Tone-burst modulated color-center-laser spectroscopy

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A new modulation technique useful for high-resolution spectroscopy with tunable infrared lasers is described. The high sensitivity of this method is demonstrated by measurements of NO $v = 0 \rightarrow 2$ overtone transitions and of transitions in the fundamental band of OH with a color-center laser operating near 2.7 μm.

Color-center lasers (CCL's) offer exciting prospects for high-sensitivity, high-resolution spectroscopy in the infrared. With a combination of three F_A(II) and F_B(II) color-center crystals mounted in a single liquid-nitrogen-cooled cryostat, continuous coverage from 3100 to 4300 cm^{-1} is available in a commercial laser system (Burleigh FCL 20) having output power levels ranging from 0.1 to 30 mW with a spectral bandwidth of ~1 MHz. Moreover, ongoing research is continually extending the spectral regions accessible with different types of color centers. Although the advantageous properties of CCL's have been clearly demonstrated for *indirect* spectroscopic applications, for example, in photoacoustic spectroscopy[1] and optogalvanic spectroscopy,[2,3] in which the relatively high average power levels available are of critical importance, a general method for achieving high sensitivity in *direct* CCL absorption spectroscopy has not yet been demonstrated. The difficulties with direct-absorption methods are a consequence of the large (several-per-cent) amplitude fluctuations present in the CCL output that, in turn, result from amplitude instabilities in the pump lasers (usually Kr^+, Ar^+, or YAG). This pump-laser instability can, in principle, be reduced substantially with the use of electro-optic amplitude stabilizers, but residual amplitude noise in the CCL still limits the video absorption sensitivity to the order of 1%. One solution to these problems with source noise in CCL absorption spectroscopy has been implemented by Litfin *et al.*,[4] who have adapted the technique of magnetic rotation spectroscopy to the CCL experiment, obtaining a substantially increased sensitivity (minimum detectable absorption ~10^{-5} cm^{-1}). With this method Carrick *et al.*[5] recently observed low-lying electronic absorption transitions in the CCH radical generated in a dc discharge. The magnetic rotation method can, however, be used only to study paramagnetic molecules, and this is, of course, a stringent limitation. In this Letter we report the development of the tone-burst modulation technique, which permits high-sensitivity CCL absorption spectroscopy measurements to be carried out for diamagnetic as well as paramagnetic species by using a comparatively simple detection system.

Tone-burst modulation is a form of frequency modulation developed initially by Pickett[6] for applications in microwave spectroscopy. Woods and co-workers have successfully used this approach to study microwave spectra of molecular ions in glow discharges.[7-9] The essence of the method is quite simple: FM sidebands (the tone) are imposed on the microwave carrier at a frequency greater than or equal to the spectral linewidth, and these sidebands (which typically contain 10% of the total radiated power) are 100% amplitude modulated at audio frequencies (the burst). When the source is off resonance with a molecular transition, the total power reaching the detector (carrier + sidebands) is the same in both the on and the off phases of the burst signal, whereas, when the source is on resonance, the absorbed power, which is proportional to the source power at that frequency, is modulated at the burst frequency. Lock-in detection then produces a signal in which the absorptions at the carrier and sideband frequencies appear with opposite sign, resembling a second-derivative line shape when $\nu_{tone} \lesssim \Delta\nu$. The advantage of this approach for microwave spectroscopy, as opposed to other FM techniques, is that it permits the source to be phase locked and frequency modulated simultaneously. To tone-burst modulate a laser, the AM tone is amplified and applied to an extracavity electro-optic phase modulator ($LiTaO_3$ or $LiNbO_3$), through which the laser beam is passed. This permits the laser to be frequency stabilized and swept in a single-mode configuration. With simple lock-in detection apparatus, high sensitivity is thus achieved without the loss of generality that accompanies the alternatives of Stark or Zeeman (magnetic-rotation) techniques.

A schematic of the modulated tone-burst CCL spectrometer is shown as Fig. 1. From 0.1 to 30 mW of infrared radiation, continuously tunable from 3100 to 4300 cm^{-1}, is produced from a CCL (Burleigh FCL-20) pumped by a Kr^+-ion laser (Spectra-Physics 171), the output of which is amplitude stabilized electro-optically (Coherent Noise Eater) to ~0.01%. The CCl can be operated with a continuously tunable single-mode output by dither-locking the intracavity étalon to the piezoelectrically driven folding mirror or with cavity mode-hop tuning (in 300-MHz increments) by ramping the étalon. Computer-controlled sweeps can be made in either case with the use of a Commodore PET CBM 3016 system interfaced to the laser drivers. The mode quality of the laser is monitored with a pair of confocal étalons (7.5 and 2 GHz). The wavelength of the laser

