out from the analyses, while in the calculation of combination differences they could be used.

When comparing the resulting constants for the upper levels of the fundamentals in Table 4, it can be noticed that the constants for the ν_3 band are anomalous. As known from the corresponding investigation on HCCI (*5*, *6*), the level $v_3 = 1$ is strongly coupled to the overtone level $v_5 = 2$

TABLE 2

Number of Assigned Lines Together with the Number of Lines Actually Used in the Analyses of the Upper States of DCCI

	Assignments			Upper state analysis		
Band	P, R	Q	J_{max}	P, R	Q	J_{max}
ν_1	244		137	186		136
ν_2	178		96	143		85
ν_3	146		80	108		80
ν_4	249	99	131	206	69	130
ν_5	229	116	122	179	66	122
$2\nu_4^0$	237		123			
$2\nu_5^0$	175		108			

Note: The number of combination differences used in ground state analysis is given in Table 3.

TABLE 3
Ground State Constants (in cm^{-1}) of DCCI

	B_0	D_0 x 10^{-8}	H_0 x 10^{-15}	Number of diff.	J_{max}	Std. dev. x 10^{-5}
Separate fits						
ν_1	0.097 074 314 3(670) [a]	1.386 91(110)	-0.26(49)	75	116	3.8
ν_2	0.097 074 240 7(1200)	1.378 68(380)	-8.88(340)	60	81	4.5
ν_3	0.097 074 516 3(2300)	1.388 04(990)	-7.33(1300)	39	68	5.7
ν_4	0.097 074 492 8(680)	1.386 39(77)	-1.05(26)	89	129	4.3
ν_5	0.097 074 491 6(930)	1.388 63(160)	0.87(84)	64	106	4.5
$2\nu_4^0$	0.097 074 218 9(640)	1.383 67(92)	-2.03(39)	91	118	4.0
$2\nu_5^0$	0.097 074 302 7(1500)	1.384 92(460)	-0.49(410)	44	80	4.8
IR fit	0.097 074 338 1(300)	1.385 34(41)	-1.29(16)	462	129	4.7
MW, Ref.(2)	0.097 074 288 0(80)	1.33(7)				
DCCI [b]	0.097 074 296 1(72)	1.384 82(20)	-1.47(10)			
HCCI, Ref.(5)	0.105 942 095 0(510)	1.733 90(86)	-2.27(42)	448	113	

[a] The error limits are one standard deviation in the units of the last digit given.

[b] Simultaneous fit of 462 differences from IR bands and 2 rotational transitions, weighted with 10^6, from Ref. (2).

by Fermi resonance. There exists also an l-type resonance between the Σ ($l_5 = 0$) and Δ ($l_5 = \pm 2$) states at the overtone level $v_5 = 2$. So, these coupled energy levels cannot be analyzed only by using the overtone $2\nu_5^0$ and the fundamental ν_3. To obtain the unperturbed molecular constants for the fundamental level $v_3 = 1$, the hot bands $2\nu_5^{0,\pm 2} - \nu_5^1$ and $\nu_3 - \nu_5^1$ appearing in the ν_5 region must be simultaneously analyzed.

TABLE 4
Results from the Analyses of the Fundamental Bands of DCCI (in cm^{-1})

	$v_1 = 1$	$v_2 = 1$	$v_3 = 1$	$v_4 = 1$, $\ell_4 = \pm 1$	$v_5 = 1$, $\ell_5 = \pm 1$
G_v	2599.123 089(10) [a]	1934.610 045(7)	525.839 908(14)	492.275 499(8)	247.673 326(8)
$B_0 - B_v$ [10^{-4}]	2.486 320(60)	3.217 334(100)	0.150 246(240)	-0.871 143(47)	-2.714 586(59)
$D_0 - D_v$ [10^{-10}]	0.805 8(88)	0.442(37)	30.357(98)	-0.508 2(75)	-3.602(11)
$H_0 - H_v$ [10^{-16}]	-4.49(35)	-35.9(36)	-11.5(110)	7.30(34)	-2.46(51)
q_t [10^{-5}]				-4.391 10(37)	-8.600 10(38)
q_t^J [10^{-10}]				0.503 6(37)	1.094 1(36)
Number of lines	186	143	108	275	245
Std.dev. [10^{-5}]	5.1	3.3	5.7	4.7	4.9

[a] The error limits are one standard deviation in the units of the last digit given.

TABLE 5
Calculated Rotational Constants (in cm^{-1}) of the Fundamental Levels of DCCI

	$v_1 = 1$	$v_2 = 1$	$v_3 = 1$	$v_4 = 1,\ \ell_4 = \pm 1$	$v_5 = 1,\ \ell_5 = \pm 1$
B_v	0.096 825 664 1(132)[a]	0.096 752 562 8(172)	0.097 059 271 6(312)	0.097 161 410 4(119)	0.097 345 754 8(131)
D_v $[10^{-8}]$	1.376 761(288)	1.380 396(570)	1.081 254(1180)	1.389 901(275)	1.420 840(310)
H_v $[10^{-15}]$	-1.021(135)	2.121(460)	10.07(120)	-2.200(134)	-1.224(151)

[a] The error limits are the sums of the standard deviations of the components used in the calculations.

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