

Absorption spectroscopy at the limit: detection of a single atom

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We investigate the sensitivity limit of absorption spectroscopy. An experiment is described in which the decrease in transmitted light intensity that is due to absorption by a single, electromagnetically confined atomic ion is observed.

Absorption spectroscopy dates back to the early 19th century when Fraunhofer observed characteristic lines in the solar spectrum (Fraunhofer lines) and to the mid-19th century when Kirchhoff and Bunsen identified specific absorption lines with certain elements.¹ Since that time, absorption spectroscopy has played an important role in the development of atomic and molecular theory and continues to be an important analytical tool in several fields of science. As with most experimental measurements, signal-to-noise ratio and resolution are of primary concern, and various advances have led to increased sensitivity. The laser led to a renewed interest in spectroscopic measurements. Not only can source brightness and resolution be greatly increased but the high spectral intensities have made it possible to observe a host of nonlinear effects that have greatly improved sensitivity and resolution.² It is always interesting to ask what the ultimate limits to a technique are. In this Letter we investigate the sensitivity limit of absorption spectroscopy when absorption is detected as a decrease in the radiation transmitted through the absorber.

There are many different kinds of sensitivity limits that could be established given the constraints of a particular experimental configuration. Here we investigate one such limit by asking the question, "What is the smallest number of atoms or molecules that one can detect by using absorption spectroscopy?" The fundamental limit is one atom or molecule, and in this Letter we describe a particular realization of this limit. Previously, the lower limit on number sensitivity was found to be about 65 atoms³ when a four-wave mixing technique⁴ was used.

We can estimate the signal-to-noise ratio in an absorption experiment in the following way. We assume that we have a collimated radiation source of power P incident upon a collection of N atoms or molecules. For simplicity, we assume that the intensity of the source at the position of the atoms is uniform with cross section A . We write the fraction of power absorbed by the atoms as ηP and assume that $\eta \ll 1$. We further assume that the detector converts the incident photons into electric current with quantum efficiency β . Therefore the total detected current is given by $I_D = P(1 - \eta)e\beta/(h\nu)$, where e is the electron charge, h is

Planck's constant, and ν is the frequency of the incident photons. We define the signal I_s as the change in detector current due to absorption. Therefore we have

$$I_s = \eta P e \beta / (h\nu). \quad (1)$$

The rms noise current can be written as

$$i_n = (i_D^2 + i_T^2 + i_{sh}^2)^{1/2}. \quad (2)$$

In Eq. (2), we have separated the statistically independent contributions from the detector noise i_D (e.g., Johnson noise), radiation-source technical noise i_T (e.g., intensity fluctuations in the radiation from a laser source), and shot noise in the detection process i_{sh} . The shot-noise contribution is simply written as $i_{sh}^2 = 2eI_D\Delta\nu$, where $\Delta\nu$ is the detection bandwidth. The contributions from i_D and i_T will depend on the specific experimental configuration, but we desire $i_D, i_T \ll i_{sh}$ for maximum signal-to-noise ratio.

If absorption is due to a particular atomic transition with resonance frequency ν_0 , then, below saturation, the absorption coefficient η is given by the expression $\eta P = N\sigma P/A$, where $\sigma = \sigma_0 K$. σ_0 is the resonant cross section for the particular transition observed. σ_0 is of the order of $\lambda^2/(2\pi)$, where λ is the wavelength at resonance.⁵ K is a factor ($K \leq 1$) that expresses the reduction of the cross section from the resonant value by (1) radiative decay into atomic states other than the lower state of the transition under investigation, (2) Doppler broadening, (3) collisional broadening, (4) detuning of the source away from ν_0 , or (5) finite bandwidth of the radiation source. We can write the signal-to-noise ratio, S/N, as

$$S/N = I_s/i_n = \frac{N\sigma_0 K e \beta P / (A h \nu_0)}{[i_D^2 + i_T^2 + 2e^2 \beta P \Delta\nu / (h \nu_0)]^{1/2}}. \quad (2)$$

Our experimental configuration is shown in Fig. 1. Since we are interested in the case when $N = 1$, a single, laser-cooled $^{198}\text{Hg}^+$ ion was confined in a miniature rf trap⁶ with inside endcap-to-endcap spacing $2z_0 = 0.064$ cm and inner ring diameter $2r_0 = 0.091$ cm. With a ring-to-endcap voltage $V_T \simeq (10 + 400 \cos \Omega t)$ V, where $\Omega/2\pi = 21.07$ MHz, the ion was confined to a space with linear dimensions $< 0.25 \mu\text{m}$.⁶ A narrow-band (width < 5 MHz) radiation source at 194

