

Sub-Doppler tunable far-infrared spectroscopy

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The first experimental observations to our knowledge of sub-Doppler linewidths in a cell made using tunable far-infrared radiation are reported. A double-resonance scheme has been used, combining CO₂-laser infrared radiation with tunable far-infrared radiation to observe a sub-Doppler line shape in an excited vibrational state of CH₃OH.

Recent progress in frequency multiplication and in nonlinear mixing of coherent radiation has made the generation of tunable far-infrared (TuFIR) radiation possible.¹ In the measurements reported here, FIR difference-frequency radiation was generated by mixing the radiation from two CO₂ lasers using the point-contact metal-insulator-metal diode.² The radiation is tuned by varying the output frequency of a waveguide CO₂ laser over its pressure-broadened gain profile.

A high-sensitivity spectrometer that uses this technique has been constructed,¹ and a minimum detectable fractional absorption of 1×10^{-4} with a 2s time constant was obtained. This sensitivity makes it possible to work at relatively low gas pressures (down to about 1 Pa); hence collisional broadening is reduced to a few hundred kilohertz. However, the Doppler broadening, especially at the higher frequencies, can easily be several megahertz, even for small polyatomic molecules. Therefore development of sub-Doppler TuFIR spectroscopy is necessary for high accuracy; this Letter is devoted to demonstrating its feasibility. The TuFIR power is too low (0.1 μ W) to permit saturation or two-photon spectroscopy schemes. A possible approach could use molecular beams,³ but since we are interested in measurements in absorption cells we decided to perform an IR-FIR double-resonance experiment, as illustrated in Fig. 1a.

The TuFIR radiation is generated in a W-Ni point-contact diode and radiates from the diode through a long wire antenna.¹ The FIR beam is collimated with a parabolic reflector and has a divergence of a few degrees. A single-pass, room-temperature, Pyrex absorption cell with a 1.9-cm internal diameter and a 55-cm length is used. The FIR-admitting cell window is high-density polyethylene, 2 mm thick, and is transparent to the FIR radiation. The other window, which admits the CO₂-laser beam, is a 2-mm-thick crystal-silicon window, which transmits about 80% of the FIR and 50% of the IR. For the superposition of the two beams, a silicon beam splitter is used, which introduces an additional loss of about 20% in the detected FIR power. A liquid-helium-cooled germani-

um bolometer is used to detect the FIR radiation. Gas pressure is measured with a capacitance manometer.

Figure 1b shows the energy levels involved in this double-resonance experiment. The FIR transition (2-3) of $(n, \tau, J, K):(0, 1, 8, 16)-(0, 2, 7, 15)$ in the excited ν_n state of CH₃OH is observed with and without the counterpropagating CO₂ laser. The counterpropagating CO₂ laser (9P36) is tuned into resonance with the absorption (1-3) of Fig. 1b: To facilitate tuning, the optoacoustic signal of this resonance is

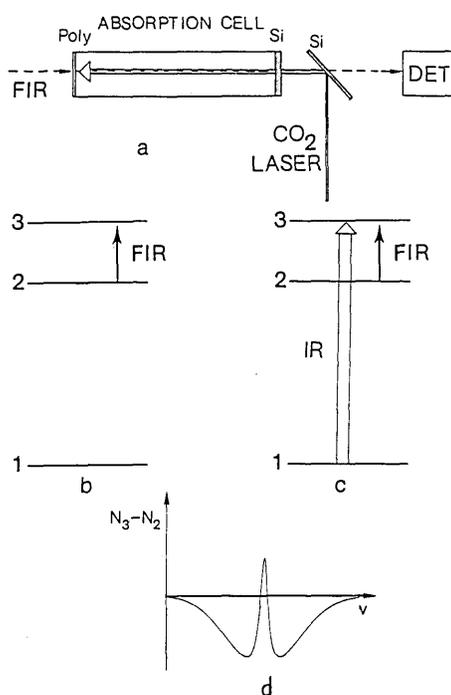


Fig. 1. a, The IR-FIR double-resonance experimental arrangement. b, In absence of IR excitation, the Doppler-broadened (2-3) transition is detected. When the velocity-selective IR radiation is added in resonance with the (1-3) transition, a sub-Doppler Lorentzian amplification curve, c, is superimposed upon the detected FIR signal.

