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Dispersion-like lineshape observed in cavity-enhanced saturation spectroscopy of HD at 1.4 μm

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Precision measurement of ro-vibrational transitions in the electronic ground state of the hydrogen molecule can be used to test quantum electrodynamics and also to determine the dimensionless proton-to-electron mass ratio. Saturation spectroscopy of the 2-0 overtone transitions of hydrogen deuterium (HD) were measured with three cavity-enhanced spectroscopy methods. With a sensitivity at the 10^{-13}cm^{-1} level, we revealed a dispersion-like lineshape instead of a conventional Lamb “dip,” which explains the significant discrepancy among previous independent measurements. The spectra can be fit well by using the Fano profile. Centers of R(1) and R(3) lines were determined as 217 105 182 111 (19)_{stat}(240)_{sys} kHz and 220 704 305 234 (20)_{stat}(240)_{sys} kHz, respectively. © 2020 Optical Society of America

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Precision measurement of atoms and molecules is a testing ground for fundamental physics [1]. Frequency references based on atomic and molecular transitions could be used for detecting dark matter [2,3] and the space-time drift of fundamental physical constants [4–6]. Simple molecules such as H_2 , H_2^+ and their isotopologues, whose energies can be calculated precisely from the quantum electrodynamics (QED) theory using a few fundamental physical constants, have played an important role in the history of quantum chemistry through increasingly refined comparisons between experimental data and theoretical predictions [7–11]. Doppler-free saturation spectroscopy of the hydrogen deuterium (HD) molecule has been successfully implemented recently by two groups, one from Amsterdam [12] using the noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) method [13–15], and the other one from HeFei by us [16] using the cavity ring-down spectroscopy (CRDS) method [17]. Lamb-dip spectra with sub-MHz width of the R(1) line in the (2,0) vibrational band of HD were observed by both groups, but two reported line positions have a deviation of 0.9 MHz, about 10 times the combined uncertainty.

Such an astonishing large discrepancy, has driven efforts to search possible reasons, either technical or physical. On one hand, the signal-to-noise level in previous CRDS measurement is lower than the NICE-OHMS one obtained by the Amsterdam group. On the other hand, since sophisticated locking and demodulation electronics is used in NICE-OHMS measurements, distortion on the spectral profile may rise from the imbalance of sidebands or drifting references [18]. In this Letter, we present new measurements of the saturation spectroscopy of HD lines using a setup that can be operated in three different cavity-based techniques: CRDS, NICE-OHMS, and cavity-enhanced absorption spectroscopy (CEAS) [19,20]. The CEAS method is naturally simpler than CRDS and NICE-OHMS, and could be used to check the consistency among different experimental methods. The sensitivity of the CRDS method was also improved by an order of magnitude over a previous study. We found an unexpected asymmetric dispersion-like line profile in the saturation spectra of the R(1) line obtained by all three methods: CRDS, CEAS, and NICE-OHMS. The discrepancy between two previous measurements is confirmed to be a result of the symmetric Lorentzian profiles being improperly applied in spectral fitting in both studies.

The experimental setup is shown in Fig. 1. It was designed to establish CRDS, NICE-OHMS, and CEAS using one optical cavity. The part for CRDS measurement is the same as that given in our previous study [16], and it will not be repeated here. The ring-down cavity has a length of 80 cm and a finesse of 120 000. Since the CEAS method directly detects the power emitted from the cavity, it is very sensitive to a fluctuation in laser power. An acousto-optic modulator (AOM) controlled by a feedback loop was used to reduce the probe laser power noise to less than 0.2%. The laser was phase modulated by an electro-optic modulator (EOM) with a modulation frequency of 19 MHz, which was used to lock the laser to the cavity by the Pound–Drever–Hall (PDH) method. The residual amplitude modulation (RAM) signal after the EOM was monitored by a detector (PD2 in Fig. 1), and a servo loop was applied to keep the EOM working at a minimum RAM [21]. In order to further decrease noise from the baseline drift, the optical cavity length was modulated

