Tunable far-infrared spectroscopy extended to 9.1 THz

Hitoshi Odashima

Department of Physics, Toyama University, Gofuku 3190, Toyama 930-8555, Japan

Lyndon R. Zink and K. M. Evenson

Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303

Received October 30, 1998

We synthesized tunable far-infrared radiation at frequencies higher than 9 THz (300 cm^{-1}) by mixing CO_2 laser, $^{15}NH_3$ laser, and microwave radiation in a W–Co metal–insulator–metal diode. We used this far-infrared radiation to accurately measure torsion–rotation transitions of CH_3OH in the 8–9-THz region. We also measured the frequency of the $aP(7,3)$ $^{15}NH_3$ laser transition.

The far-infrared (FIR) spectral region (1–10 THz) is sometimes called the gap in the electromagnetic spectrum because it is difficult to produce tunable, coherent FIR radiation. In this region, two types of spectrometer have been developed for high-resolution spectroscopy; one is based on microwave sidebands of FIR lasers with Schottky diodes[1,2] and the other uses the difference frequency of two CO_2 lasers generated in a metal–insulator–metal (MIM) diode.[3–5] The first provides more FIR power but is limited to the region below 4.5 THz because of the intrinsic capacitance of the GaAs mixer, whereas the second [which we call tunable far-infrared (TuFIR)] covers the region up to 6.5 THz, limited by the maximum frequency difference between two CO_2 lasers.[6] In a previous Letter[7] we reported the extension of the TuFIR to 7.9 THz by replacing one of the two CO_2 lasers in a traditional TuFIR spectrometer with a $^{15}NH_3$ laser. Using this FIR radiation, we observed the torsion–rotation transitions of CH_3OH up to 7.9 THz with an uncertainty of less than 1 MHz. However, we failed to observe the CH_3OH spectrum at frequencies higher than 8 THz because of reduced MIM diode efficiency at higher frequencies and reduced FIR detector sensitivity of the Ga-doped Ge (Ge:Ga) photoconductor, whose sensitivity peaks near 3 THz. In this Letter we report the further extension of tunable FIR spectroscopy to 9.1 THz with an improved ammonia–TuFIR spectrometer in which both a more sensitive Be-doped Ge photconductor[8] and a more powerful $^{15}NH_3$ laser are used.

The radiation from a CO_2 laser (frequency ν_1), a $^{15}NH_3$ laser (ν_2), and a microwave synthesized sweeper ($\nu_{mw} \leq 20$ GHz) is mixed in a W–Co MIM diode. Typical incident powers are 150 mW for the CO_2 laser, 100–150 mW for the $^{15}NH_3$ laser, and several milliwatts for the microwave radiation. The CO_2 laser is stabilized to the saturation dip in a 4.3-μm fluorescence signal of low-pressure CO_2 with the traditional $1f$ servo technique.[9] The $^{15}NH_3$ laser is stabilized to the saturated-absorption signal of low-pressure $^{15}NH_3$ with the $3f$ servo technique,[10,11] which effectively reduces the systematic frequency shift that is due to the asymmetric output power profile of our $^{15}NH_3$ laser.[12]

The W–Co MIM diode generates two tunable FIR frequencies equal to

$$\nu_{FIR} = |\nu_1 - \nu_2| \pm \nu_{mw}. \quad (1)$$

We change the synthesized FIR frequency by tuning the microwave source. Details of our $^{15}NH_3$ laser are found elsewhere,[13] and details of the ammonia–TuFIR spectrometer are described in the previous Letter,[7] except for the following changes: The generated FIR radiation is detected by a Ge:Be photoconductor, and a 35-W laser is used to pump the ammonia laser, which gives us enough power on the $^{15}NH_3$ $aP(7,3)$ line to generate radiation at 9.1 THz. Using 38-μm CH_3OH laser radiation, we confirmed that this Ge:Be photoconductor is a few times more sensitive at 7.6 THz than the Ge:Ga detector used previously. With the stronger 35-W pump laser, the $^{15}NH_3$ laser now oscillates on the $aP(7,3)$ line as well as on $aP(4,0)$, $aP(4,3)$, $aP(5,3)$, $aP(6,0)$, and $aP(6,3)$ with a typical power of 0.3–1.2 W. A grating selects the line that we want and also couples out the ammonia laser radiation.

