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The $4\nu_{CH}$ overtone of $^{12}\text{C}_2\text{H}_2$: Sub-MHz precision spectrum reveals perturbations

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The third CH stretching vibration overtone ($4\nu_{CH}$) of the acetylene molecule has been a prototype for intra-molecular dynamics studies. Using a sensitive cavity ring-down spectrometer calibrated with precise atomic transitions, the absolute line frequencies of 50 lines of this band have been determined with sub-MHz accuracy, or relatively 2×10^{-9} . The accuracy is also confirmed by the combination differences between the transitions sharing the same upper level. The improved accuracy, two orders of magnitude better than previous studies, allows us to reveal finer ro-vibrational couplings. Fitting of the rotational energies indicates that the J -dependent interactions take place after $J > 7$. The precise line positions present useful confinements to the models of the intra-molecular interactions of the acetylene molecule. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773473>]

I. INTRODUCTION

Acetylene has been a prototypical molecule in chemical dynamics studies of intra-molecular processes.^{1,2} C_2H_2 is also of great interest because of its presence in the terrestrial troposphere, planetary atmosphere, and interstellar medium.³ Rich spectra from the THz region to the ultra-violet have been reported. Overviews of the ro-vibrational spectroscopy of acetylene in its electronic ground state can be found in Refs. 4–6. The $(\nu_1 + 3\nu_3)$ band near 789 nm carries most of the infrared brightness of the $4\nu_{CH}$ manifold, and has been intensively studied. Here, ν_1 and ν_3 denote the symmetric and anti-symmetric CH stretching vibration normal modes, respectively. High-resolution absorption spectroscopy studies have been carried out with Fourier-transform infrared,^{7,8} photoacoustic,^{8,9} frequency-modulated,¹⁰ multi-pass laser absorption,^{11–14} and intra-cavity laser absorption spectroscopy.^{15,16} Using a molecular beam and a high electric field (>300 kV/cm), Barnes *et al.* recorded the Stark split spectrum of the $(\nu_1 + 3\nu_3)$ band.¹⁷ Laser-induced dispersed vibration-rotation fluorescence spectra from the $4\nu_{CH}$ manifold have also been reported by Metsälä *et al.*¹⁸ The line positions,^{7,9,15} intensities,^{8,12,16} collision-induced line shifts and broadening,^{10–14} and the ro-vibrational energy transfer mechanism^{2,18–20} have been studied.

The most precise transition frequencies of $^{12}\text{C}_2\text{H}_2$ up to date have been reported by Edwards *et al.* using a femto-second frequency comb. Forty-one lines of the $(\nu_1 + \nu_3)$ combination band of $^{12}\text{C}_2\text{H}_2$ in the 1520–1545 nm region with the accuracy of a few kHz were obtained from the Doppler-free spectrum.²¹ However, it is often too complicated to conduct Doppler-free measurement, especially for weak overtone transitions. Since the Doppler broadened profile remains symmetric, in principle, it is possible to retrieve a precise line center from a well measured line profile. We have shown that sub-MHz accuracy can be achieved from a well-determined absorption line profile using a cavity ring-down spectrometer combined with a well-calibrated and thermal-stabilized

Fabry-Pérot interferometer.^{22,23} The method can be applied to generate a large set of precise transition frequencies of atoms and molecules as secondary frequency standards over a wide spectral range. Furthermore, accurate line positions will provide a finer view of the molecular energy levels, which will lead to a better understanding of the intra-molecular interactions and resonances. In this work, we present a study of the $(\nu_1 + 3\nu_3)$ band of $^{12}\text{C}_2\text{H}_2$ in the 12 602–12 718 cm^{-1} region with sub-MHz precision. Investigation of the ground state combination differences confirms that the accuracy of upper level energies is about $2 \times 10^{-5} \text{ cm}^{-1}$, which is over one hundred times better than previous studies. The improved precision also allows us to examine the local J -dependent resonances, which have been considered to play a key role in the ro-vibrational energy transfer.