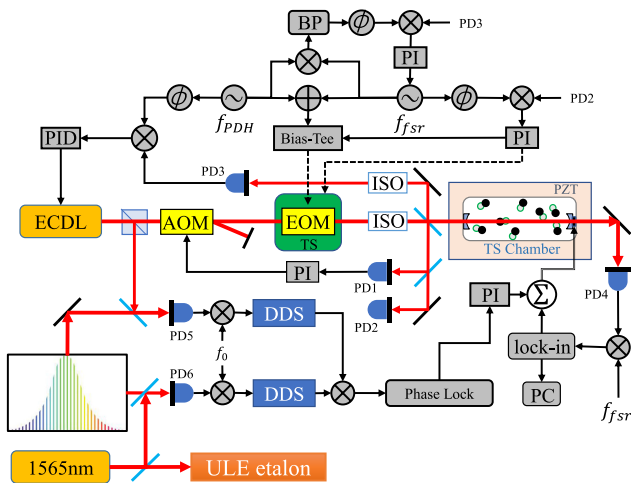


Fig. 1. Configuration of the experimental setup. AOM, acousto-optical modulator; BP, band pass; DDS, direct digital synthesizer; ECDL, external cavity diode laser; EOM, electro-optical modulator; ISO, optical isolator; PC, personal computer; PD, photodiode detector; PI, proportion integration amplifier; PID, proportional-integral-derivative; PZT, piezoelectric actuator; TS, temperature-stabilized.

at a frequency of 200 Hz by a piezo actuator (PZT), and the wavelength-modulated (wm, 1f) CEAS signal was recorded.

In the NICE-OHMS measurement, together with the 19 MHz PDH modulation, an additional frequency modulation of 199.8 MHz was applied to the EOM, which was locked to the free spectral range (FSR) of the optical cavity by the deVoe–Brewer method [22]. The laser beam transmitted through the cavity was then demodulated at the frequency of 199.8 MHz by a doubly balanced mixer (DBM). The resulted signal from the DBM was amplified, and sent to a lock-in amplifier to retrieve the wm-NICE-OHMS signal referenced to the cavity length modulation.

The probe laser frequency was calibrated by detecting its beat to an optical frequency comb synthesized by an Er-fiber oscillator operated at 1.56 μm . The repetition frequency ($f_r \approx 198$ MHz) and the carrier offset frequency ($f_0 = 250$ MHz) of the comb were both referenced to a GPS-disciplined rubidium clock. We applied the frequency comb transfer method [23] to lock the cavity length with a stable reference laser. The reference laser was a narrow-linewidth 1565 nm fiber laser (NKT) locked on an étalon made of ultra-low expansion (ULE) glass.

The temperature of the ULE étalon was stabilized, and the drift was less than 1 mK for hours. Two beat signals were recorded, one between the comb and the reference laser, and the other between the comb and the probe laser. Each beat signal was subtracted by the carrier offset frequency (f_0) from the comb, then modified by a direct digital synthesizer (DDS), and sent to a mixer to get the error signal fed to a phase locking servo. Two DDSs were adjusted to cancel the noise in the repetition frequency (f_r) of the comb. The phase locking servo controlled the length of the sample cavity by tuning a PZT attached to one of the high-reflective (HR) mirrors in the ring-down cavity. In this way, the cavity length and the probe laser frequency were locked to the reference laser through the frequency comb,