Methanol was chosen as a sample gas because of its rich torsion–rotation spectrum at frequencies above 8 THz. The absorption cell was 1.1 m long, with an 80-μm-thick polypropylene window at each end, and was filled with 1.3–2.6-Pa (10–20-mTorr) CH_3OH gas. Three transitions from 8 to 9 THz were measured. A plot of the observed absorption from the $A,(n,K,J) = (1,7,19) \leftarrow (0,6,19)$ transition at

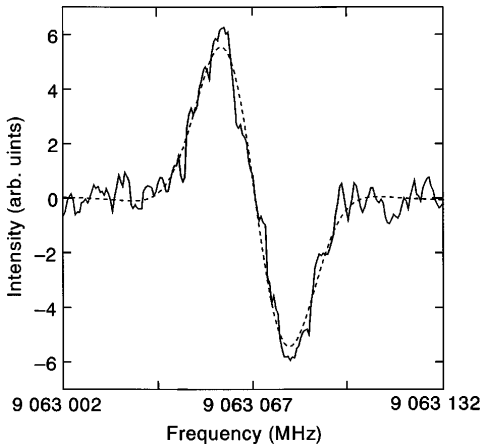

Fig. 1. Observed spectral line of the $A,(n,K,J) = (1,7,19) \leftarrow (0,6,19)$ transition of CH_3OH at 9.1 THz. Solid curve, measured spectrum; dashed curve, fitted spectrum.

Table 1. Observed Frequencies of CH_3OH

Symmetry	Transition $(n', K', J') \leftarrow (n'', K'', J'')$	Laser Line		Observed Frequency (MHz)	
		CO_2	$^{15}NH_3$	Previous Work[a]	This Work[b]
E	$(1, -4, 20) \leftarrow (0, -3, 19)$	$R(22)_{II}$	$aP(6, 3)$	8 083 391	8 083 380.39(32)
E	$(1, 2, 13) \leftarrow (0, 1, 12)$	$R(48)_{II}$	$aP(6, 3)$	8 510 236	8 510 223.84(40)
A	$(1, 7, 19) \leftarrow (0, 6, 19)$	$R(50)_{II}$	$aP(7, 3)$	9 063 076	9 063 067.34(28)

[a]The wave numbers from Ref. 14 are converted to frequencies for comparison.
[b]The numbers in parentheses are the estimated 1σ uncertainties in units of the last quoted digits.

9.1 THz is shown in Fig. 1, where n is the torsional quantum number. We assigned the observed transitions by referring to Fourier-transform spectrometer data.[14] The measured transition frequencies are listed in Table 1, together with the previous Fourier-transform spectrometer data. They are the average of several measurements and are calculated from the CO_2 and $^{15}NH_3$ laser frequencies reported in Refs. 12 and 15. The $aP(7, 3)$ $^{15}NH_3$ frequency is not reported in Ref. 12. We measured it by heterodyning the $^{15}NH_3$ laser against two reference CO_2 lasers. Its frequency is 23 762 643.94(14) MHz. The uncertainty is 1σ. Details of the frequency measurement procedure can be found in Ref. 12.

The measured $aP(7, 3)$ frequency agrees with the previous Fourier-transform spectrometer data of D'Cunha *et al.*[16] within their experimental uncertainty (6 MHz). The 1σ uncertainties of the observed CH_3OH frequencies in Table 1 are calculated from the quadratic sum of the CO_2 laser frequency uncertainty ($\leq$25 kHz),[17] the $^{15}NH_3$ laser frequency uncertainty (100–150 kHz),[12] and the statistical deviation in the repeated measurements.

