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Absorption spectrum of the $P(5)$ transition of the first overtone band of HD

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The $P(5)$ 2-0 overtone transition of the ground electronic state of an HD molecule was studied by a modified-difference spectroscopic method, and its line center was determined with the help of precisely measured C_2H_2 transition frequencies. The center was measured to be 6576.896 cm^{-1} with an accuracy better than 0.01 cm^{-1}, which is consistent with the theoretical calculation.

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I. INTRODUCTION

The HD molecule is the simplest heteronuclear diatomic molecule, and therefore many precise *ab initio* calculations have been carried out for its ground electronic state [1–4]. The allowed rovibrational transitions arise only from the breakdown of the Born-Oppenheimer approximation. Due to its very small electric-dipole transition moment (about 10^{-5} D [2,5–7]), the rotation-vibrational transitions are very weak. Historically, the HD rovibrational spectra of the 3-0 and 4-0 overtone bands were first observed in the laboratory by Herzberg [8] in 1950, and the 1-0 fundamental and 2-0 overtone bands were later observed by Durie and Herzberg [9]. A high-pressure and effectively long-path absorption cell was used in their studies for the sake of weak absorption. In the successive works, absorption lines of the 1-0 fundamental band and the 2-0, 3-0, 4-0, 5-0, and 6-0 overtone bands were extensively investigated [5–7,10–13]. Among these, it is worth noting that photoacoustic spectroscopy, a high-sensitivity technique, allows one to study the spectrum at a lower pressure with a shorter absorption path [11,13]. A series of studies on the interference effects in the spectrum of HD by HD or a foreign gas were also comprehensively studied by McKellar and co-workers [14–19]. In addition, the dipole moment of some pure rotational transitions [20–22] and the frequency of the $J=1\leftarrow0$ [23] transition were also measured.

For the first overtone band ($v=0\rightarrow v=2$), located in the 1.3–1.5-μm wavelength region, only $R(0)$ [7,9–10], $R(1)$, $P(1)$ [7,9], $R(2)$, $R(3)$, $P(2)$, and $P(3)$ [9] transitions have been studied. The recent development of tunable diode lasers in the near IR region provides low-noise laser sources for reexamining the spectrum of HD. Moreover, Nakagawa *et al.* have precisely determined the frequencies of 90 rovibrational lines of $^{12}C_2H_2$ and $^{13}C_2H_2$ in the 1.5-μm region with an uncertainty of 10^{-9}, and they provide an accurate frequency grid in this wavelength region [24]. Recently, we started a research program aimed at measuring the transition frequencies of HD the first overtone transitions. In this paper, we report our study on the $P(5)$ transition of the first overtone band with the help of the difference-spectroscopic method and only one tunable diode laser. Its frequency is determined to an accuracy of 0.01 cm^{-1}.

II. EXPERIMENTAL DETAILS

The experimental setup is shown in Fig. 1. A modified difference-spectroscopy scheme was used in this study. By using this technique, it is possible to reduce the intensity noise from the laser, and most importantly, to record the HD and C_2H_2 spectra simultaneously with one 1.5-μm external-cavity diode laser (ECDL, Environmental Optical Sensors, Inc., model 2001). The linewidth of the laser was less than 1 MHz and the single-mode frequency tuning range was 60 GHz. The frequency scan was achieved by using the stepping motor for the coarse tuning and by using the piezoelectric transducer (PZT) glued on the end mirror of the cavity for the fine tuning. The laser frequency was modulated by a 1-kHz sine signal to the PZT with a modulation depth of 21 MHz. After leaving the laser, the frequency-modulated output beam was divided into two beams by a 10%-90% beam splitter. The weak beam was sent into a 20-cm-long cell filled with 200 to 300 mTorr acetylene (C_2H_2) gas. The strong beam was sent into a multipass absorption cell (MP cell, New Focus, model 5612) with a total absorption path of up to 100 m, which was filled with HD gas (97% purity, Isotec, Inc.). The two beams, after passing through the two cells individually, were gathered separately by focusing lenses on each one of two InGaAs p-i-n diodes of the balanced photodetector (BPD, New Focus, model 1617). An output signal proportional to $(I_1-I_2)/I_2$ was then provided by the BPD, where I_1 and I_2 corresponded to the intensities of the beams through the HD cell and the C_2H_2 cell to the BPD, respectively. Through the GPIB interface and LABVIEW program, the personal computer (PC) recorded the first derivative signal obtained from the lock-in amplifier. A reflected beam from the window surface of the multipass cell was directed into a scanning Fabry-Perot (SFP) interferometer to monitor the single longitudinal-mode operation. The intensities I_1 and I_2 were previously adjusted to nearly the same intensity I_0 at a laser frequency at which both gas samples did not absorb both beams. As only the HD gas absorbed the laser beam by the amount of ΔI_1, I_1 changed its intensity to $I_0-\Delta I_1$ and the BPD output propor-