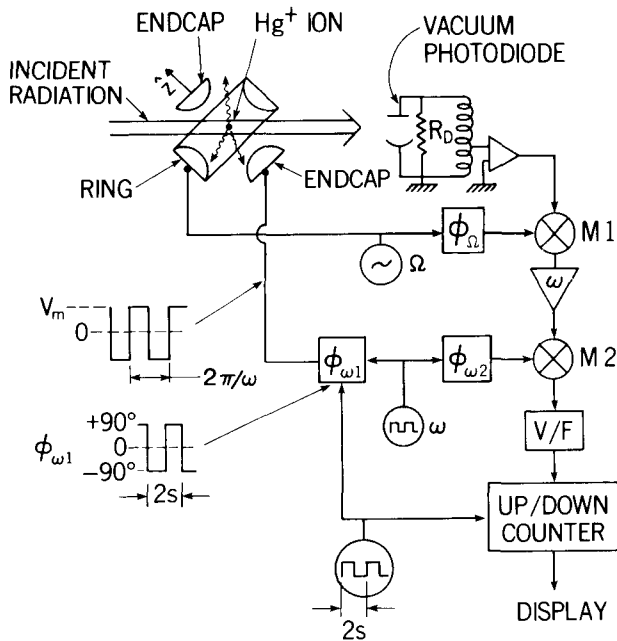


Fig. 1. Schematic diagram of the apparatus. Absorption from a single $^{198}\text{Hg}^+$ ion is detected as a change in current in the vacuum photodiode. This absorption is modulated at frequency Ω by applying a voltage V_m to one endcap electrode of the trap. To avoid a false signal from stray radiation picked up by the detector, the sign of V_m is alternated at frequency ω . To avoid drifts at the output of mixer M2, a third modulation at 0.5 Hz of the phase of ω and the sign of the signal at M2 is converted to dc by the up/down counter. V_m , ϕ_Ω , and ϕ_{ω_2} are adjusted to maximize the display output.

nm ($P \approx 3 \mu\text{W}$) was tuned near the $6s^2S_{1/2} \rightarrow 6p^2P_{1/2}$ first resonance transition in $^{198}\text{Hg}^+$ and focused through the trap and onto the ion. This radiation source was derived from sum-frequency mixing a dye laser (790 nm) and a frequency-doubled Ar^+ laser (257 nm).⁷ The detector was a vacuum photodiode with a Cs-Te photocathode. We had $\beta \approx 0.055$ (10% tube efficiency; 55% transmission from trap to detector). In order to suppress i_T from the 194-nm source, it is desirable to modulate the absorption at a high frequency.⁸ This was accomplished by applying a voltage V_m to one trap endcap. This displaced the ion from its equilibrium position in the rf trap and caused its velocity, which has a component along the direction of the 194-nm beam, to be modulated at the trap rf Ω . That is, the static electric force was compensated for by the pseudopotential force that gave rise to ion micromotion at frequency Ω .⁹ Owing to the first-order Doppler shift, the resonance frequency of the ion was modulated at Ω . Such frequency-modulation schemes were first used in nuclear magnetic resonance¹⁰ and microwave spectroscopy.¹¹ This scheme of velocity modulation is essentially identical with that developed by Saykally and co-workers.¹² As is indicated in Fig. 1, the modulated-absorption signal current was detected by a tuned circuit whose equivalent parallel resistance, $R_D \approx 300 \text{ k}\Omega$, was derived from the measured resonance Q and parallel capacitance ($\approx 3 \text{ pF}$ owing to tube and stray capacitance). Unfor-

tunately, the detector also picked up radiation from the unshielded trap electrodes, which gave a false signal that was unstable. To avoid this problem, we switched the phase of the absorption signal by 180° by switching the sign of the voltage V_m applied to the endcap at the frequency $\omega/2\pi = 2 \text{ kHz}$. Therefore, after the first mixer (M1), the absorption signal appeared at frequency ω , which we then converted to a dc voltage in M2. To avoid drifts at the output of M2, we switched the phase, ϕ_{ω_1} , of V_m by 180° every second and used a voltage-to-frequency converter (V/F) followed by an up/down counter to display the signal. The values of V_m and the phases ϕ_Ω and ϕ_{ω_2} were adjusted to give maximum absorption signal.