II. EXPERIMENTAL

The experimental setup has been presented previously.^{23,24} In brief, a CW tunable Ti:sapphire laser (Coherent 899-21) beam is carefully coupled into a 1.4 m long resonance cavity. The cavity mirrors have a reflectivity of 99.995% and one of the two mirrors is mounted on a piezoelectric actuator. The piezoelectric actuator is driven with a triangle wave from a function generator. Once the cavity mode is on resonance with the laser and the light power inside the cavity has been built up, an acousto-optic modulator will block the laser beam and initiate a ring-down event. The Ti:sapphire laser is run in a step-scan mode controlled by a personal computer. At each step, typically about 100 ring-down events are recorded with a fast digitizer. A fitting program is applied to fit the exponentially decay curve to derive the decay time τ . The sample absorption coefficient can be determined from²⁵

$$\frac{1}{c\tau(\nu)} = \alpha(\nu) - \frac{\ln R}{L}, \quad (1)$$

where c is the speed of light, ν is the laser frequency, L is the length of the cavity, and R is the reflectivity of the cavity mirror.

Precise calibration is accomplished by using the longitudinal modes of a thermo-stabilized Fabry-Pérot interferometer (FPI) built with ultra-low-expansion (ULE) glass. The transmittance peaks of the ULE-FPI, with an interval of 1497.0292 MHz, have been precisely calibrated by the Rb lines references at 780 nm²⁶ and 795 nm.²⁷ The absolute frequencies of the ULE-FPI peaks have been determined with an accuracy varying from 0.1 to 0.6 MHz in the 775–800 nm region and the day-to-day frequency drift is below 0.1 MHz.²³

The $\nu_1 + 3\nu_3$ band transitions of $^{12}\text{C}_2\text{H}_2$ in the region of 786–793 nm are recorded at a room temperature of 296.5 ± 0.5 K. The noise-equivalent minimal detectable absorption loss (α_{MDAL}) was about $2 \times 10^{-10} \text{ cm}^{-1}$. The acetylene sample has a stated purity of 99.5% and was purified with the “freeze-pump-thaw” method before use. Typically, a pure acetylene sample at 5 Pa was used in the measurements. According to the results given by Herregodts *et al.*, the self-pressure broadening and pressure shift coefficients are on the order of $0.1 \text{ cm}^{-1}/\text{atm}$ and $-0.01 \text{ cm}^{-1}/\text{atm}$, respectively.^{11,12} Under the present experimental conditions, the pressure broadening and shift are neglected.

III. RESULTS AND DISCUSSION

In total, 50 lines of the $(\nu_1 + 3\nu_3)$ band of $^{12}\text{C}_2\text{H}_2$ have been recorded. Fig. 1 illustrates the well-known $J' = 17$ and

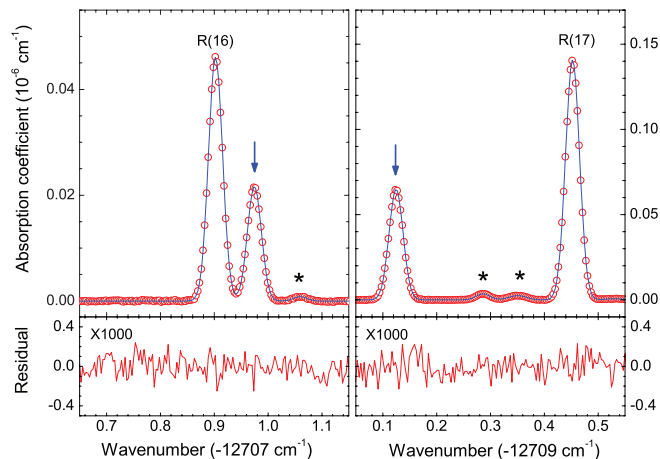


FIG. 1. R(16) and R(17) lines in the $(\nu_1 + 3\nu_3)$ band of C_2H_2 . Open circles and solid lines are the experimental and simulated spectra, respectively. The accompanying doublet lines are marked with arrows. Peaks marked with “*” are weak acetylene lines from other bands. Lower panel shows the fitting residuals (multiplied with a factor of 1000) using Gaussian line profiles in the fit.

$J' = 18$ doublets, respectively. After fitting with a Gaussian line profile, the line positions were derived from each recorded spectrum. The obtained line positions together with the statistical deviations are presented in Table I. In order to verify the accuracy of the obtained line positions, ground state combination differences from the P and R transitions

TABLE I. Line positions of the $\nu_1 + 3\nu_3$ band of $^{12}\text{C}_2\text{H}_2$ and the derived upper level energies (in cm^{-1}). Ground state rotational constants are from Ref. 21 (see also Table II). *Transitions affected by nearby acetylene lines or water lines. The position may have deviation larger than the statistical value and has not been used to determine the upper level energy.