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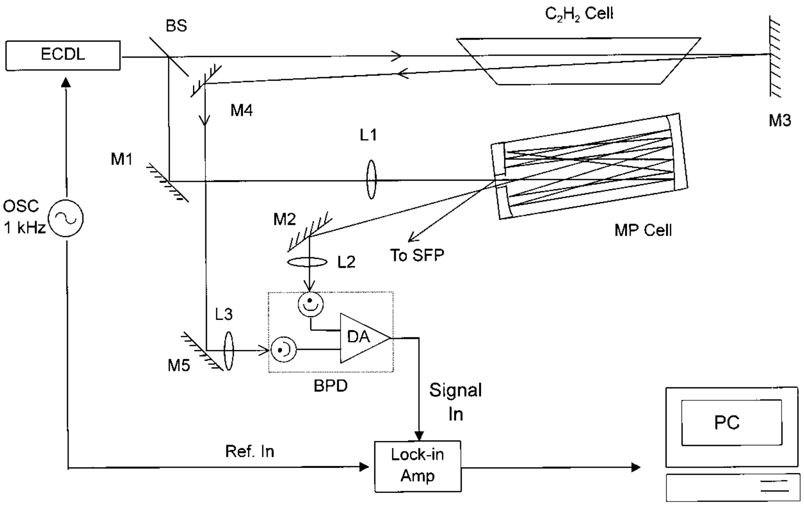

FIG. 1. Experimental setup for the spectroscopy of overtone transitions of HD molecules. ECDL, external cavity diode laser; BS, beam splitter; $M1$, $M2$, $M3$, $M4$, and $M5$, reflecting mirrors; $L1$, $L2$, $L3$, lens; BPD, balanced photodetector; OSC, oscillator; MP cell, multipass cell; SFP, scanning Fabry-Perot interferometer.

tioned to $(I_1-I_2)/I_2 \sim -\Delta I_1/I_0$. Similarly, as C_2H_2 gas absorbed the laser beam by the amount of ΔI_2, I_2 turned out to be $I_0-\Delta I_2$ and the BPD output proportioned to $(I_1-I_2)/I_2 \sim +\Delta I_2/I_0$. Since the absorption of HD and C_2H_2 was very weak (although the transition-dipole moment of C_2H_2 is relatively stronger than HD by about 250 times), the approximation $I_2=I_0-\Delta I_2 \sim I_0$ was held in the weak absorption condition. Hence two kinds of signals with opposite phases were observed, and one could identify the absorption with different gas samples. A typical recorded trace after the lock-in amplifier is shown in Fig. 2.

The HD pressure studied was from 500 to 900 Torr, limited by the safety value of the multipass cell. A disturbance to the HD spectrum by the water vapor outgassing from the cell wall or other places was inevitable since their spectra were as close by as 0.16 cm^{-1} [9,17,19]. In order to minimize this effect, we baked the multipass cell at 200 °C under evacuation for several days before filling the HD gas. Experiments showed that the appearance of H_2O lines after how many days of filling the HD gas was determined by the time duration of baking and evacuation. Generally, the time for the appearance of H_2O lines after each filling is from three days to over a week depending on the baking duration.

