

Doppler-free optical double-resonance Stark spectroscopy using modulation sidebands

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An electro-optic modulator, driven at a single radio frequency ν , is used to create sidebands ($\nu_L \pm \nu$) on the frequency ν_L of a cw single-mode CO₂ laser. Laser-induced line narrowing in molecular Stark spectroscopy is demonstrated, using double resonances of the copropagating waves at ν_L and ($\nu_L \pm \nu$) with pairs of coupled Doppler-broadened transitions. Doppler-free Stark spectra of the molecules PH₃, ¹³CH₃F, and ¹²CH₃F are used to illustrate the technique. For PH₃ it is found that the electric dipole moment vibrational difference $|\mu(\nu_2 = 1) - \mu(\nu = 0)| \leq 0.005$ D.

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We report a form of optical saturation spectroscopy for studying small splittings between molecular energy levels, with a spectral resolution far superior to that imposed in conventional spectroscopy by Doppler broadening. Our technique is based on the well-established¹⁻³ phenomenon of laser-induced line narrowing by double resonance of two copropagating laser beams with a pair of coupled Doppler-broadened transitions. Early experiments of this type were performed either with a single laser adjusted to oscillate simultaneously on two modes^{1,2} or with two separate lasers locked to a constant frequency difference.³ In our experiments only a

single laser frequency is used and the two optical frequencies, required to achieve double resonance, are produced by modulating the amplitude of the laser beam to generate sidebands. Several recent investigations of resonances in an amplitude-modulated laser beam are relevant to our study: observation of optical hole burning in solid ruby⁴; Zeeman spectroscopy in Na vapor⁵; the Zeeman effect of resonance fluorescence from I₂ vapor,⁶ using a technique originally applied with non-laser light sources.⁷ These investigations all used visible or ultraviolet light sources and most involved magnetically tuned phenomena. In contrast, our appli-

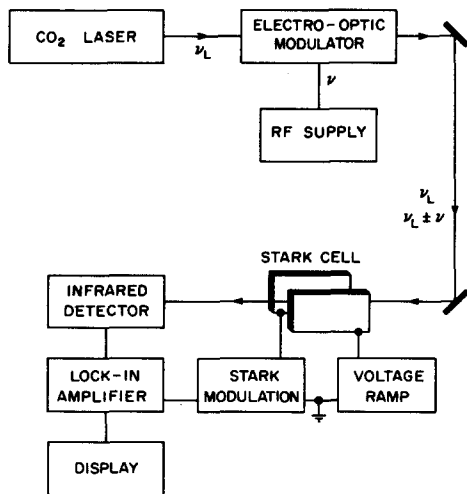


FIG. 1. Block diagram of the apparatus.

cation of the modulation sideband technique involves infrared lasers and the Stark effects of molecular vibration-rotation levels. The use of frequency-modulation sidebands, generated by piezoelectric modulation of the cavity length of an infrared laser, has been briefly reported⁸ in a study of the Stark effect of CH₄. Further applications of modulation sidebands are proposed in recent theoretical work on saturation spectroscopy.⁹

A schematic diagram of our apparatus is shown in Fig. 1. Linearly polarized infrared radiation from a cw CO₂ laser passes through an electro-optic modulator, consisting of a CdS waveplate, a CdTe electro-optic crystal and a linear polarizer. The modulator is

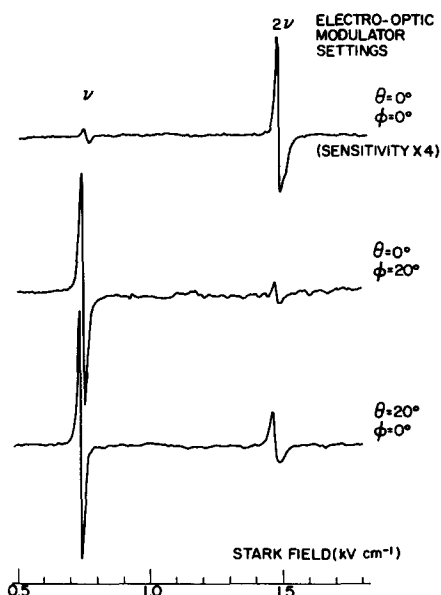


FIG. 2. Infrared double-resonance Stark spectra for PH₃ at ~6 mTorr pressure, Stark modulation 10 V cm⁻¹ at 10 kHz, and optical modulation frequency $\nu = 24.198$ MHz, illustrating the effects of applying an optical bias (waveplate retardation $\sim \pi/4$ rad, orientation ϕ) and of polarizer orientation θ . The $\nu_2 Q(14,12)$ transition of PH₃ is in resonance with the 10.16- μm R(34)CO₂ laser line. The assignment of the ν - and 2ν -type resonances is discussed in the text. The time constant of detection is 0.3 s.

driven at a fixed radio frequency ν which can range from 0.2 to 30 MHz; a rf power amplifier and resonant step-up transformer produce voltages of 1–2 kV p-p across the CdTe crystal within this frequency range, yielding a peak optical retardation of $\frac{1}{10}\pi - \frac{1}{5}\pi$ rad. The remainder of the apparatus is of the type used¹⁰ for conventional laser Stark spectroscopy. Phase-sensitive detection at the modulation frequency of the Stark field produces essentially Doppler-free resonances in derivative form as the voltage ramp is scanned.