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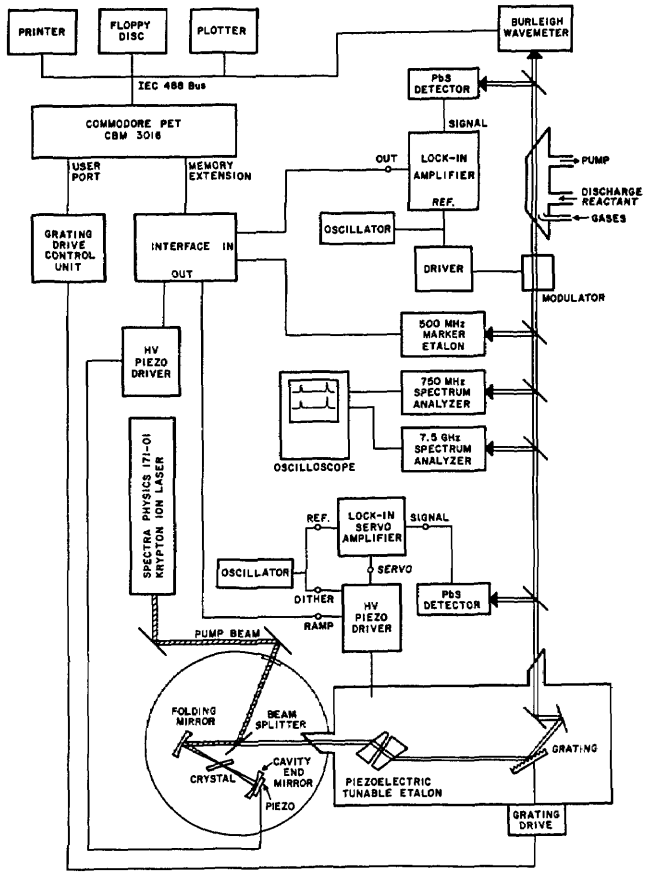

Fig. 1. Schematic of the CCL system used in this work.

is measured with an absolute accuracy of $\pm 1 \times 10^{-6}$ with a wavemeter (Burleigh WA-20). Audio and rf signal generators and a double-balanced mixer (Mini-Circuits ZFM-4 used as an amplitude modulator) generate the tone-burst modulation waveform. This is amplified to ~50 W (ENI 550L) and applied to a $LiTaO_3$ phase modulator (Lasermetrics 3126 A). The modulated infrarared radiation can then be directed through one of several sample cells, including two liquid-nitrogen-cooled glow discharge tubes (0.009 m × 1.0 m and 0.05 m × 2.0 m) and detected with a PbS, PbSe, or InSb detector. Lock-in detection at the burst frequency produces the demodulated absorption signals, which are displayed on a XY recorder.

Tone bursts applied to the phase modulator generate FM sidebands separated from the carrier by $\pm n\nu_{FM}$, where ν_{FM} is the tone frequency. In addition, AM sidebands appear at the frequencies $\nu_C \pm n\nu_{FM} \pm m\nu_{AM}$, where ν_{AM} and ν_C are the burst and carrier frequencies, respectively, and m and n are integer indices. In the time domain the modulated laser electric field $E(t)$ is given by[9]

$$E(t) = A \sin\{\omega_c t + (\mu B/2\omega_{FM}) \sin\omega_{FM} t + [\mu B/4(\omega_{FM} + \omega_{AM})] \sin(\omega_{FM} + \omega_{AM})t + [\mu B/4(\omega_{FM} - \omega_{AM})] \sin(\omega_{FM} - \omega_{AM})t\}, \quad (1)$$

where μ is the electro-optic modulation sensitivity (in radians/second volt) and B and A are the amplitudes of the tone-burst waveform and the laser, respectively.

The origin of the discrete sideband frequencies becomes evident when Eq. (1) is expanded in a converging sum of ordinary Bessel functions $J_i(K)$, yielding

$$E(t) = \sum_{m,n,p=-\infty}^{+\infty} \{(-1)^{(m-|m|+n-|n|+p-|p|)/2} \times J_{|m|}(K_1) J_{|n|}(K_2) J_{|p|}(K_3) \sin[\omega_C + m\omega_{FM} + n(\omega_{FM} + \omega_{AM}) + p(\omega_{FM} - \omega_{AM})]t\}, \quad (2)$$

where $K_1 = \mu B/2\omega_{FM}$, $K_2 = \mu B/[4(\omega_{FM} + \omega_{AM})]$, and $K_3 = \mu B/[4(\omega_{FM} - \omega_{AM})]$. This corresponds to the idealized case, in which the tone-burst waveform is assumed to be undistorted. In practice, inevitable nonidealities result from harmonic generation and intermodulation distortions in the electro-optic modulator and in the circuits used to drive it. However, because infrared linewidths (Doppler width ≅ 200 MHz) are so much larger than ν_{AM} (10–100 kHz), the effects of AM sidebands on the tone-burst modulated line shapes are generally negligible. Typically, the experiment is carried out with ~10% of the laser power in the first pair of FM sidebands, which are separated from the carrier by ±400 MHz ($\nu_{FM} > \Delta\nu_{Doppler}$). This requires ~50 V rms to be applied to the electro-optic modulator at ν_{FM}.