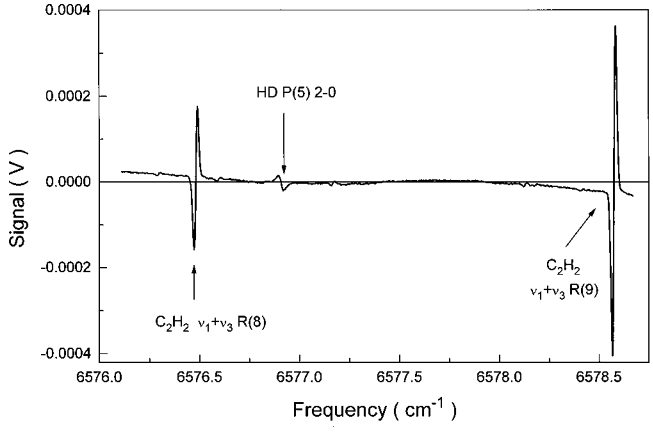

FIG. 2. Typical recorded trace ($1f$ demodulated signal) of HD (pressure: 827 Torr) $P(5)$ transition together with C_2H_2 (pressure: 214 mTorr) transitions. The frequency axis was determined by the interpolation based on the accurately measured frequency values of C_2H_2 $\nu_1+\nu_3$ $R(8)$ and $R(9)$ transitions. Two different phases for different kinds of transitions are shown in the figure.

III. RESULTS

Using frequency scanning done by the stepping motor, a typical trace of the HD and C_2H_2 spectra was obtained and shown in Fig. 2. In the figure, the HD $P(5)2$-0 and C_2H_2 $R(8)$ and $R(9)$ transitions of the $\nu_1+\nu_3$ band were observed with opposite phases. Other small transitions shown were due to C_2H_2, judging from their phases. The laser frequency was determined by the interpolation from $R(8)$ and $R(9)$ of C_2H_2 based on the assumption of linear scanning of the external-cavity diode laser. This assumption works very well, as the wavelength tuning range is only 0.6 nm around $\lambda=1520$ nm.[1] Therefore, for the determination of the center frequency of the HD $P(5)2$-0 transition, we first fit the transition profiles of C_2H_2 $R(8)$ and $R(9)$ lines separately to the first derivative of Gaussian function Y as a function of sampling sequence X by the PC, which is proportional to the tuning of laser frequency, with a polynomial background, as

$$Y=\frac{A_0(A_1-X)}{A_2^2}\exp\left[\frac{-0.5(X-A_1)^2}{A_2^2}\right]+(\text{background}),$$

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[1] For the grazing-incidence grating-type cavity of our case, $d(\sin\beta+\sin\alpha)=m\lambda$, with $m=1$, where d is the grating groove spacing, and α ($\approx 90°$) and β are the incidence angle and diffraction angle from the grating, respectively. Hence a 0.6-nm change in the wavelength around $\lambda=1520$ nm ($\beta\approx 20°$) causes a small change of about 0.55 mrad in the diffraction angle. If one expands $\sin\beta$ at $\beta=20°$, it yields

$$\sin\beta=\sin 20°+\cos 20°\times\delta\beta\propto\delta\beta.$$

Thus $\lambda=d(\sin\beta+1)$ is also linearly dependent on $\delta\beta$. This gives the conclusion that around $\lambda=1520$ nm the laser varies linearly with the change of the diffracted angle $\delta\beta$ as the tuning range of the wavelength is 0.6 nm.

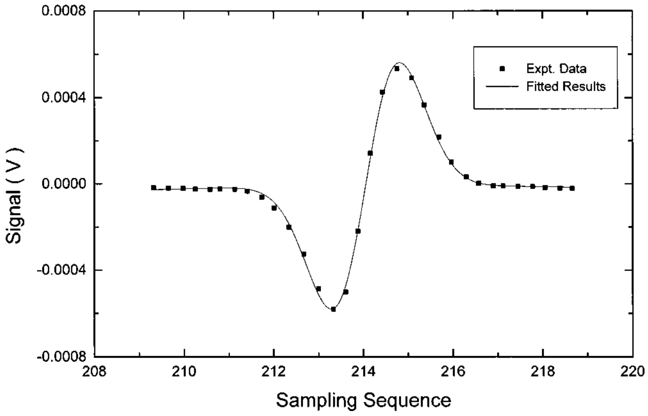

FIG. 3. Fitted C_2H_2 line profile (in its first derivative form) to first derivative of the Gaussian function with a polynomial background. Black blocks are data points. The solid line is the fitted results. The sampling sequence is proportional to the tuning frequency.

