

Precise Measurement of the Pure Rotational Submillimeter-Wave Spectrum of HCl and DCl in Their $v = 0, 1$ States

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High-resolution sub-Doppler Lamb-dip measurements were performed on the low- J pure rotational transitions of the hydrogen chloride isotopomers H^{35}Cl , H^{37}Cl , D^{35}Cl , and D^{37}Cl in the submillimeter-wave region up to 646 GHz. For the $J = 1-0$ transitions of the two HCl isotopomers, the hyperfine splitting due to the hydrogen nuclear spin-rotation interaction is resolved. Furthermore Doppler-limited lines of the DCl $J = 3 \leftarrow 2$ transition around 965 GHz as well as hyperfine-resolved rotational transitions in the first excited vibrational state were recorded up to 1.22 THz. The new frequencies were analyzed in a global fit together with FIR data yielding a set of mass-invariant rotational parameters. Isotopically invariant hyperfine parameters were obtained also from the global fit. Inclusion of the precise results from molecular beam electric resonance measurements allowed the determination of higher orders of the vibrational and rotational expansion coefficients of the chlorine and hydrogen hyperfine interactions. The precise transition frequencies reported here should be useful as secondary calibration standards in the submillimeter-wave and terahertz region. © 1998 Academic Press

1. INTRODUCTION

Highly precise sub-Doppler frequency measurements of rotational transitions in the submillimeter-wave region have not been reported often in the past. Van Dijk and Dymanus investigated the molecular beam spectra of HBr and DBr ($1, 2$) at 500 and 254 GHz, respectively. Sub-Doppler Lamb-dip measurements of frequencies up to 700 GHz were the subject of our previous work on NH_3 ($3, 4$) and CO (5). Another molecule of interest for this kind of investigation is hydrogen chloride, HCl, since it is one of the important secondary frequency standards for the FIR region (6).

Pure rotational laboratory spectra of HCl isotopomers were first reported by Burrus *et al.* (7), Cowan and Gordy (8), and Jones and Gordy (9). These investigations were later extended to higher frequencies by De Lucia *et al.* (10). The high- J rotational spectrum was measured up to 6 THz by tunable far-infrared (TuFIR) spectroscopy by Nolt *et al.* (11) for HCl and by Fusina *et al.* (12) for DCl. Both works resolved the hyperfine structure (hfs) caused by the magnetic moments of the ^{35}Cl and ^{37}Cl nuclei with spins I of $3/2$. The work on DCl analyzed the hyperfine structure consisting of electric quadrupole and nuclear spin-rotation interactions, governed by the constants eQq and C_I , respectively. Lewen *et al.* (13) measured recently the D^{35}Cl $6 \leftarrow 5$ ($v = 0$) transition at 1.936 THz using a backward-wave oscillator (BWO) mixed with the radiation from a FIR laser. FIR lines of HCl in the $v = 1$ state obtained by TuFIR spectroscopy were reported by De Natale *et al.* (14). They observed pure rotational transitions from the $3 \leftarrow 2$ at 1.8 THz up to the 9

$\leftarrow 8$ transition at 5.4 THz without resolving the chlorine hyperfine structure. Higher rotational transitions in the $v = 0$ and 1 states had been observed previously in emission by Le Blanc *et al.* (15).

A highly precise study of the hyperfine structure in H^{35}Cl and D^{35}Cl has been carried out by Kaiser (16), who measured directly the hyperfine splittings in a molecular beam resonance experiment. He determined the dipole moments and the hyperfine constants $eQq(\text{Cl})$, $eQq(\text{D})$, $C_I(\text{Cl})$, and $C_I(\text{H})$ for different vibrational and rotational states.

Recently, HCl rotational spectra were observed in the submm-wave region with the NASA Kuiper Airborne Observatory (KAO). The H^{35}Cl $J = 1 \rightarrow 0$ transition at 626 GHz was detected in absorption against the dust continuum of the molecular cloud Sgr B2 (17). IR absorption spectra were observed in atmospheres of stars (18), Earth (19), and Venus (20). Vibrationally excited HCl was recently detected in absorption in the UV spectrum of diffuse clouds toward Zeta Ophiuchi with the Hubble Space Telescope (21).

In this work, Lamb-dip spectra of the low- J pure rotational transitions up to 646 GHz for HCl and DCl are presented. In addition, the $J = 3 \leftarrow 2$ transition of DCl at 970 GHz was measured, and, for the first time, the submm-wave transitions were observed in the first excited vibrational state between 316 and 1215 GHz.

2. EXPERIMENTAL DETAILS

Details of the Cologne terahertz spectrometer have been given previously ($22, 23$). Summarized, frequency-stabi-

