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Analysis of the influence of various effects on frequency shifts of the acetylene saturated absorption lines*

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Frequency shifts of the acetylene saturated absorption lines at 1.5 μm with temperature, gas pressure and laser power have been investigated in detail. The second-order Doppler effect, the recoil effect, the Zeeman effect, the pressure shift and the power shift are taken into consideration. The magnitudes of those shifts caused by various effects are evaluated. In order to reproduce the stability of 5.7×10^{-14} obtained by Edwards, all necessary conditions are given. The results show that when there is a larger external magnetic field, the Zeeman shift could not be neglected, so that the shield should be employed. And the design of a long cavity is advantageous to reduce the influence of the second-order Doppler effect. The results also show that at least ±2.5°C temperature control for cavity can effectively prevent several effects and improve the frequency stability.

Keywords: frequency shifts, sub-Doppler spectroscopy, acetylene, cavity-enhanced absorption technique

PACC: 3300, 9575F, 4230Q, 0620H

1. Introduction

The wavelength band of 1.5 μm plays a very important role in fibre communication[1] since there is a low-loss window for coherent light. In order to take full advantage of the window, the technique of dense wavelength division multiplexing (DWDM) has been developed to narrow the channel spacing and increase the information carrying capacity.[2,3] Thus a high accurate wavelength as reference is required to prevent cross talk between channels or to calibrate optical instruments in the band.

Acetylene is an interesting candidate for frequency standard at 1.5 μm. In 1994 Labachelerie *et al*[4] for the first time, obtained the saturation spectroscopy of acetylene molecular transitions at 1.5 μm by cavity-enhanced technique.[5] Then they stabilized a laser frequency onto the obtained saturated absorption lines of acetylene.[6] The stability was of the order of 10^{-12} with a reproducibility of ±10 kHz. Subsequently, combining the above experiment with an optical comb generator, the frequency difference between two saturated absorption lines was measured with a precision of better than 100 kHz.[7] Afterwards, they measured the absolute optical frequency of 90 rovibrational lines of the acetylene 1.5 μm[8] with respect to the Rb two-photon transition at 0.778 μm with a HCN rovibration line at 1.556 μm used as an intermediate reference.[9] These measurements provide an accurate frequency atlas of acetylene 1.5 μm band with an uncertainty of $\sim 10^{-9}$. Based on these measurements, Edwards *et al*[10] in 2005, presented the more accurate frequency values for the rovibrational lines of acetylene by improving the stability of the stabilized laser to reach a minimum of 5.7×10^{-14} at 4000 s and by use of a combined frequency chain and femtosecond comb, together with a passive optical frequency comb generation. Their result provided an uncertainty of $\sim 10^{-11}$.

With the publication of the absolute frequency atlas, one can employ a stabilized laser, which is locked onto Doppler-free acetylene spectra at 1.5 μm by cavity-enhanced technique, as wavelength references. However, some effects under different experimental conditions and/or system parameters will shift the spectra frequency. In order to establish an absolute stability of acetylene-stabilized laser or to make these shifts reduce to a very low level by a suitable

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design, it is necessary to investigate various possible effects of systematic frequency shifts. Although Labachelerie *et al*[4] and Edwards *et al*[10] gave some experimental results of frequency shift under variable conditions, they have neglected some effects that can effectively cause frequency shifts. Moreover, they did not give the interpretation of the shifts theoretically. The present paper will analyse the frequency shifts of the acetylene saturated lines at 1.5 μm due to various effects, including the second-order Doppler effect, the photon-recoil effect, the pressure shift, the effect of magnetic field and the power shift. The magnitudes of these shifts are evaluated. Also, the measures to reduce the influence of various effects are discussed in detail.

2. Second-order Doppler effect

When a molecule with a velocity $\boldsymbol{v}$ absorbs a photon, in terms of conservation of momentum and energy, one can obtain the absorption frequency ν for the resonance case[11]

$$\nu = \nu_0 + \boldsymbol{k}\cdot\boldsymbol{v} - \nu_0\frac{v^2}{2c^2} + \frac{h\nu_0^2}{2Mc^2} + \cdots. \tag{1}$$

The first term ν_0 represents the eigenfrequency of the molecule in rest. The second term is the well-known first-order Doppler effect. In the case of saturated absorption, this term can be eliminated. The third term represents the second-order Doppler effect and the last term describes the photon recoil effect that will be discussed in next section.