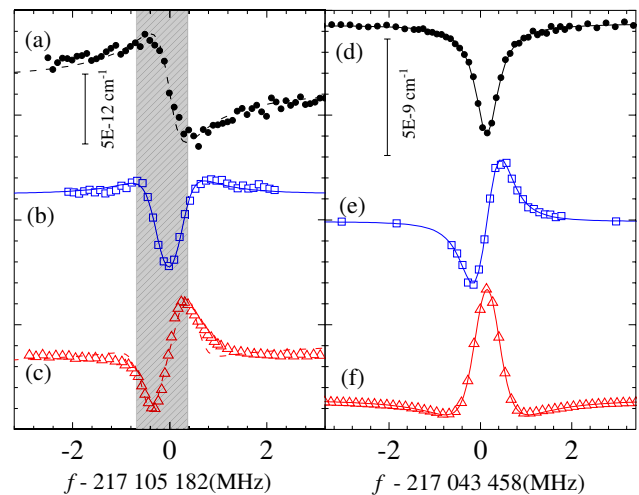


Fig. 2. Saturation spectra of the 2-0 R(1) line of HD (left panels) and the nearby R(4) line of C_2H_2 (right panels) recorded under the same experimental conditions of respective methods: CRDS (a), (d); wm-CEAS (b), (e); and wm-NICE-OHMS (c), (f). Sample pressures were about 1.5 Pa for C_2H_2 and 3 Pa for HD. The shadow shown in the left panel indicates the spectral region covered by the NICE-OHMS spectrum given in Ref. [12]. The CRDS spectrum of C_2H_2 was fitted by a Lorentzian profile, while the HD one was fitted by a Fano profile.

but the influence due to the short-time jitter of the comb was eliminated.

We used CRDS, wm-CEAS, and wm-NICE-OHMS to measure the saturation spectroscopy of the R(1) transition of HD and a nearby C_2H_2 line under same experimental conditions. The signal of the C_2H_2 line was used as a reference to optimize the experimental parameters. The acetylene sample was purified by a liquid- N_2 ethanol solution trap, and the HD sample was purified by a liquid- N_2 solution trap before use. As given in the HITRAN database [24], the R(1) line in the (2, 0) band of HD is located at 7241.849 cm^{-1} , with an intensity of 3.52×10^{-25} cm/molecule at room temperature and an Einstein coefficient of $2.15 \times 10^{-5} \text{s}^{-1}$; and the C_2H_2 line is at 7239.791 cm^{-1} , with an intensity of 4.43×10^{-24} cm/molecule and an Einstein coefficient of 0.0076s^{-1} . Taking into account a laser beam waist radius of 0.46 mm, an incident laser power stabilized at 13 mW, and a transmitted laser power of 1 mW, we estimated [25] that the intra-cavity laser power was about 135 W, and the saturation parameters for C_2H_2 and HD lines were 0.77 and 0.002, respectively.

The recorded spectra are shown in Fig. 2. The C_2H_2 spectra shown in the right side of the figure [Figs. 2(d)–2(f)] present normal CRDS, wm-CEAS, and wm-NICE-OHMS profiles [18]. Note that the wm-CEAS spectrum presents the first derivative of the CRDS profile, while wm-NICE-OHMS shows the second derivative of the CRDS profile. Obviously, the profiles of the saturated absorption spectra of the HD transition given in the left side of Fig. 2 are completely different from those of C_2H_2 . The CRDS spectrum [black circles in Fig. 2(a)] of HD is not a conventional Lamb “dip,” but has a dispersion-like profile. Meanwhile, the wm-CEAS [Fig. 2(b)] and wm-NICE-OHMS [Fig. 2(c)] profiles remain to be the first and second derivatives of the CRDS profile, respectively. Note that the CRDS spectrum directly gives the absorption coefficient, and

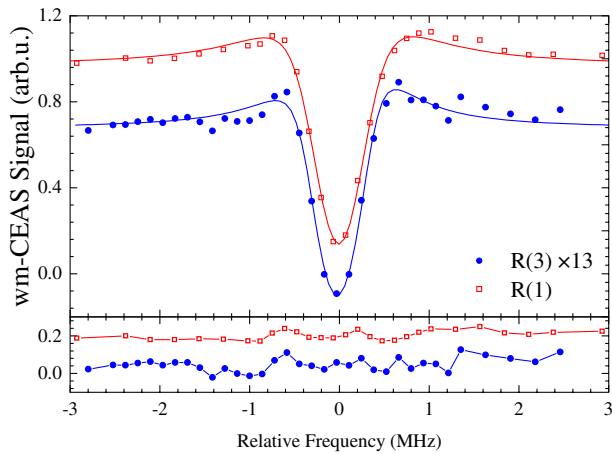


Fig. 3. wm-CEAS spectra of R(1) and R(3) (scattering points) and the simulated spectra (solid lines) using the Fano profile. Fitting residuals are given in the lower panel.

the amplitude of the CRDS spectrum is given in Fig. 2(a). Using the CRDS amplitude as a reference, we estimated the sensitivities (noise equivalent absorption coefficient) of the CRDS, CEAS, and NICE-OHMS methods obtained in this work are: $3 \times 10^{-13} \text{ cm}^{-1}$ (2700 scans in 135 h), $1 \times 10^{-13} \text{ cm}^{-1}$ (80 scans in 4 h), and $4 \times 10^{-14} \text{ cm}^{-1}$ (370 scans in 12 h), respectively.

