# PRESSURE SHIFT AND BROADENING OF METHANE LINE AT 3.39 $\mu$ STUDIED BY LASER-SATURATED MOLECULAR ABSORPTION*

R. L. Barger and J. L. Hall
Joint Institute for Laboratory Astrophysics,† Boulder, Colorado 80302

(Received 21 October 1968)

We study broadening and the anomalously small shift of a 3.39-$\mu$ rotation-vibration line of methane at millitorr pressures. Saturation by the laser intracavity field allows investigation of the *very* sharp natural linewidth, without Doppler broadening. Two lasers were independently locked to this transition with an offset of less than ±1 kHz, a reproducibility of $\pm 1\times 10^{11}$.

By the use of laser saturation of molecular absorption, we have obtained at 3.39 $\mu$ an emission feature in laser power centered on a methane vibration-rotation line. In this paper we report measurements of the broadening and exceptionally low shift of the line due to pressure, temperature, and other experimental conditions, and measurements of the reproducibility of line center. The emission feature is a very sharp Lorentzian line, its width being determined by collisional and interaction time effects. In this preliminary work we have obtained widths as narrow as 150 kHz half-width at half-maximum intensity, i.e., $\Delta\nu_{1/2}/\nu \approx 1\times 10^{-9}$ (the ultimate attainable half-width, as would be determined by the radiative lifetime, is $\Delta\nu_{1/2}/\nu \approx 1\times 10^{-12}$). We have stabilized to the line center with a reproducibility of better than $\pm 1\times 10^{-11}$. This reproducibility is 2.5 orders of magnitude better than that of the primary standard of length, which is defined by the 6057-Å line of $\mathrm{Kr}^{86}$.

Several reviews of laser-stabilizing methods are available.[1,2] For a discussion of laser-wavelength standard *accuracy* problems the reader is referred to a recent paper by one of us (J.L.H.).[3] Essentially all previous absolute methods rely on an atomic transition as the fundamental wavelength reference. Molecules are attractive as the reference on several counts. First, molecular vibration-rotation transitions have characteristically longer radiative lifetimes. Second, we deal with absorption from a thermally accessible state, a fact which will be an important aid to understanding the residual effects of collisions. Third, we may select a system with a favorable branching ratio to maximize the absorption per unit linewidth, and fourth, as mentioned by many workers,[4] the richness of molecular spectra makes more likely an "accidental" coincidence within the 2- or 3-ppm tuning range of the typical laser. By now, many such overlaps are known.[4,5]

The $\mathrm{CH}_4$ absorption of the 3.39-$\mu$ radiation of the helium-neon laser is a remarkably happy case.[6] It is a transition [$P(7)$ line of the $\nu_3$ band] which starts from a level that is well populated thermally even at liquid-nitrogen temperatures and below. The natural lifetime is estimated to be about 10 msec.[7] The absorption coefficient is very large, about 0.18 $\mathrm{cm}^{-1}\ \mathrm{Torr}^{-1}$,[7] so that relatively modest laser power densities are required to obtain usable saturation. The transition lies about 100 MHz blue of the helium-neon line center,[7] but one can pressure-shift the laser into very good coincidence with the methane absorption. See Fig. 1(a). In addition, the high helium pressure ($\simeq$12 Torr) greatly increases the laser homogeneous width and thus allows single frequency oscillation. Even at these pressures the 3.39-$\mu$ laser line has high gain, which allows the use of an intracavity gas cell to obtain high power density and high sensitivity to small absorption. Uehara, Sakurai, and Shimoda[8] have shown that this methane line is also free from Stark shift. Magnetic interaction with the earth's field is expected to produce about $\frac{1}{2}$ kHz of splitting. Spin-rotation interaction may be of the order of 3 kHz.