The first-order Doppler effect of the molecular velocity broadens the spectral line, whereas the line centre is not shifted. The spectral line is shifted, however, by the second-order Doppler effect.[12] The frequency shift $\Delta\nu$ at the Maxwell distribution of molecular velocity can be written as

$$\frac{\Delta\nu}{\nu_0} = -\frac{v^2}{2c^2} = -\frac{3kT}{2Mc^2}, \tag{2}$$

where T is the temperature, k is Boltzmann constant, c is light velocity in vacuum, and M is the molecular mass. The value of $\Delta\nu/v_0T$ for acetylene is $-5.36\times10^{-15}\,\mathrm{K}^{-1}$, which gives a fixed shift of 1.597×10^{-12} at 298 K.

The gas in the laser beam is heated by absorption of laser radiation. Therefore, the gas temperature in the laser beam is somewhat higher than the wall temperature. A Poisson equation

$$\nabla^2 t = \frac{q}{\kappa}, \tag{3}$$

where q is the absorbed laser power in a unit volume and κ is the thermal conductivity, can be used to calculate the temperature distribution in the gas. On the assumption that the beam of radius A is of a cylindrical symmetry with a constant absorption, the temperature distribution inside the beam of radius $A(r<A)$ is

$$t(r) = t(A) + \frac{q}{4\kappa}(A^2 - r^2); \tag{4}$$

while the temperature distribution outside the beam of radius A ($r>A$), where the term q/κ in Eq.(3) becomes zero, is

$$t(r) = t(A) - \frac{A^2 q}{2\kappa}\ln\left(\frac{r}{A}\right). \tag{5}$$

Thus, the average temperature rise in the laser beam ($r<A$) is

$$\overline{\Delta t} = \frac{Q}{2\pi\kappa L}\left(\frac{1}{4} + \ln\frac{B}{A}\right), \tag{6}$$

with respect to the temperature at $r=B$ outside the beam. $Q=\pi A^2 Lq$ is the total power absorbed in the cavity of length L.

When the mean free path is much shorter than the beam radius, i.e. high pressure, the thermal conductivity κ is independent of the gas pressure, but it is proportional to the square root of the temperature. When calculating a small temperature change, the temperature dependence of the conductivity can be ignored. The value of the conductivity for acetylene is $0.02135\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ at a temperature of 298 K.[13] For a 10 cm confocal cavity with the cavity mirrors of 20 mm diameter and $Q=1$ mW, $\overline{\Delta t}$ is 0.304 K. However, for acetylene-saturated absorption, a low pressure in absorption cavity is used. In this case, the mean free path becomes longer and independent of the gas pressure and temperature, so the thermal conductivity will become smaller and proportional to the gas pressure. Thus $\overline{\Delta t}$ for the saturated absorption is roughly estimated to be ten times as large as the value calculated above, up to ∼3 K. This may result in a frequency shift of 1.61×10^{-14}. In order to obtain a stability of 5.7×10^{-14}, the variation in absorbed power must be within 3.5 mW.

In Fig.1, the frequency shifts of the acetylene are calculated for various lengths of the confocal cavity, L, and the change of the absorbed power, ΔQ, by using Eqs.(2) and (6). The results show that, in the case of same ΔQ, a short confocal cavity has a larger frequency shift than the long one. Thus a longer cavity is advantageous to reduce the second-order Doppler effect and improve the stability.

