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NOTE

Tunable Far-Infrared Spectroscopy of HF, $H^{35}Cl$, and $H^{37}Cl$ in the 6 to 9 THz Region

The frequencies of pure rotational transitions of light molecules, such as HF and HCl, fall in the far-infrared region (1–10 THz). Below 6.5 THz, their rotational transition frequencies have been measured with an accuracy of a few hundred kilohertz (*1, 2*), using a tunable far-infrared (TuFIR) spectrometer (*1, 3*). The tunable, coherent far-infrared radiation is produced by a difference frequency generation of two CO_2 lasers. However, in the 6.5–10 THz region, few accurate data have been reported, because the TuFIR technique had an upper limit of 6.5 THz (*4*) due to the range of available CO_2 laser frequencies. Recently, we extended the TuFIR technique to higher frequencies over 9 THz (*5, 6*) by replacing one of two CO_2 lasers in a regular TuFIR spectrometer with a $^{15}NH_3$ laser. This modification has allowed us to produce difference frequencies to over 9 THz. In this note, we report extended measurements of the rotational transition frequencies of HF, $H^{35}Cl$, and $H^{37}Cl$ in the 6–9 THz region using this ammonia–TuFIR spectrometer.

In the ammonia–TuFIR spectrometer, tunable, coherent far-infrared radiation is generated by mixing radiation from a CO_2 laser, a $^{15}NH_3$ laser, and a microwave-synthesized sweeper in a W–Co metal–insulator–metal (MIM) diode. This spectrometer enables us to measure far-infrared transitions up to 9.1 THz with an accuracy dependent on locating the center of an absorption line (usually better than 1 MHz). Details of the ammonia–TuFIR spectrometer have been described in Ref. (*5, 6*). We used a 2-cm long absorption cell in which the sample gas was flowing at a pressure of 0–7 Pa (0–50 mTorr). For HCl measurements, HCl gas with natural abundances of 75.8% $H^{35}Cl$ and 24.2% $H^{37}Cl$ was used. The observed frequencies were calculated from CO_2 laser frequencies (*7*) and $^{15}NH_3$ laser frequencies (*6, 8*). The averaged frequencies of several measurements are shown in Table 1 along with the laser transitions and the 2σ estimated experimental uncertainties. These uncertainties were calculated from a quadratic sum of the statistical uncertainty and the difference frequency uncertainty. The $J = 13 \leftarrow 12$ transitions of $H^{35}Cl$ and $H^{37}Cl$ were not observed because the generated far-infrared radiation was absorbed by atmospheric water vapor. The observed frequencies were fitted using some previous data (*1, 2, 9*) to develop the following $^1\Sigma$ effective Hamiltonian:

$$H_{\text{eff}} = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 - L[J(J+1)]^4 + M[J(J+1)]^5. \quad [1]$$

The redetermined rotational parameters are summarized, along with the best previous parameters, in Table 2.

TABLE 1
Observed Frequencies of HF, $H^{35}Cl$, and $H^{37}Cl$ (MHz)

HF	Transition	CO_2 laser	$^{15}NH_3$ laser	Observed Frequency[a]	obs.–calc.[b]
	$J = 6 \leftarrow 5$	$R(50)_{II}$	$aP(4,0)$	7 341 700.96(35)	−0.12
	$7 \leftarrow 6$	$R(52)_{II}$	$aP(6,3)$	8 542 410.96(98)	0.36
$H^{35}Cl$	Transition	CO_2 laser	$^{15}NH_3$ laser	Observed Frequency	obs.–calc.
	$J = 11 \leftarrow 10$	$P(10)_{II}$	$aP(5,3)$	6 801 958.73(23)	−0.07
	$12 \leftarrow 11$	$R(16)_{II}$	$aP(5,3)$	7 403 057.80(35)	0.18
	$14 \leftarrow 13$	$R(20)_{II}$	$aP(7,3)$	8 591 531.68(46)	−0.12
$H^{37}Cl$	Transition	CO_2 laser	$^{15}NH_3$ laser	Observed Frequency	obs.–calc.
	$J = 11 \leftarrow 10$	$P(10)_{II}$	$aP(5,3)$	6 791 867.06(22)	−0.10
	$12 \leftarrow 11$	$R(48)_{II}$	$aP(4,3)$	7 392 100.67(52)	0.24
	$14 \leftarrow 13$	$R(20)_{II}$	$aP(7,3)$	8 578 884.52(63)	−0.17

[a] The numbers in parentheses are the estimated 2σ uncertainties in units of the last quoted digits.

[b] The frequencies are calculated from the rotational parameters in Table 2.

TABLE 2
Rotational Parameters of HF, $H^{35}Cl$, and $H^{37}Cl$ (MHz)[a]

HF	This Work	Previous Work[b]
B	616 365.217(87)	616 365.200(10)
D	63.5548(21)	63.5524(4)
H	$4.9027(129)\times10^{-3}$	$4.898(2)\times10^{-3}$
L	$4.483(194)\times10^{-7}$	$4.44(2)\times10^{-7}$
M	$3.08(82)\times10^{-11}$	$2.94(8)\times10^{-11}$
$H^{35}Cl$	This Work	Previous Work[c]
B	312 989.225(16)	312 989.2443(154)
D	15.82997(18)	15.83050(32)
H	$4.8980(57)\times10^{-4}$	$4.931(19)\times10^{-4}$
$H^{37}Cl$	This Work	Previous Work[c]
B	312 519.063(26)	312 519.0954(126)
D	15.78236(30)	15.78333(27)
H	$4.882(11)\times10^{-4}$	$4.947(16)\times10^{-4}$

[a] The numbers in parentheses are the estimated 2σ uncertainties in units of the last quoted digits.

[b] Ref. [*9*].

[c] Ref. [*1*].

In summary, we have successfully applied an ammonia–TuFIR spectrometer for the observation of the rotational transitions of HF, $H^{35}Cl$, and $H^{37}Cl$ in the 6–9 THz region. The accurately measured frequencies of strong absorption lines of these stable molecules should be useful for calibration standards in this frequency region.

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