J''	P(J'')	J''	R(J'')	J'	$E(J')$	δ^a
P(3)	12 668.464 656(06)	R(1)	12 680.230 896(17)	2	12 682.584 181	1
P(4)	12 665.959 296(13)	R(2)	12 682.431 813*	3	12 689.491 575	
P(5)	12 663.403 430(21)	R(3)	12 684.581 836(09)	4	12 698.701 344	16
P(6)	12 660.796 969(14)	R(4)	12 686.680 974(17)	5	12 710.213 253	1
P(7)	12 658.140 120(21)	R(5)	12 688.729 300(14)	6	12 724.027 226	5
P(8)	12 655.433 072(09)	R(6)	12 690.726 872(10)	7	12 740.143 170	16
P(9)	12 652.673 608(16)	R(7)	12 692.671 507(17)	8	12 758.558 612	3
P(10)	12 649.866 583(16)	R(8)	12 694.567 926(19)	9	12 779.278 026	14
P(11)	12 647.008 765(12)	R(9)	12 696.412 751(16)	10	12 802.297 757	0
P(12)	12 644.100 972(12)	R(10)	12 698.206 902*	11	12 827.618 237	
P(13)	12 641.140 829*	R(11)	12 699.946 956(25)	12	12 855.236 340	
P(14)	12 638.136 147(28)	R(12)	12 701.642 970(08)	13	12 885.160 205	30
P(15)	12 635.079 528(13)	R(13)	12 703.285 232(06)	14	12 917.381 003	8
P(16)	12 631.976 544(12)	R(14)	12 704.880 052(10)	15	12 951.904 066	14
P(17)	12 628.827 654(12)	R(15)	12 706.427 688(18)	16	12 988.729 177	15
P(18)	12 625.607 144(30)	R(16)	12 707.902 463(34)	17	13 027.829 993	21
	12 625.679 355(26)		12 707.974 721(39)	17	13 027.902 227	2
P(19)	12 622.463 214(31)	R(17)	12 709.452 576(17)	18	13 069.354 073	34
	12 622.135 519(25)		12 709.124 698(24)	18	13 069.026 286	58
P(20)	12 619.055 824(39)	R(18)	12 710.737 659(13)	19	13 112.960 504	25
P(21)	12 615.688 418(15)	R(19)	12 712.061 191(17)	20	13 158.952 008	8
P(22)	12 612.324 040(25)	R(20)	12 713.386 328*	21	13 207.290 826	
P(23)	12 608.928 989(29)	R(21)	12 714.678 836(46)	22	13 257.942 409	8
P(24)	12 605.495 158(26)	R(22)	12 715.930 975(18)	23	13 310.897 742	19
P(25)	12 602.028 206(06)	R(23)	12 717.148 215*	24	13 366.161 515	

^aGround state combination difference, $\delta = |\nu + E_{gs}(J'') - E(J')|$ (in 10^{-6} cm^{-1}), where ν is the observed line position, E_{gs} and E are the energies of the lower and upper levels of the transition, respectively.

TABLE II. Ro-vibrational constants of the $\nu_1 + 3\nu_3$ band of $^{12}\text{C}_2\text{H}_2$ (in cm^{-1}).^a (a) Ground state parameters, from Edwards *et al.*²¹ (b) Parameters from Zhan and Halonen.⁹ (c) This work, from a fit of the upper-level energies $J' \leq 16$. (d) This work, from a fit of the upper-level energies $J' \leq 7$.

	G_v	B_v	$D_v \times 10^6$	$H_v \times 10^{12}$	rms ^b
(a)		1.176 646 497 4(14)	1.627 067(13)	1.90(6)	
(b)	12 675.676 9(40)	1.150 961(42)	1.877(86)	274(45)	0.015
(c)	12 675.678 51(59)	1.151 181(12)	0.987(43)	0	0.001 3
(d)	12 675.676 713(26)	1.151 254 0(21)	1.207(33)	0	0.000 025

^aValues in parentheses are 1σ standard deviations at the last digit.