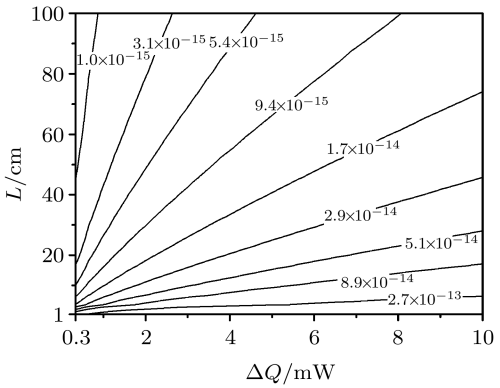


Fig.1. The frequency shift caused by second-order Doppler effect as a function of L and ΔQ on the assumption that the diameter of cavity mirrors is 20 mm.

3. Recoil effect

The last term of Eq.(1) describes the photon recoil effect. The origin of a recoil effect in the saturated spectroscopy is a direct consequence of the transfer of momentum of the photon to the molecule, and vice versa. A photon of frequency ν has a momentum $h\nu/c$ where h is Planck's constant. When a molecule in the lower state absorbs a photon, the photon momentum $h\nu/c$ would be transferred to the absorber. Accompanying the momentum transfer, the part photon energy $(h\nu)^2/2Mc^2$ must be additionally transferred to absorber in the form of kinetic energy. Thus the frequency of absorption $\nu_{\rm a}$ is higher than the proper frequency ν_0 of the molecule.

$$\nu_{\rm a} = \nu_0(1+\varepsilon). \tag{7}$$

When, on the other hand, a molecule in the excited state emits a photon, the molecule will obtain a kinetic energy $(h\nu)^2/2Mc^2$, and the photon energy needed for the excitation is diminished by this recoil. Then the frequency of emission $\nu_{\rm e}$ is lower than the proper frequency ν_0 of the molecule.

$$\nu_{\rm e} = \nu_0(1-\varepsilon), \tag{8}$$

where ε is the coefficient of frequency shift caused by the recoil effect. The value of ε for acetylene at 1.5 μm is

$$\varepsilon = \frac{h\nu_0}{2Mc^2} = 1.7\times10^{-11}. \tag{9}$$

For linear absorption, the absorption line or profile is simply shifted towards the blue by the recoil shift ε. The shifted value, $\nu_0+\varepsilon\nu_0$, should be adopted as the standard of frequency. However, for the Doppler-free saturated signal based on cavity-enhanced absorption technique at 1.5 μm, there is a strong standing wave interacting with a group of molecules of the same velocity ($v_z = 0$). The recoil effect leads to a doublet structure of the respective resonance line as has been found theoretically[14–16] and experimentally.[17–19] The two saturated resonances are separated by 2ε. The centre frequency between saturated resonances is the proper frequency ν_0. The doublet structure is disadvantageous for determining the exact centre of transition. At low resolution, the unresolved doublet structure may lead to line asymmetries caused by different sizes of the components. With progressively increasing resolution, the signal is reduced.

Kol'chenko *et al*[14] have investigated the recoil effect in saturated absorption. The peak frequency of saturated absorption is found to be

$$\nu = \nu_0 + \frac{\gamma_2-\gamma_1}{\gamma_2+\gamma_1}\varepsilon\nu_0, \tag{10}$$

where γ_1 and γ_2 are the decay rates of the lower and upper states of the transition, respectively. The ratio of the decay rates is dependent on the gas pressure, the temperature and the laser power. The frequency shift caused by the recoil effect as a function of the ratio of γ_1 to γ_2 is given in Fig.2. The magnitude of the fixed frequency shift is of the order of 10^{-12}–10^{-11}. A change in γ_1/γ_2 by several percent due to any change in these parameters will produce a frequency shift about $\pm1\times10^{-12}$. It is true that the saturated absorption frequency is within 10^{-11} of the proper frequency ν_0, nevertheless it varies by 10^{-13} to 10^{-12}.

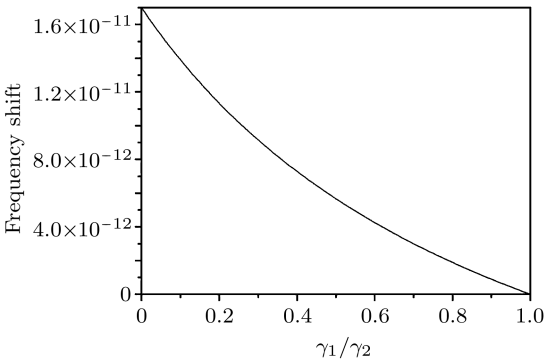


Fig.2. The frequency shifts of the acetylene caused by the recoil effect versus the ratio of γ_1 to γ_2.