Our work is based on the synthesis of this background with an idea of Lee and Skolnick,[9] who reported saturation of the absorption of pure neon placed within the cavity of a He-Ne oscillator. Their point is that the absorption profile is so sharp that a Doppler shift is generally required to bring the laser frequency into resonance with the absorber. As the laser frequency approaches the natural (molecular) absorption frequency, absorbers with smaller longitudinal velocities are involved. Ultimately, at line center, both counter-running cavity waves interact with the same zero-longitudinal-velocity subgroup. For suitably large cavity power density, this doubled interaction rate will reduce the actual number of resonant absorbers and thus give rise to an

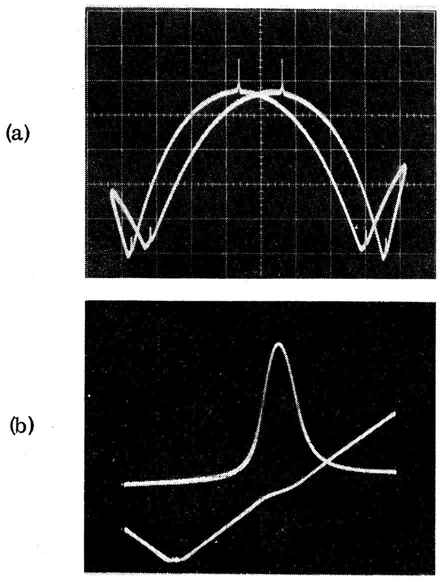

FIG. 1. (a) Output power versus laser-cavity tuning. Only the upper 20% of the 1-mW output is displayed in the full ten divisions. The horizontal axis is calibrated as 28 MHz/div by the cusps where the order of the interferometer changes by 1 and the frequency jumps by 200 MHz. The saturated absorption peak is about 2% amplitude and 400 kHz wide, and is nicely centered on the Ne$^{20}$ Doppler gain curve. (b) Upper trace is output power versus cavity tuning, similar to (a) except here the scale is 2 MHz/div. Lower trace (ordinate is the "optical" oscillation frequency (beat frequency against a local oscillator laser) versus the same cavity sweep as the upper trace. The frequency "hangup" occurs as the oscillation frequency is strongly pulled by the methane's rapidly varying phase shift.

"emission" feature precisely at line center. It is important to note that even if the two running waves are of unequal intensity, there is no systematic shift of line center, assuming the cell to be isothermal. The linewidth of the interaction is seen to be the homogeneous width due to collisions, natural decay rate, intensity broadening, Stark and Zeeman broadening, etc. For very favorable absorber systems, nearly free from the above-mentioned sources of broadening, one may observe the linewidth anticipated on the basis of the finite interaction time. This time should scale proportional to the laser spot size and inversely with the thermal velocity of the absorber molecules. In the experiments to be described, the corresponding partial linewidth is in the neighborhood of 100 kHz half-width at half-maximum $(1\times10^9)$.

*Experiment*. —Since much of our success in these measurements is directly due to the novel experimental techniques employed, it may be of interest briefly to summarize the salient features of the apparatus. To minimize environmental disturbances, all experiments have been carried out in an isolated underground laboratory (vault). The three lasers, Nos. 1 and 3 with and No. 2 without methane cells, and the methane-gas handling system are mounted on a 3-ton, 4-ft×12-ft, cast-iron–surface table. The cavities of lasers Nos. 1 and 3 are about 60 cm long. They are spaced with three fused-silica rods, 19 mm in diameter, which are cemented into lightweight aluminum plates with an acoustically lossy epoxy. The cavity is divided roughly equally between the rf excited helium-neon gain cell and the methane absorption cell. Power densities up to $2\frac{1}{2}$ W/cm$^2$ are obtained in the methane cell. Mirrors are scanned with electrostrictive crystals to give frequency modulation at frequencies up to 10 kHz. With methane inside the cavity, the phase shift accompanying the extremely sharp absorption slows the cavity tuning rate at line center by a factor of about 3. See Fig. 1(b). Thus to obtain a proper line shape we must program the scan over the line as a frequency input rather than a cavity-tuning input.