^bThe root-mean-square value of the differences between the observed and calculated line positions.

to the same upper level are calculated and shown in the last column of the table. The ground state rotational level energies have been calculated using the parameters given by Edwards *et al.*²¹ The averaged combination difference is only $1.4 \times 10^{-5} \text{ cm}^{-1}$, and coincides with the estimated experimental uncertainty. A few transitions (marked with “*” in Table I) are affected by nearby acetylene transitions or water lines. As a result, these line positions may have a systematic deviation, which can reach up to $2 \times 10^{-4} \text{ cm}^{-1}$. These lines are excluded from the determination of the upper energy levels.

The band is labeled as $\nu_1 + 3\nu_3$ because the dominant normal mode state in the compositions of its upper vibrational state is (1030^00^0) , with the notation $(V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5})$, where V_i ($i = 1-5$) is the vibrational quanta, and ℓ is the corresponding vibrational angular momentum. The rotational energies of the (1030^00^0) vibrational state can be interpreted with the usual energy level formula:

$$E(J) = G_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3, \quad (2)$$

where G_v is the vibrational term, B_v , D_v , and H_v are rotational and centrifugal distortion constants. The ro-vibrational constants can be derived from a fit of the energies given in Table I. Because the $J' > 16$ energy levels are perturbed, only the levels of $J' \leq 16$ are included in the fit and the resulted spectroscopic parameters are given in Table II (row “c”). The

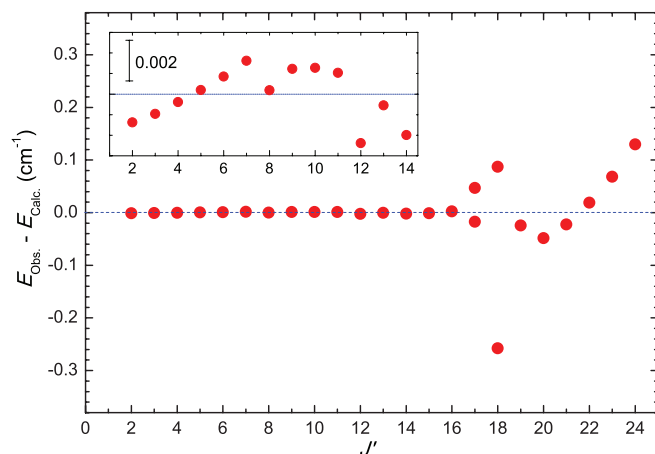


FIG. 2. Differences between the observed and calculated ro-vibrational energies of the (1030^00^0) state. The “c” set of parameters in Table II were used in the calculation. Note for the $J' = 17$ and $J' = 18$ doublets, deviations of both interacting levels are shown here.

energies of the rotational levels of the (1030^00^0) state can be calculated with these parameters and the deviations between the calculated and observed energies are shown in Fig. 2.

As shown in Fig. 2, there is a systematic deviation of the $J' > 20$ levels of the (1030^00^0) state, which has been interpreted by Zhan and Halonen⁹ as due to a Coriolis resonance with a Π_u vibrational state at $12\,671.5 \text{ cm}^{-1}$ (the (0040^00^0) state). The well-known splits of the $J' = 17$ and $J' = 18$ levels were first reported by Smith and Winn,⁷ and later attracted more studies.^{8,9,11,12,15,20} In our spectrum recorded under very low sample pressures, the doublets are well resolved and the R(16) and R(17) lines are shown in Fig. 1. The concomitant levels of the doublets are also marked in the same figure. The energies of the upper levels are calculated using the ground state levels²¹ and the line positions given in Table I. Smith and Winn⁷ have proposed candidates for the perturber as $(2\nu_1 + 3\nu_2 + \nu_5^1)$ or $(3\nu_2 + 2\nu_3 + \nu_5^1)$. Based on the observed energies and the calculated unperturbed bright state energies, Hurtmans *et al.*¹⁵ proposed that the dark state may be the (0504^01^1) vibrational state with predicted $G_v = 12\,678.6 \text{ cm}^{-1}$ and $B_v = 1.145 \text{ cm}^{-1}$. Using a two-level model and the energy of the bright state calculated with the parameters given in Table II, we can determine the energy of the perturber level (dark state) and the off-diagonal interaction matrix element. The respective results for the $J' = 17$ and $J' = 18$ levels are presented in Table III.