Typical tone-burst modulated absorption line shapes are shown in Figs. 2 and 3. The $R(1/2)_{1/2}$ spin doublet of the $v = 0 \rightarrow 2$ overtone band[10] of NO at 3728.7 cm^{-1}, observed in a single-pass 2-m cell with 140 mTorr of NO at 300 K, is shown in Fig. 2. This signal corresponds to a 1% maximum absorption of the total laser power. When known absorption coefficients for NO overtone transitions are used, this indicates that a detection limit of $2 \times 10^{13}/cm^3$ for NO is obtainable. Multipassing could reduce this to $\sim 4 \times 10^{11}$ cm^{-3}. In Fig. 3 the $R(7/2)_{1/2}$ transition[11] of the $v = 0 \rightarrow 1$ band of OH at 3728.62 cm^{-1}, generated in a 20-mA dc glow discharge through 500 mTorr of H_2O in an ambient-temperature 1-m cell, is shown and illustrates the applicability of this technique to the detection of radicals produced in discharges. In these early experiments, the factor limiting the detection sensitivity was the modulated background that is due to the presence of standing waves in the optical system. These waves were minimized by tilting all optical surfaces to avoid reflections as much as pos-

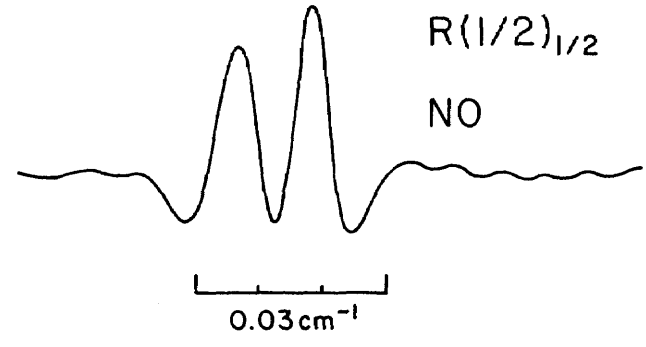

Fig. 2. The $R(1/2)_{1/2}$ doublet of NO ($v = 0 \rightarrow 2$) observed at 3728.7 cm^{-1} in a single pass through a 2-m cell containing NO at 140 mTorr using a 30-msec time constant.

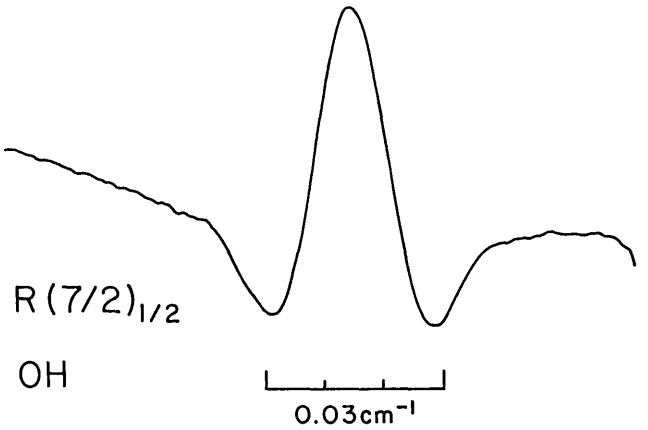

Fig. 3. The $R(7/2)_{1/2}$ transition of OH ($\nu = 0 \rightarrow 1$) observed at 3728.62 cm^{-1} in a single pass through a 1-m cell containing a discharge with 500 mTorr of H_2O at 20 mA using a 300-msec time constant.

sible. Furthermore, when an additional frequency modulation of the laser at ~3 MHz was incorporated, the largest background of the noise that is due to standing waves could be averaged out with appropriate adjustment of the amplitude. An improvement of ~5 in the sensitivity was realized in this manner; however, residual étalons in the system were still the cause of the background noise level.

Unfortunately, electrical breakdown of the $LiTaO_3$ electro-optic crystal occurred at a relatively early phase of this work, precluding a more extensive examination of the operating parameters of this experiment. Nevertheless, it appears that fractional absorptions of about 1×10^{-5} could readily be detected by this method. Because of its simplicity, sensitivity, and general applicability, tone-burst modulated infrared-laser spectroscopy should be of substantial value for spectroscopic and kinetic studies of reactive molecules.

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