Excellent automatic frequency locks are obtained with specially designed high-stability servo systems. We lock laser No. 1 to line center (zero-slope point) by using the central zero of the first derivative with respect to frequency of the laser power. Using laser No. 2 as a local oscillator, we obtain beat frequencies between lasers Nos. 1 and 2 and between lasers Nos. 2 and 3. Signals proportional to beat frequency are obtained with linear frequency-to-voltage converters and fed into the servos to perform the locks. We call this technique "frequency-offset locking." With the No. 1-No. 2 frequency-offset lock held constant at, say, 5000.0 kHz, the frequency of the No. 2-No. 3 can be varied from $\frac{1}{4}$ to about 15 MHz to scan over the methane line of the No. 3 laser. Frequency-offset locking yields beat frequencies with about ±50-Hz fluctuations for a $\frac{1}{10}$-sec averaging time. The line-center lock has total frequency excursions of about 1 kHz. Thus, with the "frequency-offset locking" technique, stability can be transferred from one laser to another with almost no loss of precision.[10] (The average offset frequencies drift by less than 1 kHz/h.)

Data have been taken in the form of $X$-$Y$ plots of the derivative with respect to frequency of laser No. 3's output power. Some representative first-derivative line shapes are shown in Fig. 2. The modulation used, 50-kHz peak-to-peak, is small enough that no important correction for finite modulation width is required. The linewidth was measured at 15 methane pressures between 0.02 and 48 mTorr. In another set of experiments at a constant 13-mTorr methane pressure, xenon was used as the pressure-broadening agent. Xenon pressure ranged from 0 to 88 mTorr. The resulting line shapes, similar to those of Fig. 2, are all accurately described by the Lorentz derivative function. The broadening results may be well expressed by the following (least-squares fitted) linear relation

$$\Delta\nu_{\frac{1}{2}} = 150\text{ kHz} + (13.9 \pm 0.4\text{ kHz/mTorr}) \times P_{\mathrm{Xe}} + (16.3 \pm 0.6\text{ kHz/mTorr}) \times P_{\mathrm{CH}_4}.$$

Here $\Delta\nu_{1/2}$ is the half-width at half-maximum intensity of the Lorentz power signal. This half-width, according to the arguments given by Bennett,[11] corresponds approximately to twice the half-width of each Lorentz hole. Thus for pure $\mathrm{CH}_4$ self-broadening we report 8.1 ± 0.3 kHz/mTorr as the "phase-memory" linewidth $\Gamma_2$ ($\Gamma_2 = 1/\pi T_2$ in the usual resonance jargon, $T_2$ being the polarization coherent relaxation time).

Gerritsen and Ahmed[12] report the slope of the absorption linewidth versus pressure to be 7.4 ± 0.5 kHz/mTorr for pure methane. The small difference between these two results, 0.7 ± 0.8 kHz/mTorr, may well arise from a small error in absolute calibration of the pressure measurement. (Our measurements were made with a high-pressure ion gauge calibrated for methane against a McCloud gauge using a capacitance manometer as the null detector.) However, the sign of the difference is not inconsistent with the possibility that phase and frequency shifts of interest to us can arise from weaker collisions than those which affect the high-pressure experiments of Ref. 12. It will be very interesting for us to study the signal size (as well as linewidth) as a function of saturation parameter and pressure, since we should be able to determine separately the rate of energy loss, $\Gamma_1$, and the rate of loss of phase coherence, $\Gamma_2$.

We now turn to the interesting question of the line shift with pressure, power, and other experimental conditions, that is, to the question of accuracy and freedom from spurious systematic frequency offsets. We are easily able to measure pressure-induced broadening as reported above. However even with excellent digital data (similar to those illustrated in Fig. 2) and computer line-shape analysis, we are not yet able reliably to measure the pressure-induced shift