Our previous and present experimental results show that the third-order generation, in which tunable FIR radiation is obtained with two infrared lasers and microwave radiation, works at frequencies up to 9.1 THz, Second-order generation, mixing radiation from two infrared lasers in a W–Ni MIM diode, provides higher-frequency operation and more FIR power but has limited tunability.[3] Because of the wider tuning range ($\pm$20 GHz) of third-order generation, this ammonia–TuFIR spectrometer provides nearly complete coverage of the 6–9-THz region and is a practical tool for high-resolution spectroscopy. We have used it to measure high-J rotational transitions of HF and HCl, which are reported elsewhere.[18]

The spectrum in Fig. 1 shows a good signal-to-noise ratio at 9.1 THz; however, to observe the FIR spectrum at frequencies higher than 9.1 THz we needed a more efficient $^{15}NH_3$ laser, which operates on lower-frequency lines and provides enough power for frequency stabilization (~100 mW) and FIR generation (~150 mW). At higher frequencies, more-sensitive detection of a lower FIR power is required, because the MIM diode efficiency is reduced. We measured our Ge:Be detector sensitivity at 10.7 THz, using the 28-μm H_2O vapor laser line. It has only 3% of the sensitivity that it has near its peak at 7.6 THz. A Si:B photoconductor[8] whose sensitivity peaks near 11 THz should be used near 10 THz. We believe that this TuFIR technique will be applicable at frequencies up to ~10 THz with a Si:B detector and that the gap in the electromagnetic spectrum will disappear.

The authors thank I. G. Nolt of NASA Langley Laboratory for his preparation of the Ge:Be detector. This research was supported by NASA contract W-19, 167. K. M. Evenson's e-mail address is evenson@boulder.nist.gov.

References

1. D. D. Bicanic, B. F. J. Zuidberg, and A. Dymanus, Appl. Phys. Lett. **32,** 367 (1978).
2. G. A. Blake, K. B. Laughlin, R. C. Cohen, K. L. Busarow, D.-H. Gwo, C. A. Schmuttenmaer, D. W. Steyert, and R. J. Saykally, Rev. Sci. Instrum. **62,** 1693 (1991).
3. K. M. Evenson, D. A. Jennings, and F. R. Petersen, Appl. Phys. Lett. **44,** 576 (1984).
4. I. G. Nolt, J. V. Radostitz, G. DiLonardo, K. M. Evenson, D. A. Jennings, K. R. Leopold, M. D. Vanek, L. R. Zink, A. Hinz, and K. V. Chance, J. Mol. Spectrosc. **125,** 274 (1987).
5. F. Matsushima, H. Odashima, D. Wang, S. Tsunekawa, and K. Takagi, Jpn. J. Appl. Phys. **33,** 315 (1994).
6. F. Matsushima, K. M. Evenson, and L. R. Zink, J. Mol. Spectrosc. **164,** 517 (1994).
7. H. Odashima, M. Tachikawa, L. R. Zink, and K. M. Evenson, Opt. Lett. **22,** 822 (1997).
8. E. E. Haller, Infrared Phys. Technol. **35,** 127 (1994).
9. C. Freed and A. Javan, Appl. Phys. Lett. **17,** 53 (1970).
10. L. R. Zink, F. S. Pavone, R. Meucci, M. Prevedelli, and M. Inguscio, Opt. Commun. **77,** 41 (1990).
11. J. L. Hall, H. G. Robinson, T. Baer, and L. Hollberg, in *Advances in Laser Spectroscopy*, F. T. Arecchi, F. Strumia, and H. Walther, eds. (Plenum, New York, 1981), p. 99.
12. H. Odashima, M. Tachikawa, L. R. Zink, and K. M. Evenson, J. Mol. Spectrosc. **188,** 245 (1998).
13. M. Tachkawa and K. M. Evenson, Opt. Lett. **21,** 1247 (1996).
14. G. Moruzzi, B. P. Winnewisser, M. Winnewisser, I. Mukhopadhyay, and F. Strumia, *Microwave, Infrared and Laser Transitions of Methanol* (CRC Press, Boca Raton, Fla., 1995), Table 9.2.
15. A. G. Maki, Che-Chung Chou, K. M. Evenson, L. R. Zink, and J.-T. Shy, J. Mol. Spectrosc. **167,** 211 (1994).
16. R. D'Cunha , S. Urban, and K. Narahari Rao, J. Mol. Spectrosc. **111,** 352 (1985).
17. T. D. Varberg and K. M. Evenson, IEEE Trans. Instrum. Meas. **42,** 412 (1993).
18. H. Odashima, L. R. Zink, and K. M. Evenson, "Tunable far-infared spectroscopy of HF, $H^{35}Cl$, and $H^{37}Cl$ in the 6 to 9 THz region," J. Mol. Spectrosc. (to be published).