From Eq. (3), in order to maximize S/N, we want to make P as large as possible until saturation is reached. When the incident radiation exceeds saturation intensity, the numerator of Eq. (3) reaches a constant value given by $\sigma_0 K P / (A h \nu_0) \approx \gamma/2$, where γ^{-1} is the radiative lifetime of the upper state. Increasing P further only increases i_{sh} , thereby reducing S/N. If we assume that the incident radiation is just at saturation intensity, and if we neglect i_T in Eq. (3), Eq. (3) becomes (for $N = 1$)

$$S/N = (\pi\sqrt{2})^{-1} \frac{e\beta\gamma/(2\Delta\nu^{1/2})}{[4k_B T/R_D + e^2\beta\gamma A/(\sigma_0 K)]^{1/2}} \quad (4)$$

The factor $(\pi\sqrt{2})^{-1}$ accounts for the modulation scheme used but makes the simplifying assumption that the atomic absorption changes linearly between zero and its maximum value as the atomic-resonance frequency is modulated through its full extent. We have made the identification $i_D^2 = 4k_B T \Delta\nu/R_D$, where k_B is Boltzmann's constant and T is the effective temperature of the input circuit. For the first resonance transition in Hg^+ , $\gamma^{-1} = 2.3 \text{ nsec}$, and $\sigma_0 = 6.0 \times 10^{-11} \text{ cm}^2$. The ion was at the center of our focused Gaussian laser beam ($w_0 \approx 5 \mu\text{m}$). $K \approx 1$, which was the key to this experiment. Therefore, we calculate that the second term in the denominator of Eq. (4) is negligible. This was verified by a direct measurement of i_{sh}/i_D . We determined that the detector-noise temperature was $T \approx 600 \text{ K}$ ($\approx 3\text{-dB}$ noise figure) by measuring photon shot noise on the detector and assuming that $i_T \ll i_D$ at 21.07 MHz. Making the identification $\Delta\nu = (2\tau)^{-1}$, where τ is the integration time per point out of the up/down counter, we calculate that $S/N \approx 12.6$ ($\eta \approx 2.5 \times 10^{-5}$) for $\tau = 50 \text{ sec}$ from Eq. (4). This compares reasonably well with the data of Fig. 2, where we measured $S/N \approx 5.7$. For the maximum signal, the laser is tuned halfway down the resonance line and the absorption of the single ion is modulated between a few percent and nearly 100% of the maximum absorption at frequency Ω . The disagreement between theory and experiment may be due to two causes. First, the simple theory assumes that the absorption signal occurs only at frequency Ω and neglects signal content at harmonics of Ω . Second, we have neglected loss of signal due to radiative decay from the $^2P_{1/2}$ state to the metastable $^2D_{3/2}$ level. Data similar to those of Ref. 6 indicate this may account for reduction in signal by a factor of about 2 in the present experiment.

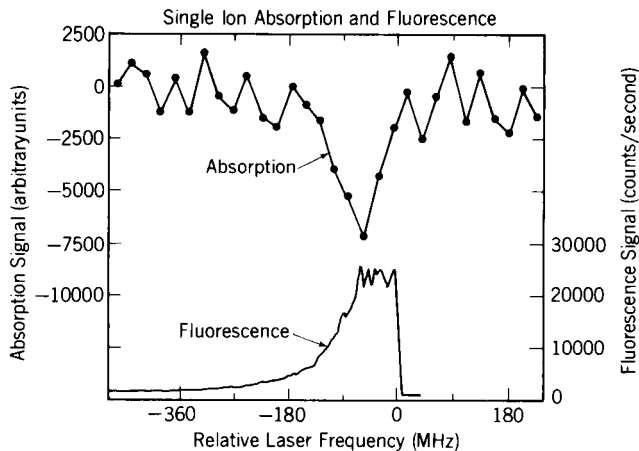


Fig. 2. Absorption signal observed as the 194-nm source is tuned through ν_0 . Lower trace shows the simultaneously observed fluorescence scattering; the flat-topped appearance of this curve is due to the frequency modulation of the ion resonance. Integration times per point are 50 and 10 sec in the upper and lower traces, respectively.