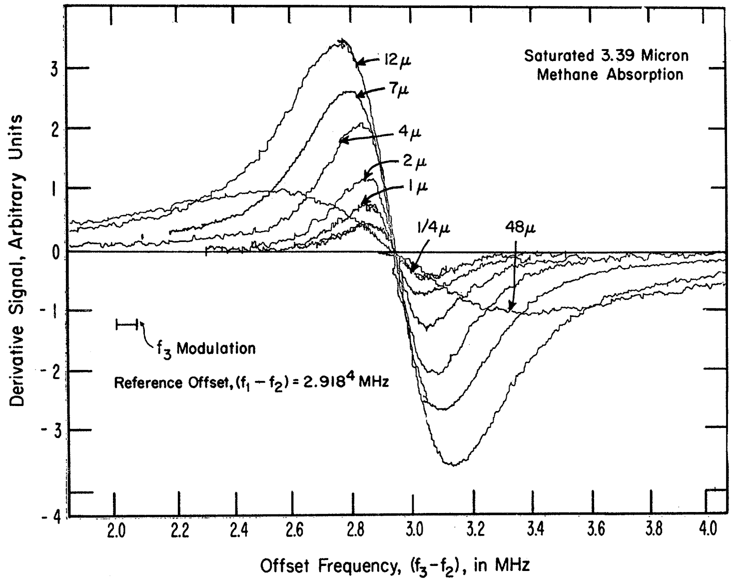

FIG. 2. First derivative of the output power of laser No. 3 versus offset-lock frequency $f_3 - f_2$. The several curves are labeled by the $\mathrm{CH}_4$ (in mTorr) in laser No. 3. Laser No. 1 was stabilized to the center of its methane line. Laser No. 2, local oscillator for both optical-heterodyne detectors, was stabilized against laser No. 1 with a $2.918^4$-MHz offset. The curves are very accurately described by the Lorentz-derivative function.

in pure $CH_4$. The present best value is 75 ± 150 Hz/mTorr. Thus the shift-to-width ratio for $CH_4$-$CH_4$ interaction is 1:200 rather than the roughly 1:4 ratio usually obtained for Van der Waals interactions. Our result, an upper limit, is obviously already pleasant in connection with wavelength-standards applications of this work. We believe this remarkably small shift can be directly understood in terms of the high symmetry of the methane molecule, the beautifully regular spacing of the relevant rotational energy levels, and the low kinetic energy of the collision partners. Interestingly enough, xenon also gives an unmeasurable shift, 29 ± 150 Hz/mTorr.

To develop some appreciation of the accuracy of the lock-to-line center, we have looked for a frequency difference between lasers Nos. 1 and 3 with the lasers independently line-center locked. The finite slope of the laser power curves beneath the methane peaks contributed less than $\frac{1}{2}$-kHz offset. For methane pressures below about 10 mTorr, we observe an asymmetric power broadening.[13] This disappears for low power density (below ~$\frac{1}{2}$ W/cm$^2$), where adequate signal-to-noise ratio is still obtained. Shift of the zero-slope point is about 1 kHz at a power density of 1 W/cm$^2$. Thus, we have extrapolated to the limit of low power for various methane pressures. We find no frequency difference to within our experimental uncertainties of ±1 kHz between the two independently locked methane saturated-absorber systems. This demonstrated reproducibility of ±1 part in $10^{11}$ is better by 2.5 orders of magnitude than the present primary standard of length, and to our knowledge is 2 orders of magnitude better than any figure previously reported for wavelength reproducibility.[14]

Some early experiments with two separated interaction regions ("Ramsey two-cavity method") were partially successful in demonstrating the expected interference effects at very low pressures, but the relative phase of the excitation in the two interaction zones could not be adequately controlled in those first experiments. Probably the two most interesting directions for further immediate progress are the following: (a) to enlarge the beam diameter in the interaction region and to refrigerate the methane, both of which sharpen the resonance, and (b) to build a ratio-type experiment outside the laser cavity. Our interesting, but still preliminary, results on the second approach will be reported at a later time. In addition to the interest as a potential wavelength standard, these techniques should allow study of gas-phase collision effects with a sensitivity never before available.

The authors are happy to express their appreciation to their colleagues R. N. Zare and P. L. Bender for their interest and their useful comments. One of us (J.L.H.) has profited greatly from several conversations with D. W. Halford on frequency standards and related topics.

---

*Work supported in part by National Aeronautics and Space Administration, Advanced Development Division, Goddard Space Flight Center, Greenbelt, Md., and in part by the National Bureau of Standards, of which the authors are staff members.

†Of the University of Colorado and the National Bureau of Standards.