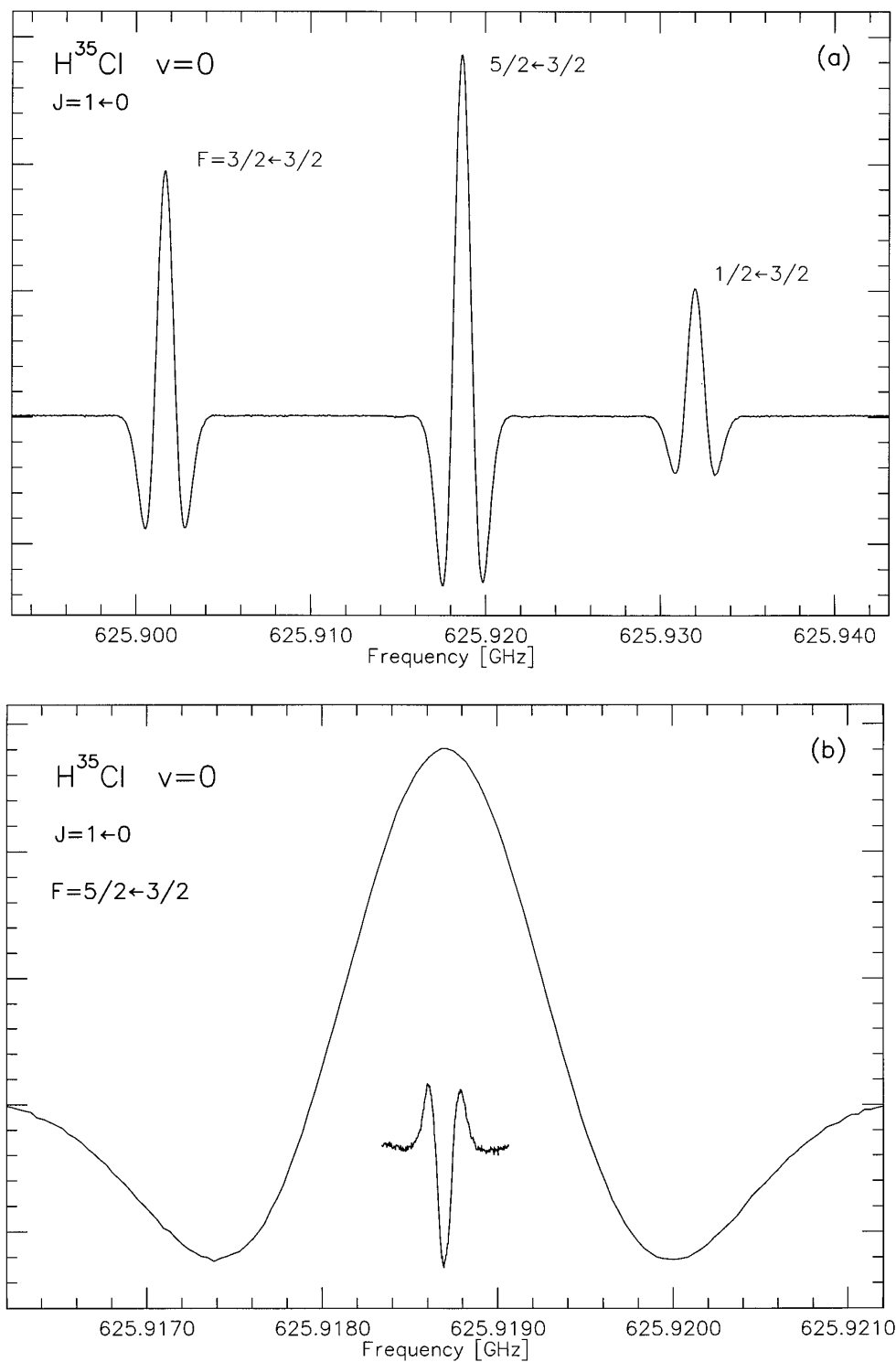


FIG. 1. The H^{35}Cl $J = 1 \leftarrow 0$ rotational transition at 625.9 GHz. Panel (a) shows the Doppler-limited spectrum of all three hyperfine transitions and (b) in comparison the Lamb-dip measurement for the strongest hfs line. The width of the Doppler profile is 1.3 MHz, and that of the Lamb-dip 90 kHz.

lized backward-wave oscillators were used in the frequency region between 300 GHz and 1.3 THz. The absorption signals were detected by a liquid helium-cooled, mag-

netically tuned InSb hot electron bolometer providing enhanced sensitivity up to 1.6 THz. Commercially available HCl and DCl gases were used in a 3.9-m absorption