A novel aspect of our technique is the capability of optimizing features in the Stark spectra by adjusting either the angle ϕ , between the retardation axis of the waveplate and the polarization vector of the incident laser radiation, or the angle θ , by which the linear polarizer is uncrossed with respect to the incident radiation. In the simplest case, where $\phi = \theta = 0^\circ$, virtually all of the radiation reaching the Stark cell is concentrated at the two sideband frequencies $(\nu_L + \nu)$ and $(\nu_L - \nu)$, apart from a small amount of radiation transmitted at the carrier frequency ν_L , due to optical imperfections. If the Stark field is directed parallel to the original polarization vector of the laser beam, the sidebands will excite a pair of perpendicular transitions having $\Delta M = \pm 1$, yielding the overall selection rule $|\Delta M| = 2$ and the resonance condition that the two Stark sublevels differing in M by 2 should be separated by a frequency difference of 2ν . For a level (J, K) of a symmetric-top molecule having electric dipole moment μ and displaying a first-order Stark effect, the electric field at which this 2ν -type resonance occurs is $h\nu J(J+1)/\mu K$.¹¹ Alternatively, if the linear polarizer is displaced from $\theta = 0^\circ$, or if an optical bias is applied by rotating the waveplate away from $\phi = 0^\circ$, further strong resonances appear, involving the carrier frequency ν_L

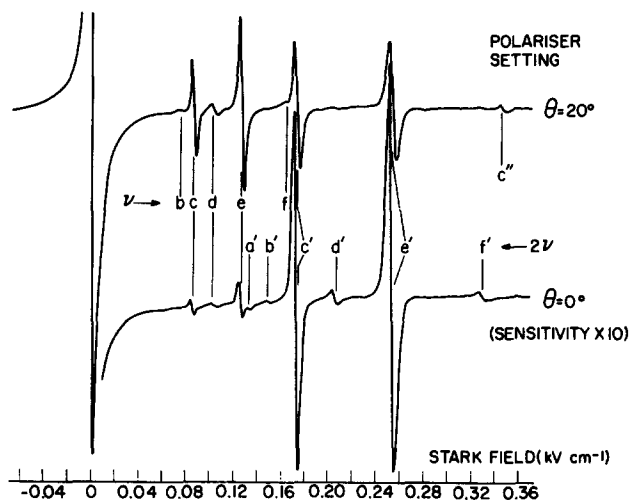


FIG. 3. Infrared double-resonance Stark spectra for ¹³CH₃F at ~5 mTorr pressure, Stark modulation 5 V cm⁻¹ at 10 kHz, zero optical bias, and optical modulation frequency $\nu = 24.205$ MHz, showing the zero-field level-crossing signal and both direct and collision-induced Stark resonances. The $\nu_2 R(4,3)$ transition of ¹³CH₃F is in resonance with the 9.66- μm P(32) CO₂ laser line. The resonances are labelled a, b, c, \dots in the style of Ref. 12, a prime being used to distinguish the 2ν -type resonances (optimized at $\theta = 0^\circ$) from the ν -type resonances (optimized at $\theta = 20^\circ$). The resonance labelled c'' is discussed in the text. The time constant of detection is 0.1 s.

and either of the sidebands ($\nu_L \pm \nu$); the Stark sublevels coupled by the radiation field in this case differ by ν , so that the ν -type resonant electric field for a symmetric top is $\frac{1}{2}h\nu J(J+1)/\mu K$. Such effects are illustrated in Fig. 2, showing results for the ν_2 Q(14, 12) transition of phosphine, PH_3 , which lies close (\sim MHz) to the 10.16- μm R(34) CO_2 laser line. Linewidths of \sim 1 MHz FWHM are obtained, corresponding to 100-fold laser-induced line narrowing with respect to the normal Doppler linewidth.¹²

Figure 3 displays a further example of the technique. The infrared double-resonance Stark spectrum of the ν_3 R(4, 3) transition of $^{13}\text{CH}_3\text{F}$, which differs in frequency by -25.8 MHz from the 9.66- μm P(32) CO_2 laser line,¹⁰ was studied by Brewer *et al.*,¹³ using two lasers locked to a fixed frequency difference. Our results, obtained with just a single laser beam amplitude modulated at 24.205 MHz, faithfully reproduce the previous results,¹³ including the appearance of collision-induced resonances *a, b, d*, and *f*. Figure 3 shows that the ν -type resonances (*a, b, c, ...*) are greatly enhanced with respect to the 2ν -type signals (*a', b', c', ...*) when the polarizer is rotated from $\theta = 0^\circ$ to 20° .¹¹ The weak resonance labelled *c''* is a 2ν -type $|\Delta M| = 1$ signal due to a pair of $\Delta M = 0$ and $\Delta M = \pm 1$ transitions, produced by uncrossing the polarizer. The strong zero-field level-crossing signal, which always accompanies the optical double-resonance signals, is also shown in Fig. 3.