We expect the signal to show a dispersion shape as the frequency of the 194-nm source is tuned through the resonance frequency ν_0 . Only half of the dispersion feature (Fig. 2) was observed because the ion rapidly heated when the frequency of the 194-nm source was tuned above the resonance frequency ν_0 .¹³ This caused a significant decrease in scattering owing to increased Doppler broadening and decreased spatial overlap of the laser beam with the ion; i.e., K became very small. If we simultaneously observed the fluorescence scattering (lower trace in Fig. 2), the absorption signal first reached its maximum amplitude (minimum of upper curve in Fig. 2) and then returned to zero at the resonance frequency, as indicated by the sudden drop in fluorescence in the lower trace. This verified that the signal was mostly due to frequency modulation rather than to amplitude modulation (achieved by moving the ion in and out of the laser beam) since the maximum signal for amplitude modulation would be achieved at ν_0 . The frequency modulation also accounts for the flat-topped shape of the fluorescence curve in Fig. 2. The optimum value of V_m was independently verified by observing the intensity modulation of the fluorescence signal at 21.07 MHz by measuring time correlations of the photons scattered by the single ion.

S/N in the present experiment could be increased by a factor of about 4 if i_D could be reduced so that the noise was dominated by i_{sh} . When i_{sh} dominates, Eq. (4) tells us that we can improve S/N by decreasing the laser spot size A . Stronger focusing in this experiment was prevented by the size of the input windows to the trap. In order just to maintain saturation we must reduce P accordingly. In the limit where A ap-

proaches σ_0 , the absorption of the input beam by the ion would approach several percent. In this limit, the detector could be a photomultiplier tube operated in the photon-counting mode. i_D would be replaced by tube dark counts, and S/N would approach the square root of the number of detected counts. If we can neglect i_D and i_T , the choice of absorption or fluorescence detection is straightforward. If the fraction ϵ of fluorescence photons striking the detector is greater than η , fluorescence detection gives the greater S/N. The reverse is true for $\eta > \epsilon$. We have assumed that β is the same for the absorption and fluorescence detectors.

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References

1. A concise historical review is given by R. A. Sawyer, *Experimental Spectroscopy*, 3rd ed. (Dover, New York, 1963), pp. 1-17.
2. See, for example, K. Shimoda, ed., *High Resolution Laser Spectroscopy* (Springer-Verlag, Berlin, 1976); R. A. Keller, ed., *Laser-based Ultrasensitive Spectroscopy and Detection V*, Proc. Soc. Photo-Opt. Instrum. Eng. 426 (1983); M. D. Levenson, *Nonlinear Laser Spectroscopy* (Academic, New York, 1982).
3. J. Bialas, R. Blatt, W. Neuhauser, and P. E. Toschek, Opt. Commun. 59, 27 (1986).
4. S. Le Boiteux, D. Bloch, M. Ducloy, A. Pesnelle, S. Runge, and M. Perdrix, Opt. Commun. 52, 274 (1984).
5. See, for example, R. Loudon, *The Quantum Theory of Light* (Oxford U. Press, London, 1973), p. 287.
6. J. C. Bergquist, R. G. Hulet, W. M. Itano, and D. J. Wineland, Phys. Rev. Lett. 57, 1699 (1986).
7. H. Hemmati, J. C. Bergquist, and W. M. Itano, Opt. Lett. 8, 73 (1983).
8. J. J. Snyder, R. K. Raj, D. Bloch, and M. Ducloy, Opt. Lett. 5, 163 (1980); L. Hollberg, Ma Long-Sheng, M. Hohenstatt, and J. L. Hall, Proc. Soc. Photo-Opt. Instrum. Eng. 426, 91 (1983); E. A. Whittaker and G. C. Bjorklund, Proc. Soc. Photo-Opt. Instrum. Eng. 426, 81 (1983); M. Ducloy and J. J. Snyder, Proc. Soc. Photo-Opt. Instrum. Eng. 426, 87 (1983).
9. H. G. Dehmelt, Adv. At. Mol. Phys. 3, 53 (1967); 5, 109 (1969); D. J. Wineland, W. M. Itano, and R. S. Van Dyck, Jr., Adv. At. Mol. Phys. 19, 135 (1983).
10. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
11. R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562L (1947).
12. C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, Phys. Rev. Lett. 50, 727 (1983).
13. R. E. Drullinger, D. J. Wineland, and J. C. Bergquist, Appl. Phys. 22, 365 (1980).