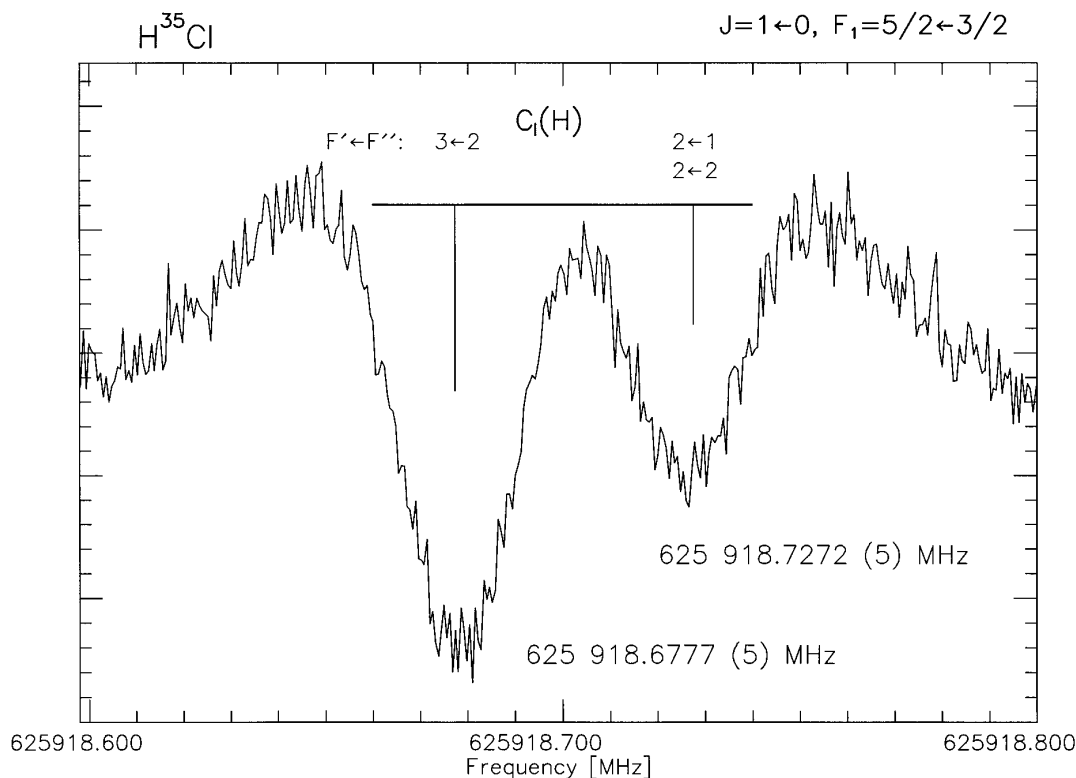


FIG. 2. Higher resolution measurement of the Lamb-dip shown in Fig. 1b. Calculated frequencies and relative intensities of the hydrogen hyperfine components are indicated. The linewidth of the Lamb-dips is about 25 kHz. The accuracy of the frequency positions is estimated to 500 Hz.

cell. These samples contain the chlorine isotopomers in natural abundance, i.e., 75.77% for ^{35}Cl and 24.23% for ^{37}Cl (24). For the Lamb-dip measurements, the sample pressure was maintained between 5 and 10 μbar , whereas higher pressures up to 40 μbar were used for the Doppler-limited measurements. Especially for the weak transitions in the excited vibrational state, higher sample pressures yielded better signal-to-noise ratios.

Figures 1 and 2 show in a sequence of recordings the effect of increased frequency resolution. In Fig. 1a the Doppler-limited complete hyperfine pattern of the H^{35}Cl $J = 1 \leftarrow 0$ transition is presented, whereas Fig. 1b depicts the strongest and central component $F = 5/2 \leftarrow 3/2$ recorded in the Doppler and sub-Doppler mode. The experimental uncertainty for the Lamb-dips is estimated to 3 kHz. The minimum linewidth of the Lamb-dips (about 90 kHz) is limited mainly by the internal line structure due to the hydrogen hyperfine interaction. This nuclear spin-rotation interaction could be resolved for the $F_1 = 5/2 \leftarrow 3/2$ lines of H^{35}Cl and H^{37}Cl after technical improvement of the KVARZ synthesizers. Figure 2 displays this result for the H^{35}Cl transition. In the case of the other HCl lines

the spin-rotation splitting is smaller and could not be fully resolved.

The increased resolution provided by saturation-dip spectroscopy is demonstrated in Fig. 3 where the partly resolved chlorine hfs in the Doppler-limited spectrum for the D^{35}Cl $J = 2 \leftarrow 1$ transition at 646.5 GHz is far better resolved by the Lamb-dip spectra. Finally, Fig. 4 displays the Doppler-limited recording of the $J = 3 \leftarrow 2$ transition of D^{35}Cl in the $v = 1$ state. Tables 1 and 2 list the determined frequencies of the newly measured transitions. The frequencies were determined by fitting a parabolic function to the measured lines.

3. ANALYSIS AND DISCUSSION

For HCl, only the pure rotational part of the Hamiltonian plus the hyperfine interactions due to nuclear spins of the Cl isotopes have to be considered here. The hydrogen hyperfine interaction was observed in a later stage of the measurements and is also included in the analysis. The electric quadrupole and the nuclear spin-rotation interaction are expressed by the corresponding isotopically invariant parameters as re-