Comparing our previous CRDS spectra reported in Ref. [16] and that shown in Fig. 2(a), we realized that the insufficient signal-to-noise ratio (SNR) in a previous work prevented us from recognizing the asymmetric lineshape. The asymmetry becomes evident in the present CRDS spectrum [Fig. 2(a)] when the noise level is reduced by an order of magnitude. The symmetric Lorentzian function was improperly applied to fit the spectrum in Ref. [16], which yielded a line center considerably blue shifted. Comparing the NICE-OHMS spectrum given in this work [Fig. 2(c)] and that reported by Cozijn *et al.* [12], we find that the spectrum in Ref. [12] covered only part of the whole spectrum [shadow region in Fig. 2(c)]. For this reason, and because a Lorentzian function was improperly applied to fit the “dip” that is actually in the “peak” region of the direct absorption spectrum, the line center reported in Ref. [12] should be red shifted.

We have also recorded the saturation spectrum of the R(3) line at 7361.903 cm^{-1} . The R(3) line is about nine times weaker than the R(1) line. As shown in Fig. 3, the observed wm-CEAS lineshape of the R(3) line is similar to R(1).

In order to investigate the saturated spectroscopy of the HD lines quantitatively, here we preferred to use spectra recorded by the wm-CEAS method for two reasons. First, wm-CEAS and wm-NICE-OHMS spectra obtained in this work have better SNR than CRDS. Second, compared to wm-NICE-OHMS, wm-CEAS is relatively simpler and less sensitive to the experimental conditions [18]. The obtained spectra of HD lines have an obvious dispersion-like lineshape. We found that the spectra could be fit well by a profile based on the Fano function [26]

$$\phi(\nu) = \frac{\left(\frac{\nu-\nu_0}{\Gamma/2} + q\right)^2}{\left(\frac{\nu-\nu_0}{\Gamma/2}\right)^2 + 1}, \quad (1)$$

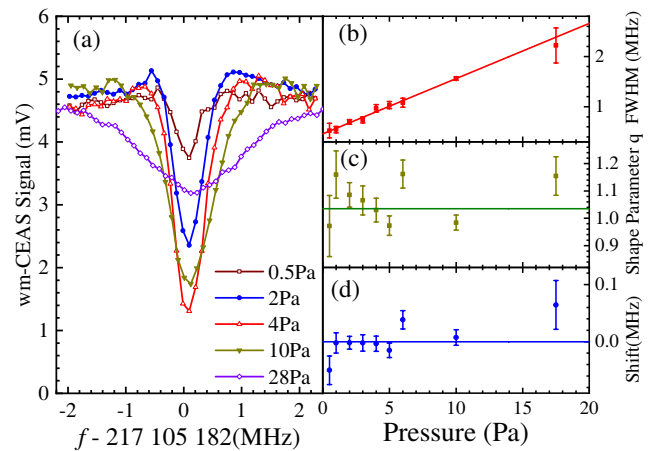


Fig. 4. (a) R(1) line of HD recorded at different sample pressures. Spectra were fit with the Fano profile. Linewidths (FWHM), shape parameters, and line centers are given in (b)–(d).

where ν_0 is the line center, Γ is the linewidth (full width at half maximum, FWHM), and q is the shape parameter that characterizes the asymmetry of the line profile. The Fano profile due to the collision-induced continuum has been observed in Doppler-broadened infrared absorption spectra of HD at high pressures [27]. The solid line shown in Fig. 2(b) presents the fitting result. The same parameters obtained from the fit were applied to simulate the CRDS and wm-NICE-OHMS spectra, shown as dashed lines in Figs. 2(a) and 2(c). Good agreement between the experimental and simulated spectra indicates the consistency among different measurements.