[1] A. D. White, IEEE J. Quantum Electron. QE-1, 349 (1965).

[2] G. Birnbaum, Proc. IEEE 55, 1015 (1967).

[3] J. L. Hall, IEEE J. Quantum Electron. QE-4 (to be published).

[4] R. N. Zare (Joint Institute of Laboratory Astrophysics), private communication; K. M. Baird (National Research Council of Canada, Ottawa, Canada), private communication; G. Gould (Polytechnic Institute of Brooklyn), private communication; V. P. Chebotayev, in the Proceedings of the Fifth International Conference on Quantum Electronics, Miami, Florida, May, 1968 (to be published).

[5] C. B. Moore, to be published.

[6] Methane has also been suggested for an absolute standard by K. Shimoda, in Conference on Precision Electro-Magnetic Measurements, Boulder, 1968, U. S. Atomic Energy Commission Report No. CONF 66 0644 (U. S. Government Printing Office, Washington, D. C., 1968).

[7] H. J. Gerritsen, in the Proceedings of the Third International Congress on Quantum Electronics, Paris, 1963, edited by P. Grivet and N. Bloembergen (Columbia University Press, N.Y., 1964), p. 581.

[8] K. Uehara, K. Sakurai, and K. Shimoda, to be published. Result quoted in Ref. 6.

[9] P. H. Lee and M. L. Skolnick, Appl. Phys. Letters 10, 303 (1967).

[10] These techniques will be reported in more detail at a later time.

[11] W. R. Bennett, Jr., in the Proceedings of the Third International Congress of Quantum Electronics, Paris, 1963, edited by P. Grivet and N. Bloembergen (Columbia University Press, N.Y., 1964), p. 450.

[12] H. J. Gerritsen and S. A. Ahmed, Phys. Letters 13, 41 (1964).

[13] These very interesting changes in line shape at high power are presently being investigated.

[14] Our "material" fractional linewidth is (within a factor of 2 or so) equal to that of the hydrogen maser, the present standard of excellence for reproducibility. Our cavity $Q$ of $20\times10^6$ is about 50 times higher than that of a "typical" H maser. Our measured signal-to-noise ratio is about 50 dB in a 1-Hz bandwidth, about

the same as the H maser. However, a refrigerated photocell and a He-Ne optical preamplifier should each add about 10 dB. The higher cavity $Q$ will require greater bandwidth in the cavity stabilizing feedback loop, but the signal-to-noise ratio should be ample. With a methane cell of four-times larger aperture, cooled to 76°K, we should closely approximate the H-maser stability.

---

# MANY-BODY THEORY FOR TIME-DEPENDENT PERTURBATIONS IN ATOMIC SYSTEMS*

N. C. Dutta, T. Ishihara, C. Matsubara, and T. P. Das
Department of Physics, University of California, Riverside, California

(Received 5 November 1968)

A many-body approach for the calculation of time-dependent properties of atoms is developed and applied to helium atom. The refractive indices and excitation energies so obtained are in excellent agreement with experiment.

The Brueckner-Goldstone many-body perturbation theory has been used with great success in the past for the calculation of time-independent properties of atoms.[1-3] The purpose of the present Letter is to extend this theory to the calculation of the response of atomic and molecular systems to time-dependent external perturbations. Such a study is of great current interest because of the potential applicability[4] of this response in the calculation of the properties[5-8] of interacting atomic systems. The utilization of diagrammatic techniques in the present method enables us to include and interpret many-electron effects as well as one-electron effects in a systematic way. The procedure is illustrated by the calculation of the frequency dependent polarizability of helium atom. The choice of helium has been dictated by two main reasons. First, helium is the simplest many-body system in which the theory could be tested. Secondly, the results of a number of variational calculations[9-13] and experimental measurements[14-16] are available for both the static and dynamic polarizabilities and optical excitation energies[17] of this atom which can be compared with our theory.