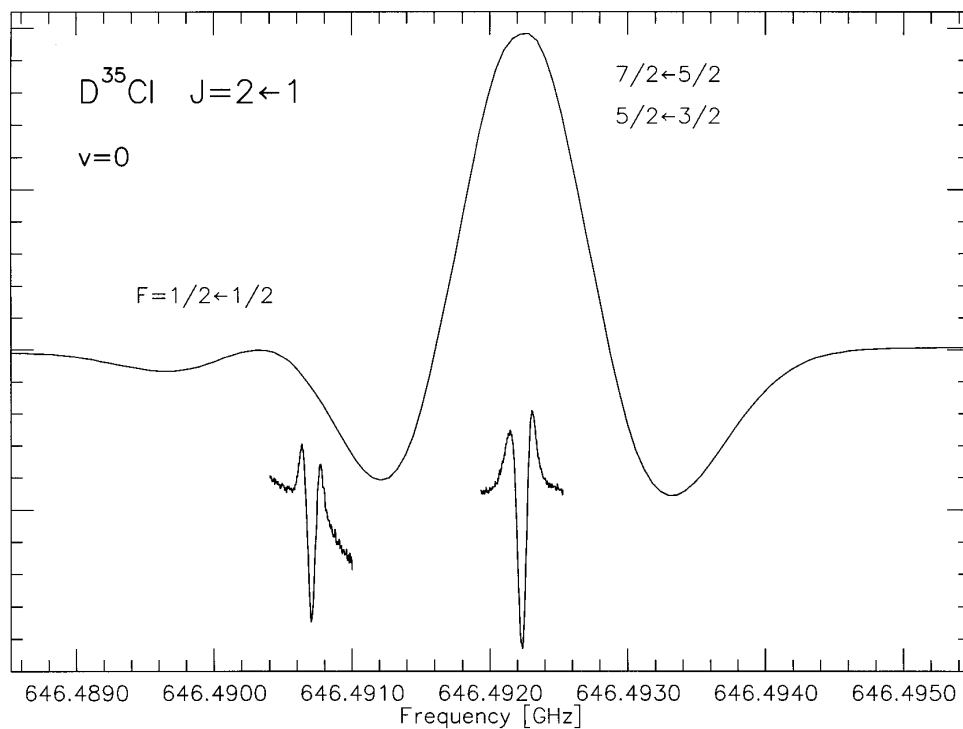


FIG. 3. Comparison of the Doppler-limited and Lamb-dip spectrum of the $D^{35}\text{Cl}$ $J = 2 \leftarrow 1$ transition at 646.5 GHz. The higher experimental resolution of the chlorine hyperfine splitting achieved by the Lamb-dip measurements is clearly visible.

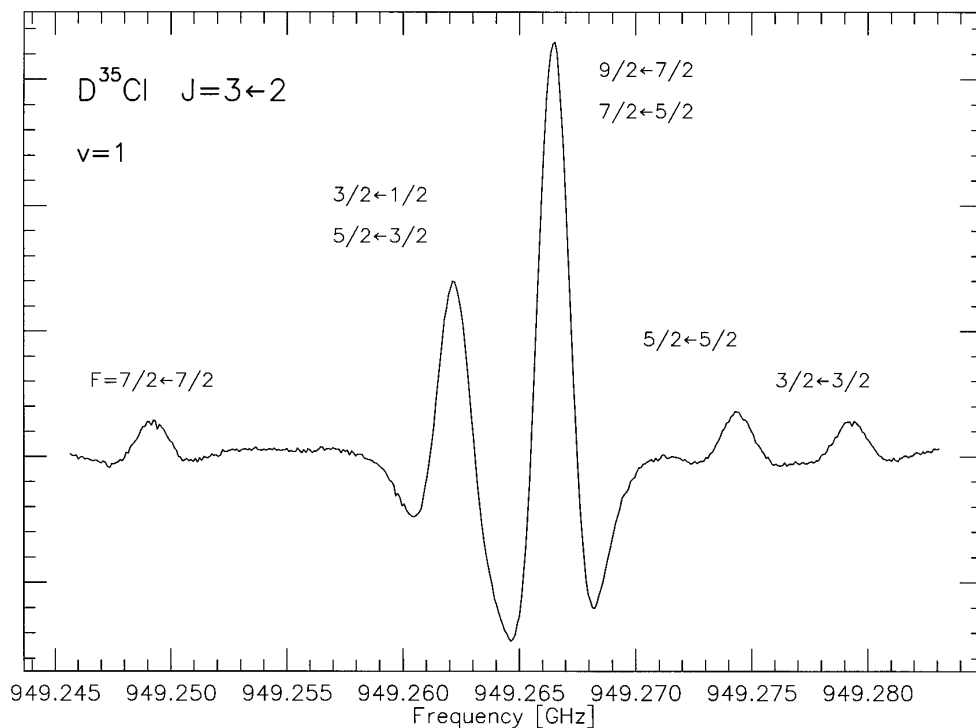


FIG. 4. The $J = 3 \leftarrow 2$ transition of $D^{35}\text{Cl}$ in the $v = 1$ state at 969.49 GHz.

TABLE 1
Observed Frequencies of Sub-Doppler HCl and DCl Lines in the $v = 0$ State

$J' F_1' F' \leftarrow J'' F_1'' F''$	ν_{exp}^a [MHz]	O–C ^b [kHz]	ν_{exp} [MHz]	O–C [kHz]	ν_{exp} [MHz]	O–C [kHz]	ν_{exp} [MHz]	O–C [kHz]
	H ³⁵ Cl		H ³⁷ Cl		D ³⁵ Cl		D ³⁷ Cl	
1 1.5 \leftarrow 0 1.5	625 901.6584(30)	-0.5	624 964.3694(30)	0.6	323 282.2085(30)	-2.2	322 338.9345(30)	1.6
1 2.5 3 \leftarrow 0 1.5 2	625 918.6777 (5)	0.3	624 977.7815 (5)	0.2	323 299.1290(30)	1.4 ^c	322 352.2639(30)	-2.9 ^c
1 2.5 2 \leftarrow 0 1.5 1	625 918.7272 (5)	-0.4 ^c	624 977.8311 (5)	-0.3 ^c	323 299.1290(30)	1.4 ^c	322 352.2639(30)	-2.9 ^c
1 2.5 2 \leftarrow 0 1.5 2	625 918.7272 (5)	-0.4 ^c	624 977.8311 (5)	-0.3 ^c	323 299.1290(30)	1.4 ^c	322 352.2639(30)	-2.9 ^c
1 0.5 \leftarrow 0 1.5	625 932.0081(30)	1.3	624 988.2821(30)	1.7	323 312.4994(30)	2.5	322 362.7986(30)	0.9
2 1.5 \leftarrow 1 0.5					646 473.881(10)	-5.7	644 585.768(10)	-4.2
2 2.5 \leftarrow 1 2.5					646 475.282(10)	-5.8	644 586.870(10)	-4.7
2 1.5 \leftarrow 1 2.5					646 487.255(10)	-0.9	644 596.301(10)	-2.0
2 0.5 \leftarrow 1 0.5					646 490.695(10)	1.1	644 599.017(10)	0.1
2 3.5 \leftarrow 1 2.5					646 492.2290(50)	4.6 ^c	644 600.2292(50)	4.3 ^c
2 2.5 \leftarrow 1 1.5					646 492.2290(50)	4.6 ^c	644 600.2292(50)	4.3 ^c
2 1.5 \leftarrow 1 1.5					646 504.167(10)	-5.8	644 609.635(10)	-1.9
2 0.5 \leftarrow 1 1.5					646 520.978(10)	-4.3	644 622.880(10)	-1.6