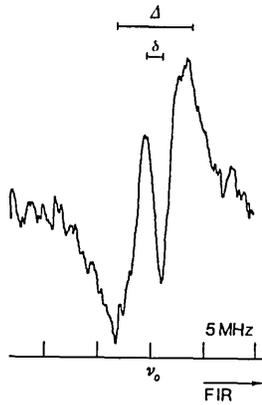


Fig. 2. The FIR absorption curve and sub-Doppler emission signal. The CH_3OH absorbing gas was at a pressure of 2.5 Pa; the FIR radiation was frequency modulated, and a derivative signal was recorded (time constant, 400 msec).

monitored in a separate absorption cell. At room temperature approximately 1% of the molecules are in the excited vibrational state, and the Doppler-broadened absorption of the (2-3) transition is detected. When the CO_2 radiation enters the absorption cell, a selected velocity group of molecules is excited to level 3. As a result a narrow, sub-Doppler, Lorentzian amplification curve is superimposed upon the broader Gaussian absorption curve, as illustrated in Fig. 1c.

In the first experimental scheme, the FIR radiation was frequency modulated, and the derivative of the absorption (or, in the pumped case, emission) signal was observed following phase-sensitive detection. A typical experimental recording is shown in Fig. 2. A broad curve is recorded with a width Δ of 7.4 MHz, consistent with a computed Doppler FWHM of 5.5 MHz plus additional pressure broadening. The narrower superimposed curve is recorded with a width δ of approximately 1.1 MHz. The measured width is essentially caused by homogeneous collisional broadening. It is worth noting that the actual Lorentzian width is $\sqrt{3}$ times the difference between maximum and minimum derivative points, or about 1.9 MHz. To obtain high accuracy it will be necessary to lock the CO_2 laser to the center of this line.

In a second experimental scheme, the Doppler-broadened absorption contribution to the signal was eliminated by amplitude modulating the counterpropagating CO_2 laser beam with a mechanical chopper. The detection was in phase with the modulation in order to record only the signal from the molecules excited by the CO_2 laser. In this scheme no derivative of the signal is introduced. A typical Lorentzian-shaped sub-Doppler recording is shown as curve c of Fig. 3. Here the CO_2 laser frequency was tuned to near the center of the (1-3) transition, so that the FIR recording is nearly at the center of the (2-3) transition. In curves a and b of Fig. 3 the CO_2 frequency was detuned, and the FIR recordings are shifted correspondingly. As expected, the ratio $\Delta\nu_{\text{FIR}}/\Delta\nu_{\text{IR}}$ is equal to the ratio between the two frequencies. The two shifts have opposite signs because the two beams are counterpropagating.

The effect of changing the gas pressure is illustrated in Figs. 4 and 5. The CO_2 power entering the absorption cell was kept constant at about 500 mW, with a cross section of about 30 mm^2 and a power density of approximately 1.7 W/cm^2 . The width increases almost linearly from 2.5 MHz (FWHM) at 2.7 Pa (20 mTorr) to 4.3 MHz (FWHM) at 13.3 Pa (100 mTorr). The values of the widths are equal to those measured with the derivative system (using the $\sqrt{3}$ factor mentioned earlier). The line shape is also affected by a residual Doppler broadening caused by the imperfect overlap of the two beams. The saturation broadening due to the CO_2 pump power is negligible at our experimental conditions. In fact, by doubling the pump power we have observed broadening of only a few percent at the lowest pressures, and the broadening was unobservable at pressures higher than 4 Pa. From the sub-Doppler recordings we obtain (Fig. 5) a pressure self-broadening parameter of 150(7) kHz/Pa [20(1) MHz/Torr] (FWHM), assuming that collisions are the only cause of broadening. This value is consistent with our recent result with linear absorption spectroscopy⁴ even though a quantitative comparison is difficult because of the nonequilibrium velocity distribution created in the case of the sub-Doppler measurement.⁵

An infrared-submillimeter double-resonance experiment was previously reported.⁶ In that case the tunable radiation was generated by mixing the output from an optically pumped laser with microwave radiation in a Schottky diode. That experiment used FIR frequencies more than four times lower than the one that we have generated in the present work. As a consequence, the Doppler broadening was observed to affect the line shape only at low pressures, and sub-