The total Hamiltonian $\mathcal{H}$ for an $N$-electron atom in the presence of a time-dependent perturbation $\mathcal{H}_2(t)$ is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2(t), \tag{1}$$

where

$$\mathcal{H}_0=\sum_{i=1}^{N}(T_i+V_i),$$

and

$$\mathcal{H}_1=\sum_{i>j}^{N}\frac{1}{r_{ij}}-\sum_{i=1}^{N}V_i. \tag{2}$$

$T_i$ is the sum of the kinetic energy and nuclear Coulomb potential. The single-particle potential $V_i$, which is in principle arbitrary, is chosen so as to make the perturbation expansion as convergent as possible. To obtain the expectation value of any operator $\mathcal{O}$ for this system, namely,

$$\langle\mathcal{O}\rangle=\langle\Psi(t)|\,\mathcal{O}\,|\Psi(t)\rangle, \tag{3}$$

we need the normalized eigenfunction $\Psi(t)$ of the total Hamiltonian $\mathcal{H}$ in Eq. (1). In obtaining $\Psi(t)$ it is convenient to work in the interaction representation involving the time-development[18] operator $U(t,t_0)$:

$$\Psi(t)=U(t,t_0)\Psi(t_0), \tag{4}$$

where

$$U(t,t_0)=\sum_n U_n(t,t_0),$$

$$U_n(t,t_0)=[(-i)^n/n!]\int_{t_0}^{t}dt_1\cdots \times\int_{t_0}^{t}dt_n\,T\{\mathcal{H}_I(t_1)\cdots\mathcal{H}_I(t_n)\} \tag{5}$$

and $\mathcal{H}_I(t)=e^{i\mathcal{H}_0t}(\mathcal{H}_1+\mathcal{H}_2)e^{-i\mathcal{H}_0t}$, and $T$ is Wick's chronological operator.[18] Using the adiabatic hypothesis,[18] Eq. (3) can be rewritten as

$$\langle\mathcal{O}\rangle=\langle U(t,-\infty)\Phi_0|\,\mathcal{O}_I\,|U(t,-\infty)\Phi_0\rangle =\langle\Phi_0|T(\textstyle\sum_n S_n\mathcal{O}_I)|\Phi_0\rangle_L, \tag{6}$$

where $L$ indicates that the summation is over linked terms only and $S_n=U_n(\infty,-\infty)$. $\Phi_0$ is the $N$-particle ground-state eigenfunction of $\mathcal{H}_0$ and is a Slater determinant composed of the lowest $N$ one-electron states in the potential $V_i$. Using the complete set of eigenstates of $\mathcal{H}_0$, each term in Eq. (6) can be represented by Feynman-like dia-

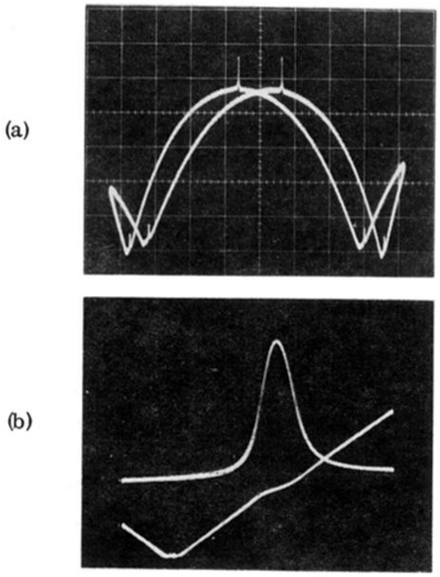

FIG. 1. (a) Output power versus laser-cavity tuning. Only the upper 20% of the 1-mW output is displayed in the full ten divisions. The horizontal axis is calibrated as 28 MHz/div by the cusps where the order of the interferometer changes by 1 and the frequency jumps by 200 MHz. The saturated absorption peak is about 2% amplitude and 400 kHz wide, and is nicely centered on the $Ne^{20}$ Doppler gain curve. (b) Upper trace is output power versus cavity tuning, similar to (a) except here the scale is 2 MHz/div. Lower trace (ordinate is the "optical" oscillation frequency (beat frequency against a local oscillator laser) versus the same cavity sweep as the upper trace. The frequency "hangup" occurs as the oscillation frequency is strongly pulled by the methane's rapidly varying phase shift.