^aIn brackets: Estimated uncertainties of the experimental frequencies. F' and F'' values are omitted for unresolved hydrogen hyperfine splittings.

^bO–C: Observed minus calculated frequencies.

^cCalculated frequency taken as the weighted average of the hfs components.

cently employed by Saleck *et al.* (25). For a diatomic molecule, the rovibrational matrix elements are most conveniently expressed by Dunham-type series involving isotopically invariant parameters U_{ij} :

$$\begin{aligned} \langle J'F; v | H_{\text{Rot}} | JF; v \rangle \\ = \delta_{J'J} \sum_{i,j=0}^{\infty} \mu^{-(i/2+j)} U_{ij} (v + 1/2)^i [J(J+1)]^j. \end{aligned} \quad [1]$$

Here μ is the reduced mass in atomic mass units. If the breakdown of the Born–Oppenheimer approximation has to be taken into account, the rotational constant U_{01} should be replaced by the expression (26)

$$U_{01} = U_{01}^e + U_{01}^A \left(1 - \frac{M_A^0}{M_A} \right) + U_{01}^B \left(1 - \frac{M_B^0}{M_B} \right), \quad [2]$$

where A and B denote the isotopes of the different nuclei and M_A^0 and M_B^0 the atomic masses of the reference isoto-

pomer, here $^1\text{H}^{35}\text{Cl}$. U_{01}^A and U_{01}^B are the corrections to the Born–Oppenheimer approximation; their conversion to Watson's Δ_{01} constants is given by (26)

$$\Delta_{01}^A = - \frac{M_A^0}{m_e U_{01}^{\text{BO}}} U_{01}^A \quad [3]$$

and analogously for Δ_{01}^B . U_{01}^{BO} is defined as $U_{01}^e + U_{01}^A + U_{01}^B$. The explicit matrix elements for the hfs interactions used here are given in Ref. (25). Besides the atomic masses, the magnetic moments of the two chlorine nuclei (24) were included in the fitting procedure. In the case of the electric quadrupole moments, the more accurately known ratio $Q(^{35}\text{Cl})/Q(^{37}\text{Cl})$ was taken from Ref. (27) instead of their absolute values.

Together with the $v = 0$ frequencies reported by TuFIR spectroscopy up to 6 THz (11, 12), the new line positions were subjected to a global least-squares fit, where each line was weighted proportionally to the inverse square of its ex-

TABLE 2
Observed Frequencies of Doppler-Limited HCl and DCl Lines in the $v = 0, 1$ States