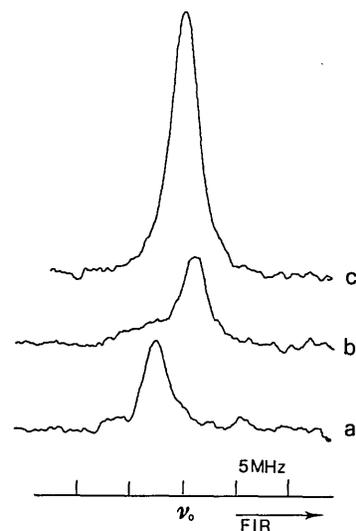


Fig. 3. The sub-Doppler signal of CH_3OH . The exciting CO_2 -laser beam was mechanically chopped at 500 Hz and was used as a reference for lock-in detection of the FIR signal. The gas pressure was about 2.4 Pa. The CO_2 laser was tuned at the center of the (1-3) absorption in c. An IR detuning of -17 and +27 MHz was introduced in b and c, respectively. Correspondingly, a FIR detuning is recorded of +1.4 MHz in b and of -2.1 MHz in a.

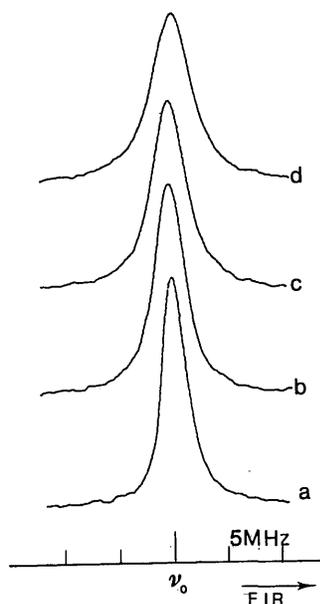


Fig. 4. Pressure broadening of the sub-Doppler double-resonance signal: a, 1.13 Pa; b, 3.76 Pa; c, 5.41 Pa; d, 7.52 Pa.

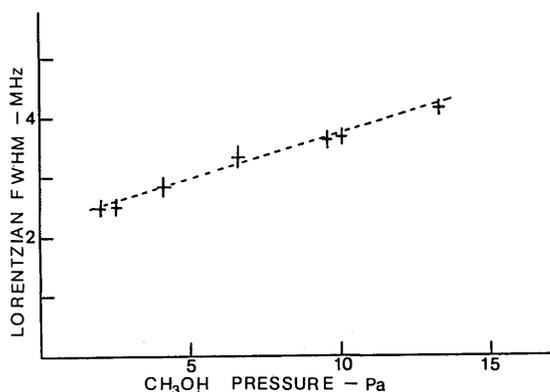


Fig. 5. FWHM of the sub-Doppler signal as a function of pressure. The dashed line corresponds to a broadening parameter of 150(7) kHz/Pa.

Doppler recordings were obtained only by using molecular beams.³ Similar double-resonance studies of CH₃OH have been performed using an optically pumped laser as the source of FIR radiation.⁷⁻⁹ Because the FIR lasers have limited tunability, they were able to observe the gain profile and not the complete absorption (or emission) curve. The value obtained for the pressure broadening of the gain curve in Ref. 7 is close to the present result. However, the present result is more accurate not only because of the larger tunability but also because of the much higher accuracy of the frequency.

In the research reported in Refs. 7-9 the frequency tuning is achieved by changing the length of the laser cavity. This procedure is misleading because pulling effects, for instance, can significantly reduce the actual tunability. Our present results demonstrate the feasibility of sub-Doppler tunable FIR spectroscopy by means of a double-resonance scheme. Here the coupled, velocity-selected transition (vibrational) is in the IR, but in general it could be in the visible or the UV (electronic). The FIR source could be locked to a narrow dip related to the saturation of the IR transition. This could be important in view of transferring reference signals from one region to the other and is a generalization of the effect observed in the optically pumped lasers.¹⁰

The good signal-to-noise ratio obtained with the second experimental scheme opens the possibility of extending this technique to the study of collisional energy transfer between molecular sublevels. In addition, the sub-Doppler resolution could yield information on the effect of the velocity on the collisional energy-transfer process.

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