We purposely changed the laser polarization from linear to circular, reducing half of the laser power, but did not observe any change in the lineshape. Note that the result obtained by CRDS is actually a weighted average over different laser powers, since the intra-cavity light power decays during a ring-down event. Therefore, the agreement among three methods also indicates that the lineshape is not sensitive to the laser power.

A series of spectra of the R(1) line were recorded under different sample pressures, and they are shown in Fig. 4(a). When the pressure increases, a significant pressure broadening is observed, but the lineshape is substantially unchanged. The spectra were fitted by using the Fano profile. The values of linewidth, shape parameter q , and line center obtained from the fit are depicted in Figs. 4(b)–4(d). A linear fit of the linewidths obtained at different pressures yields a collision-induced pressure broadening coefficient of $0.109(4) \text{ MHz/Pa}$. The width at the zero pressure limit is $0.473(28) \text{ MHz}$, agreeing with the calculated [28] transit-time broadening width of 0.7 MHz of HD at room temperature. The q parameter and line center show no detectable pressure dependence. Therefore, we use a simple weighted average of the positions, and the statistical uncertainty is 19 kHz .

The present line profile model is rather simplified. Recently, Dupré [29], Komasa *et al.* [30], and Jóźwiak *et al.* [31] independently calculated the hyperfine feature of the R(1) line, which shows a width (FWHM) of 0.3 MHz . The recoil shift of this HD line is 35 kHz , which results in a doublet in the saturation spectroscopy [32]. Other contributions to the uncertainty budget include: frequency calibration 0.4 kHz , pressure shift $<3 \text{ kHz}$, second-order Doppler shift $<5 \text{ kHz}$, and the

uncertainty from the locking servo is less than 2 kHz. Here we conservatively give a systematic uncertainty of 0.24 MHz, which is the half-width of the line at the zero pressure limit. With that, the center frequencies of the R(1) and R(3) lines are 217 105 182.111(19)_{stat.}(240)_{sys.} MHz and 220 704 305.234(20)_{stat.}(240)_{sys.} MHz, respectively.

Recently, the calculated R(1) and R(3) line centers have been updated by Pachucki and his colleagues [33] as 217 105 180.2(0.9) MHz and 220 704 303.2(0.9) MHz, respectively, which are both red shifted by 2 MHz from the experimental results given here. Fasci *et al.* [34] gave the R(1) position as 217 105 181.581(94) MHz from Doppler broadened spectra with a width over 1 GHz. In parallel to this work, the R(1) line was also remeasured by the Amsterdam group using the wm-NICE-OHMS method [35]. They got a profile very similar to the NICE-OHMS spectrum obtained in this work, indicating the consistency among different measurements. The Amsterdam group took into account the crossovers among hyperfine substructures, applied a hypothesis of a mechanism refilling the ground state population, presented numerical results mimicking the observed spectrum, and gave a revised R(1) position of 217 105 181 901(50) kHz. The Amsterdam value deviates from ours by -0.11 MHz, which is smaller than the systematic uncertainty given here, but two times the joint statistical uncertainty.

In conclusion, we performed cavity-enhanced saturation spectroscopy measurements of ro-vibrational transitions of HD at 1.4 μm using three different methods, CRDS, NICE-OHMS, and CEAS, with sensitivities at the 10^{-13}cm^{-1} level. We obtained consistent results from all methods and revealed that the spectrum has a linewidth over 0.5 MHz but a very asymmetric dispersion-like lineshape. The Fano profile was applied to fit the spectra, and positions of the R(1) and R(3) lines were determined with a statistical uncertainty of 0.02 MHz.

If the uncertainty in the line-profile model can be eliminated, we can foresee an experimental uncertainty of 20 kHz or less. For example, the linewidth will decrease by a factor of four if we decrease the temperature of the sample cell from 300 K to 20 K. From the theoretical point of view, an accuracy of several kHz would be soon feasible [33]. A comparison of the experimental and calculated results will give a most precise test of QED in neutral molecules. According to the sensitivity coefficients between the infrared transition of HD and related physical constants given by Pachucki and Komasa [16,36], it will also allow a determination of the proton-to-electron mass ratio with an accuracy below 1×10^{-10} .

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