where A_0, A_1, and A_2 are the height, the line center, and the half-width [equal to the half-width at half maximum (HWHM)/$(2\ln 2)^{1/2}$,] respectively. A typical fit is shown in Fig. 3. The choice of a Gaussian function was due to the Doppler broadening domination in the low pressure (200–300 mTorr) for the C_2H_2 gas sample used in our experiment. Second, we set the fitted $R(8)$ and $R(9)$ lines' center as the precisely measured values [24], i.e.,

$$\nu_{R(8)}=6576.481\,654\ \ \mathrm{cm}^{-1},$$

$$\nu_{R(9)}=6578.575\,892\ \ \mathrm{cm}^{-1}.$$

Then, the interpolation yielded the frequency axis of our spectrum, as shown in Fig. 2. Finally, since high pressure up to 1 atm was used for the HD gas sample, the HD $P(5)2\text{-}0$ line profile was fitted to the first derivative of the Lorentzian function with the polynomial background as (as shown in Fig. 4)

$$Y=\frac{A_0(X-A_1)}{A_2^2}\,\frac{1}{\{1+[(X-A_1)/A_2]^2\}^2}+(\text{background}),$$

where A_0, A_1, and A_2 are the height, the line center, and the half-width at half maximum, respectively. The pressure of the HD gas studied was from 500 to 900 Torr at a temperature of 298 K (related to the density from 0.83 to 1.08 amagat). Since the signal-to-noise ratios of spectra under 650 Torr were bad, we neglected them in our analysis. The plots of the fitted center and the HWHM vs pressure are shown in Fig. 5. The errors shown in the figure are 1σ standard deviation of a set of fitted values for several repeated measurements. Hence the standard deviation of the determination of line center is less than 0.004 cm^{-1} over the pressure range studied. It shows the precise determination of the line centers.

From the plot of fitted line center vs pressure (Fig. 5), it is found that an increasing tendency in the fitted center occurs, contrary to other observations [10]. A linear fit to the relation of pressure shift (ν) with pressure (P), i.e., $\nu=a+bP$ (in Torr) was made to obtain $a=6576.896(8)\ \mathrm{cm}^{-1}$, which is consistent with the theoretical value of 6576.902 cm^{-1} of the calculation result by Wolniewicz [4], and

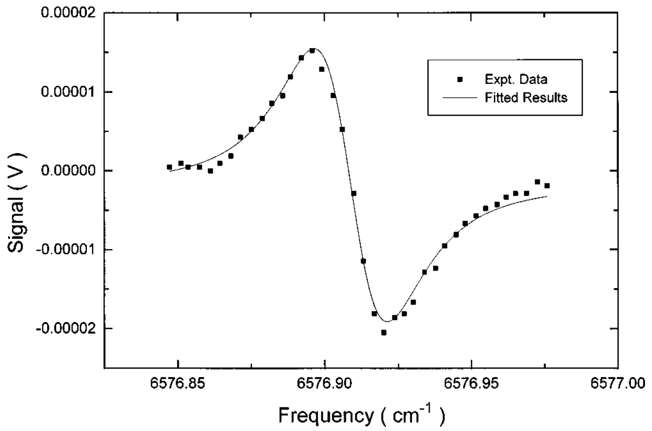

FIG. 4. Fitted HD $P(5)$ 2-0 line profile (in its first derivative form) to first derivative of a Lorentzian function with a polynomial background. Black blocks are data points and the solid line is fitted results. The frequency axis was obtained from the interpolation.