As shown in Table II, the accuracy of the ro-vibrational line positions calculated from the “c” set of parameters has improved an order of magnitude over previous studies, but is still almost two orders of magnitude worse than the experimental accuracy. The inset of Fig. 2 shows an enlarged view of the deviations between the observed and calculated energies for $J' = 2-14$ levels. Apparently, the deviations of the $J' \leq 7$ levels have a regular dependence on the J' value, while irregular trend of the deviations for $J' > 7$ levels indicates that there are perturbations, which have not been found before. At least two local resonances occur at $J' = 8$ and $J' = 12$, respectively. Payne *et al.* have revealed through IR-UV double resonance spectroscopy that the $J' = 12$ level is a “gateway”

TABLE III. Observed energies and the calculated diagonal and off-diagonal matrix elements of the $J' = 17$ and $J' = 18$ doublets (cm^{-1}).

J	E_1 , obs.	E_2 , obs.	E_1^0 , bright	E_2^0 , dark	W^a
17	13 027.829 99	13 027.902 23	13 027.847 5	13 027.884 7	0.031 0
18	13 069.354 07	13 069.026 29	13 069.267 0	13 069.113 4	0.144 8

^aOff-diagonal interaction matrix element.

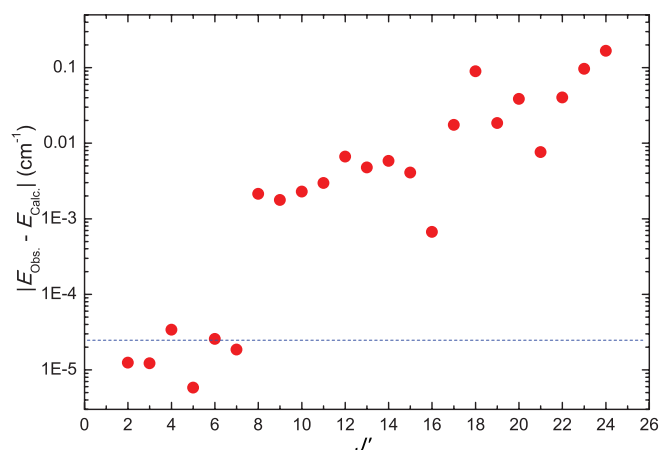


FIG. 3. Absolute differences between the observed and calculated vibrational energies of the (1030^0_0) state. The “d” set of parameters in Table II were used in the calculation. The dashed line indicates the experimental uncertainty level (1σ).

for the anomalous odd- J rotational energy transfer and have concluded that there are intra-molecular ro-vibrational energy transfer channels at $J' = 12$ level of the (1030^0_0) state.^{19,20} The local perturbation at $J' = 12$ revealed here agrees well with such statement.

The perturbations starting at the $J' = 8$ level can be more easily identified from Fig. 3. The figure shows the absolute deviations between the observed and calculated energies but the “d” set of parameters shown in Table II are used in the calculation. These spectroscopic parameters are determined from a fit of the $J' \leq 7$ energy levels. The mean deviation of the fit is $2.5 \times 10^{-5} \text{ cm}^{-1}$, consistent with the experimental uncertainty, which is indicated by a dashed line in Fig. 3. A large jump in the deviation occurs at $J' = 8$, from 10^{-5} cm^{-1} to 10^{-3} cm^{-1} . It provides a definite proof of the existence of perturbations starting from here, which have been masked in previous studies with lower spectral precision. At present stage, we cannot give a conclusive interpretation of the resonances with a satisfied accuracy, because the obtained spectral results are still limited and the interactions involved here are rather complicated. A systematic investigation on the intra-molecular interactions will be carried out based on the precise spectroscopy of the ro-vibrational transitions over a broader spectral range.

IV. SUMMARY

In conclusion, the high-precision and high-sensitivity of the cavity ring-down spectrometer have allowed us to determine the absolute frequencies of 50 lines of the $\nu_1 + 3\nu_3$ band of $^{12}\text{C}_2\text{H}_2$ with $2 \times 10^{-5} \text{ cm}^{-1}$ accuracy (relatively 2 ppb). These transitions can be applied as frequency references in the

786–793 nm region. The analysis presented in this work also gives an example that the precision spectroscopy in the frequency domain can provide an insight of the intra-molecular perturbations and coincides with the energy-transfer dynamics revealed from time-resolved studies. Although decisive assignments of the perturbers may need a systematic investigation of the vibration-rotation interactions in the molecule, the precise positions of ro-vibrational transitions provide a useful confinement on such studies.

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