J'	$F' \leftarrow J''$	F''	ν_{exp}^a [MHz]	O-C ^b [kHz]	ν_{exp} [MHz]	O-C [kHz]	ν_{exp} [MHz]	O-C [kHz]	ν_{exp} [MHz]	O-C [kHz]
			H³⁵Cl		H³⁷Cl		D³⁵Cl		D³⁷Cl	
			$v = 1$				$v = 1$			
1	1.5 \leftarrow 0	1.5	607 674.093(250)	-10			316 541.156(200)	-71	315 627.583(200)	-83
1	2.5 \leftarrow 0	1.5	607 691.205(250)	-350 ^d			316 558.354(200)	-73	315 641.138(200)	-81
1	0.5 \leftarrow 0	1.5	607 705.152(250)	-51			316 572.013(200)	-28	315 651.924(200)	-21
2	2.5 \leftarrow 1	2.5	1 214 983.846(300)	-247 ^c			632 993.560(200)	-128 ^c	631 164.772(200)	-32 ^c
2	1.5 \leftarrow 1	0.5	1 214 983.846(300)	-247 ^c			632 993.560(200)	-128 ^c	631 164.772(200)	-32 ^c
2	0.5 \leftarrow 1	0.5	1 215 002.106(100)	38 ^c	1 213 205.080(100)	14 ^c	633 011.524(100)	-78 ^c	631 178.821(100)	-101 ^c
2	3.5 \leftarrow 1	2.5	1 215 002.106(100)	38 ^c	1 213 205.080(100)	14 ^c	633 011.524(100)	-78 ^c	631 178.821(100)	-101 ^c
2	2.5 \leftarrow 1	1.5	1 215 002.106(100)	38 ^c	1 213 205.080(100)	14 ^c	633 011.524(100)	-78 ^c	631 178.821(100)	-101 ^c
2	1.5 \leftarrow 1	1.5	1 215 014.067(500)	-393			633 023.667(150)	-91	631 188.396(200)	-101
			D³⁵Cl		D³⁷Cl		D³⁵Cl		D³⁷Cl	
			$v = 0$				$v = 1$			
3	3.5 \leftarrow 2	3.5	969 468.312(50)	-16	966 635.680(50)	-8	949 249.321(100)	89	946 505.757(150)	131
3	2.5 \leftarrow 2	3.5	969 475.895(500)	-206	966 641.255(500)	-556				
3	1.5 \leftarrow 2	0.5	969 481.041(50)	-13 ^c	966 645.648(100)	-70 ^c	949 262.180(100)	-6 ^c	946 515.745(150)	-90 ^c
3	2.5 \leftarrow 2	1.5	969 481.041(50)	-13 ^c	966 645.648(100)	-70 ^c	949 262.180(100)	-6 ^c	946 515.745(150)	-90 ^c
3	4.5 \leftarrow 2	3.5	969 485.296(50)	-30 ^c	966 649.075(50)	20 ^c	949 266.516(100)	21 ^c	946 519.258(150)	25 ^c
3	3.5 \leftarrow 2	2.5	969 485.296(50)	-30 ^c	966 649.075(50)	20 ^c	949 266.516(100)	21 ^c	946 519.258(150)	25 ^c
3	2.5 \leftarrow 2	2.5	969 493.035(50)	-3	966 655.148(50)	-12	949 274.458(100)	79	946 525.446(150)	5
3	1.5 \leftarrow 2	1.5	969 497.858(50)	8	966 658.970(50)	20	949 279.297(100)	21	946 529.266(150)	-33
3	1.5 \leftarrow 2	2.5	969 509.827(150)	3	966 668.369(200)	-16				

^{a,b,c}See footnotes of Table 1.

^dLine given 10 times lower weight in the fit.

perimental uncertainty. The uncertainties of the DCl lines reported by Fusina *et al.* (12) were increased 10 times in order to give both TuFIR works comparable weights in the fit. The center frequencies of nonresolved hyperfine splittings were calculated by use of their intensity-weighted averages. For all sub-Doppler frequencies the average was taken over the chlorine and hydrogen hfs, whereas for the Doppler-limited lines the average was calculated with respect to the unresolved chlorine hfs.

The hyperfine constants reported by Kaiser (16) were included in the fit by converting them to isotopically invariant hyperfine parameters and varying them within the uncertainties stated in Ref. (16). In this procedure, it was necessary to include three parameters for the dependence of the hfs constants when comparing the H³⁵Cl to the D³⁵Cl iso-

pomer. These Born–Oppenheimer corrections were adopted analogously to the Born–Oppenheimer corrections to U_{01} in Eq. [2]:

$$eq_{ij} = eq_{ij}^e + eq_{ij}^A \left(1 - \frac{M_A^0}{M_A} \right) + eq_{ij}^B \left(1 - \frac{M_B^0}{M_B} \right) \quad [4]$$

$$C_{ij} = C_{ij}^e + C_{ij}^A \left(1 - \frac{M_A^0}{M_A} \right) + C_{ij}^B \left(1 - \frac{M_B^0}{M_B} \right). \quad [5]$$

To include Kaiser's data, the parameters $eq_{00}^H(\text{Cl})$, $C_{00}^H(\text{Cl})$, and $C_{00}^H(\text{H})$ were found to be necessary in the fitting procedure. While the breakdown of the Born–Oppenheimer approximation for the nuclear quadrupole coupling constant of ³⁵Cl has already been recognized and analyzed by