$$b=(1.5\pm0.4)\times10^{-5}\ \ \mathrm{cm}^{-1}/\mathrm{Torr},$$

which can be converted to $(12.5\pm0.3)\times10^{-3}\ \mathrm{cm}^{-1}$/amagat and about the same order of pressure shift of $R(0)2\text{-}0$, $(-13.0\pm0.8)\times10^{-3}\ \mathrm{cm}^{-1}$/amagat, which was experimentally obtained by McKellar [10] but with the opposite sign. The reason is not clear and still under investigation. One possible cause is due to the strong neighbor absorption of H_2O, which was identified to be the transition $(5,3,2)\rightarrow(6,4,3)$, corresponding to the upper and lower (J, Ka, Kc), respectively, of the $(120)\rightarrow(000)$ band [25]. We believe that this also affected the determination of the line center of HD. It is found that at the same HD pressure, the fitted line centers shifted to a high frequency for the latter observation. This probably can be explained by the gradual increase of H_2O vapor. From the plot of fitted linewidth vs pressure (Fig. 5), it seems no obvious variation was observed, and the values fluctuated around 0.022 cm^{-1} (half-width), close to the theoretical value of Doppler width.

The Fano line-shape function was also fit to understand the collision-induced line-shape effect. But the result showed that a very large Fano's line-shape parameter was obtained, which means no collision-induced Fano shape effect was observed for this transition, and this is similar to the observation of the $R(0)2\text{-}0$ transition by McKellar [10].

In order to realize the accuracy of this method, other known transitions of C_2H_2 and H_2O near 1520 nm were also determined by the same method and compared with their measured values, with resulting differences smaller than 0.01 cm^{-1}. Therefore it is believed that the HD spectrum observed by this method yields an accuracy better than 0.01 cm^{-1}. The background caused by high-pressure HD gas samples and H_2O absorption lines limited the accuracy to

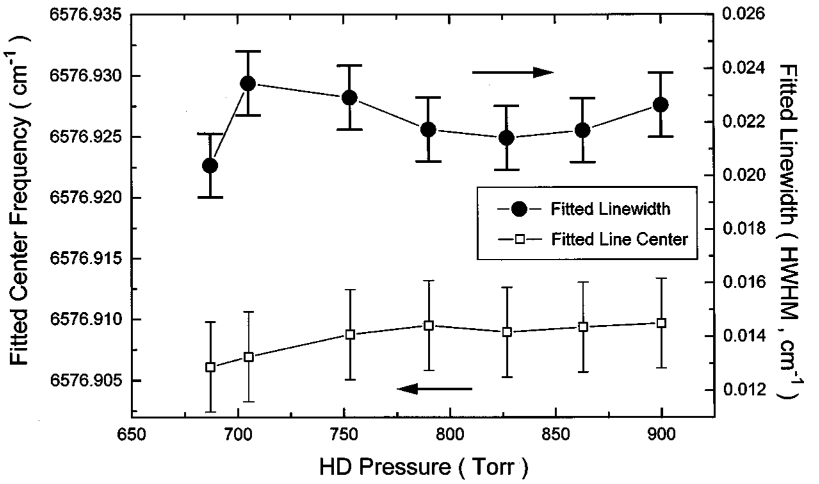

FIG. 5. The fitted-center frequency and the fitted linewidth (half-width) of HD vs pressure. The error bars given are 1σ standard deviation of several repeated measurements.

which line center could be determined. The absorption coefficient was not measured due to the need to realign multipass cell as the pressure varied.

IV. SUMMARY AND CONCLUSION

In conclusion, we have successfully determined the transition frequency of HD $P(5)2\text{-}0$ with the help of a modified difference spectroscopy. To further study this topic, we plan to directly measure this line frequency against the well-measured C_2H_2 $\nu_1+\nu_3$ $R(8)$ line, which is only 0.42 cm^{-1} lower. For the case of very weak absorption of HD, the use of a higher power 1.5-μm laser amplified by the Er-doped fiber amplifier [26] and the Fabry-Perot cavity-enhanced absorption method [27], as well as a high sensitivity technique such as noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [28] may be considered for the study of sub-Doppler spectroscopy of HD in the future.

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