The modulation sideband technique has also been applied to the ν_3 Q(12, 2) Stark resonance of $^{12}\text{CH}_3\text{F}$ with the 9.55- μm P(20) CO_2 laser line. Separate signals from $\nu = 0$ and $\nu_3 = 1$ vibrational states are clearly resolved, in good agreement with the results of Brewer's two-laser technique.^{3, 13} In contrast, our results for the ν_2 Q(14, 12) transition of PH_3 (Fig. 2) do not show any separation of contributions from the two vibrational states; this places an upper limit of 0.005 D on the electric dipole moment difference, $|\mu(\nu_2 = 1) - \mu(\nu = 0)|$. Other applications of the modulation sideband technique include the determination of $\mu(\nu_2 = 1)$ for $^{15}\text{NH}_3$ from the quadratic Stark effect of the ν_2 *asR*(2, 0) transition and studies of extremely small ($\sim 10^{-5}$ D) rotationally induced electric dipole moments such as those of the tetrahedral molecule GeH_4 ; these will be reported in detail elsewhere.¹⁴

Finally, we wish to stress the advantages and potential scope of this new technique. It is capable of sub-MHz resolution of atomic and molecular level splittings, without imposing severe demands on stability and calibration of laser frequency, as only the *difference* between carrier frequency ν_L and sideband frequencies ($\nu_L \pm \nu$) is critical. Furthermore, the technique employs only a single laser and does not require that two spatially separated laser beams be used. Thus, although

our results do not indicate improvement in accuracy and sensitivity over those obtained by using the two-laser method,¹³ the apparatus is considerably simpler. As an adjunct to conventional laser Stark spectroscopy, the optical double-resonance method is best applied to very small Stark effects and to transitions which lie so close to the laser frequency that their Stark pattern would not be resolved at the small electric fields required to achieve a single-photon resonance. It has the advantage of giving *separate* Stark shifts for upper and lower states and, in the case of a first-order Stark effect, of producing a much simpler spectral pattern than that from conventional Stark spectroscopy. The technique is by no means restricted to infrared laser frequencies or to investigation of the Stark effect, and should find extensive application in studies of Zeeman effects, collisional processes, hyperfine structure, etc., associated with transitions throughout the optical spectrum.

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¹H.R. Schlossberg and A. Javan, *Phys. Rev.* **150**, 267 (1966); *Phys. Rev. Lett.* **17**, 1242 (1966).

²M.S. Feld and A. Javan, *Phys. Rev.* **177**, 540 (1969).

³R.G. Brewer, *Phys. Rev. Lett.* **25**, 1639 (1970).

⁴A. Szabo, *Phys. Rev. B* **11**, 4512 (1975).

⁵K. Takagi, R.F. Curl, and R.T.M. Su, *Appl. Phys.* **7**, 181 (1975).

⁶M. Broyer, J.C. Lehmann, and J. Vigué, *J. Phys. (Paris)* **36**, 235 (1975).

⁷A. Corney and G.W. Series, *Proc. Phys. Soc. (London)* **83**, 207 (1964); **83**, 213 (1964).

⁸A.C. Luntz and R.G. Brewer, *J. Chem. Phys.* **54**, 3641 (1971).

⁹M. Sargent, P.E. Toschek, and H.G. Danielmeyer, *Appl. Phys.* **11**, 55 (1976); M. Sargent and P.E. Toschek, *Appl. Phys.* **11**, 107 (1976).

¹⁰S.M. Freund, G. Duxbury, M. Röhmed, J.T. Tiedje, and T. Oka, *J. Mol. Spectrosc.* **52**, 38 (1974).

¹¹The assignment of resonances at a field of $h\nu J(J+1)/\mu K$ is ambiguous, since a ν -type $|\Delta M| = 1$ process involving the carrier wave and one of the sidebands yields a resonance field which is identical to that of the 2ν -type $|\Delta M| = 2$ process. We have observed the two processes at separate fields in second-order Stark effects, such as that of the $^{15}\text{NH}_3 \nu_2 \text{asR}(2, 0)$ transition.

¹²The asymmetric distortion of derivative line shapes, which is evident at higher Stark fields, is attributed to small inhomogeneities which existed in the Stark field.

¹³R.G. Brewer, R.L. Shoemaker, and S. Stenholm, *Phys. Rev. Lett.* **33**, 63 (1974); R.L. Shoemaker, S. Stenholm, and R.G. Brewer, *Phys. Rev. A* **10**, 2037 (1974).

¹⁴W.A. Kreiner, B.J. Orr, U. Andresen, and T. Oka (unpublished).