TABLE 3
Isotopically Invariant Rotational and
Hyperfine Parameters for HCl

Parameter	This Work ^a	Previous ^a	Unit
U_{01}^e	311 094.692 (12)	311 097.57 (24) ^b	MHz u
U_{01}^{Cl}	0.6918 (26)		MHz u
U_{01}^{H}	-20.5097 (50)		MHz u
U_{11}	-8 912.261 (34)	-8 919.281 (591) ^b	MHz u ^{3/2}
U_{21}	37.530 (19)	45.4317 (4617) ^b	MHz u ²
U_{02}	-15.28221 (34)	-15.28870 (339) ^b	MHz u ²
U_{12}	0.17979 (75)	0.20601 (196) ^b	MHz u ^{5/2}
$U_{03} \times 10^4$	4.779 (25)	4.7838 (63) ^b	MHz u ³
$U_{13} \times 10^5$	-2.52 (56)	-1.573 (130) ^b	MHz u ^{7/2}
$eq_{00}^e \times Q(^{35}\text{Cl})$	-66.77574 (19)	-66.7751 (30) ^c	MHz
$eq_{10} \times Q(^{35}\text{Cl})$	-1.65439 (41)	-1.6556 (63) ^c	MHz u ^{1/2}
$eq_{20} \times Q(^{35}\text{Cl})$	0.00922 (21)	0.0092 (24) ^c	MHz u
$eq_{01} \times Q(^{35}\text{Cl})$	-0.004461 (74)		MHz u
$eq_{11} \times Q(^{35}\text{Cl})$	-0.00066 (17)		MHz u ^{3/2}
$eq_{00}^{\text{H}} \times Q(^{35}\text{Cl})$	-0.02897 (23)		MHz
$eq_{00}^{\text{Cl}} \times Q(^{35}\text{Cl})$	0.188 (72)		MHz
$C_{00}^e(\text{Cl})$	92.266 (50)		kHz u
$C_{10}(\text{Cl})$	7.696 (95)		kHz u ^{3/2}
$C_{20}(\text{Cl})$	0.333 (39)		kHz u ²
$C_{01}(\text{Cl})$	0.0168 (40)		kHz u ²
$C_{00}^{\text{H}}(\text{Cl})$	4.36 (46)		kHz u
$eq_{00} \times Q(\text{D})$	0.18863 (21)		MHz
$eq_{10} \times Q(\text{D})$	-0.00324 (58)		MHz u ^{1/2}
$C_{00}^e(\text{H})$	-7.414 (15)		kHz u
$C_{10}(\text{H})$	0.139 (11)		kHz u ^{3/2}
$C_{01}(\text{H})$	0.0056 (19)		kHz u ²
$C_{00}^{\text{H}}(\text{H})$	0.137 (25)		kHz u
derived:			
U_{01}^{BO}	311 074.8744 (78)	311 076.637 (815) ^b	MHz u
Δ_{01}^{Cl}	-0.14177 (53)	-0.278 (168) ^b	
Δ_{01}^{H}	0.121125 (29)	0.1315 (10) ^b	
$Y_{10}(\text{H}^{35}\text{Cl})$	2 991.799 (33)	2 990.89141 (270) ^d	cm ⁻¹
$Y_{10}(\text{H}^{37}\text{Cl})$	2 145.727 (24)	2 145.11386 (163) ^d	cm ⁻¹
r_e^{BO}	1.27460658 (53)	1.2746084 (15) ^b	10 ⁻¹⁰ m
$r_e(\text{H}^{35}\text{Cl})$	1.27456598 (53)		10 ⁻¹⁰ m
$r_e(\text{D}^{35}\text{Cl})$	1.27458697 (53)		10 ⁻¹⁰ m

^aValues in brackets: 1 σ .

^bCoxon and Ogilvie (29). Values in brackets: 1 σ .

^cH³⁵Cl value from Kaiser (16).

^dCalculated from mass-reduced U_{10} values (29).

Kaiser (16) and Bunker (28), the additional parameters for the nuclear spin-rotation interaction are regarded here as statistically important in the fit to achieve best agreement with the constants reported by Kaiser (16).

The resulting isotopically invariant parameters are shown in Table 3 and the calculated frequencies (O - C) in Table 4. The weighted rms for all 133 lines included in the fit is 1.6 kHz. The rotational parameters are compared to the values reported by Coxon and Ogilvie (29). This work analyzed about 900 rotational and vibrational-

rotational transitions leading to an extended set of mass-invariant parameters including higher orders of the U_{ij} parameters and a larger number of Born-Oppenheimer correction constants. Therefore the agreement for most rotational parameters is only moderately good owing to the very different data sets and the different set of constants fitted in Ref. (29). Concerning the vibrational dependence of $eQq(^{35}\text{Cl})$, our values agree very well with the ones reported by Kaiser.

Derived parameters, such as U_{01}^{BO} , Y_{10} ($\approx \omega_e$), and equilibrium bond lengths r_e , are also included in Table 3. These values are determined here for the first time from measurements of pure rotational submm-wave transitions only, i.e., independent of IR works. The error calculation of the r_e values takes into account the uncertainty of Planck's constant h . The nine-digit numbers calculated for the equilibrium bond distances r_e stem from the high accuracy of the various U_{01} parameters and are considered to be of purely numerical importance. However, the different r_e values exhibit a variation larger than the measurement accuracy and hence reveal a deviation from the Born-Oppenheimer approximation as discussed in previous work (e.g., 30).

The specific hyperfine constants for the $v = 0$ and 1 states calculated from the isotopically invariant hfs parameters are listed in Table 4. The rotational and vibrational dependences of the hfs constants are very well reproduced as can be seen by a comparison with Kaiser's (16) data. In a second fit we ignored Kaiser's work and fitted only $eq_{00}(\text{Cl})$, $eq_{10}(\text{Cl})$, $C_{00}(\text{Cl})$, and $C_{00}(\text{H})$. The resulting hfs constants are given in the third column in Table 4. Compared to the earlier microwave (10) and TuFIR (12) work, our new measurements led to improved values for the hfs constants.

In addition to the hfs parameters already mentioned, we included the eq_{00}^{Cl} term to correct for the change of eq_{00} with the change of the chlorine isotope. The fitted value given in Table 3 is regarded here to be of numerical importance. However, we found a slightly better agreement between the observed and calculated frequencies of H³⁷Cl and D³⁷Cl by including this parameter. It would be of interest to perform a molecular beam electric resonance experiment on H³⁷Cl or D³⁷Cl to investigate this effect more precisely.

4. CONCLUSION

Precise transition frequencies in the submm-wave and terahertz region were measured applying Lamb-dip and conventional Doppler-limited spectroscopy. In addition, submm-wave rotational transitions in the first excited vibrational state were observed for all four stable isotopomers for the first time. The set of isotopically invariant

TABLE 4
Calculated Hyperfine Constants Obtained from the Parameters in Table 3
in Comparison to Values Reported in Other Works

Constant	This Work ^a	This Work ^b	Previous	Unit
H³⁵Cl				
$v = 0$ eQq	-67.60916 (30)	-67.6178 (274)	-67.800 (95) ^c	MHz
eQq ($J=1$)	-67.61895 (39)	-67.6178 (274)	-67.61893 (47) ^d	MHz
$v = 1$ eQq	-69.26187 (85)	-69.186 (65)		MHz
eQq ($J=1$)	-69.27302(103)	-69.186 (65)	-69.27289 (93) ^d	MHz
$v = 0$ $C_I(\text{Cl})$	53.829 (53)	53.61 (37)	68 (10) ^c	kHz
$C_I(\text{Cl})$ ($J=1$)	53.849 (53)	53.61 (37)	53.851 (42) ^d	kHz
$v = 1$ $C_I(\text{Cl})$	58.559(133)	53.61 (37)		kHz
$C_I(\text{Cl})$ ($J=1$)	58.578(133)	53.61 (37)	58.597 (45) ^d	kHz
$v = 0$ $C_I(\text{H})$	-41.877(139)	-41.37 (37)		kHz
$C_I(\text{H})$ ($J=1$)	-41.811(143)	-41.37 (37)	-41.80 (25) ^d	kHz
$v = 1$ $C_I(\text{H})$	-41.076 (191)	-41.37 (37)		kHz
$C_I(\text{H})$ ($J=1$)	-41.010 (193)	-41.37 (37)	-41.09 (24) ^d	kHz
H³⁷Cl				
$v = 0$ eQq	-53.278253 (236)	-53.2931 (216)	-53.436 (95) ^e	MHz
eQq ($J=1$)	-53.28596 (31)	-53.2931 (216)		MHz
$v = 1$ eQq	-54.57988 (67)	-54.528 (51)		MHz
eQq ($J=1$)	-54.58865 (81)	-54.528 (51)		MHz
$v = 0$ $C_I(\text{Cl})$	44.738 (44)	44.56 (31)	56 (10) ^c	kHz
$C_I(\text{H})$	-41.814 (139)	-41.31 (37)		kHz
D³⁵Cl				
$v = 0$ $eQq(\text{Cl})$	-67.388420 (254)	-67.3961 (232)	-67.4605 (955) ^e	MHz
$eQq(\text{Cl})$ ($J=1$)	-67.393356 (276)	-67.3961 (232)	-67.39338 (9) ^d	MHz
$v = 1$ $eQq(\text{Cl})$	-68.57757 (57)	-68.521 (48)		MHz
$eQq(\text{Cl})$ ($J=1$)	-68.58301 (61)	-68.521 (48)	-68.5831 (10) ^d	MHz
$v = 0$ $C_I(\text{Cl})$	27.4233 (252)	27.578 (189)	28.32 (582) ^e	kHz
$C_I(\text{Cl})$ ($J=1$)	27.4284 (252)	27.578 (189)	27.426 (7) ^d	kHz
$v = 1$ $C_I(\text{Cl})$	29.128 (49)	27.578 (189)		kHz
$C_I(\text{Cl})$ ($J=1$)	29.134 (49)	27.578 (189)	29.121 (62) ^d	kHz
$v = 0$ $eQq(\text{D})$	0.18746 (64)			MHz
$eQq(\text{D})$ ($J=1$)	0.18746 (64)		0.18736 (30) ^d	MHz
$v = 1$ $eQq(\text{D})$	0.18510(142)			MHz
$eQq(\text{D})$ ($J=1$)	0.18510(142)		0.1848 (38) ^d	MHz
$v = 0$ $C_I(\text{D})$	-3.2848 (136)	-3.2666 (289)		kHz
$C_I(\text{D})$ ($J=1$)	-3.2822 (137)	-3.2666 (289)	-3.295 (46) ^d	kHz
$v = 1$ $C_I(\text{D})$	-3.2395 (156)	-3.2666 (289)		kHz
$C_I(\text{D})$ ($J=1$)	-3.2368 (160)	-3.2666 (289)	-3.25 ^d	kHz
D³⁷Cl				
$v = 0$ $eQq(\text{Cl})$	-53.104080 (200)	-53.1182 (183)	-53.0023 (539) ^e	MHz
$C_I(\text{Cl})$	22.7588 (209)	22.888 (157)	19.13 (512) ^e	kHz
$eQq(\text{D})$	0.18746 (64)			MHz
$v = 1$ $eQq(\text{D})$	0.18511 (142)			MHz
$v = 0$ $C_I(\text{D})$	-3.2752 (136)	-3.2568 (288)		kHz

^aValues calculated from parameters in Table 3. In brackets: 3σ .

^bValues from fit without inclusion of Kaiser's (16) results. See text. In brackets: 3σ .

^cDe Lucia et al. (10).

^dFrom Kaiser (16). In brackets: values between 3.5 and 5σ . See Ref. (16).

^eFusina et al. (12). In brackets: 1σ .

parameters reproduces the measured frequencies very well and the hyperfine constants agree with the results from previous work. The experimental frequencies should be useful for calibration purposes. HCl is observed in many terrestrial and extraterrestrial environments; these as well as laboratory experiments require accurate reference frequencies.

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