4. Pressure shift

A phenomenological constant ϕ is assumed to describe the frequency shift at pressure p in the following

equation,

$$\nu = \nu_0 + \phi p. \tag{11}$$

Swann and Gilbert[20] have measured ϕ of the acetylene at 1.5 μm. Their result showed that many of the lines exhibit a shift ϕ near +2.18 kHz/Pa. However, the measurements performed used high-pressure cell (6.7–65.8 kPa). It is invalid for the saturated absorption where the acetylene pressure in the absorption cell is typically in the range of 1.33–5.52 Pa. Labachelevie *et al*[8] claimed that apparent pressure dependence of the frequency in the above pressure range was not found. For Edwards' system,[10] the frequency shift in changing from 1 Pa cell to 3 Pa cell is +1.0 kHz. Thus we have deduced that the slope of the frequency shift caused by pressure variation is 485 Hz/Pa.

The temperature dependence of the pressure shift has not been studied experimentally or theoretically. Moderate thermal changes can slightly modify the pressure shift of a molecular spectral line by changing the collision frequency. The collision-induced pressure shift is given by

$$\nu - \nu_0 = \frac{1}{2\pi} N \bar{v} \sigma_{\mathrm{s}}, \tag{12}$$

where N is the density of collision partners; $\bar{v}$ is the mean relative velocity and σ_{s} is the cross section. In a closed cell containing only the gas, the density is fixed and σ_{s} can be taken as a constant. The mean relative velocity is proportional to the square root of the temperature. Using Eq.(12), the curve of the pressure shift versus the change of the temperature is obtained, as shown in Fig.3. The result shows that the percentage change of the amount of relative pressure shift, which is caused by the temperature change, is almost a half of the percentage change of the temperature. Thus in order to reproduce the stability of 5.7×10^{-14} at the temperature of 298 K and the pressure of 2.66 Pa, the gas temperature must be stable within ± 2.5°C.

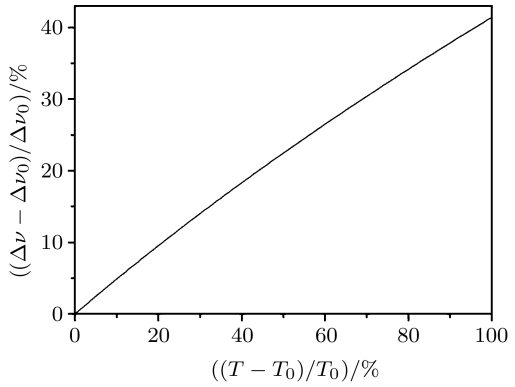


Fig.3. The percentage change of the amount of relative pressure shift as a function of the percentage change of the relative temperature. $\Delta\upsilon_0$ and $\Delta\upsilon$ are the pressure shifts measured at temperatures T_0 and T, respectively. T_0 and T are in degree of Kelvin.

5. Electromagnetic fields effect

The acetylene molecule is a linear symmetric X_2Y_2 molecule, which belongs to the point group $D_{\infty\nu}$. Since, for almost all known linear polyatomic molecules, the angular momentum of electrons about the internuclear axis is zero and the electronic ground state is $^1\Sigma$, the influence of a possible electronic angular momentum on the vibration-rotational spectrum need not be taken into account. The hyperfine structure arising from the internal magnetic field is much smaller than those normally found in atoms and can be neglected. This is simply due to the nature of the molecular chemical bond, where unpaired electrons in atoms pair up with electrons from another atoms. Magnetic moments of the acetylene are proportional to the overall rotational angular momentum and are 1/1000 that of an electron. Thus a large external magnetic field of 0.1 T would cause a Zeeman splitting of less than 1 MHz. The slope is about 10 MHz/T.

Because the acetylene lacks a nuclear quadrupole moment, electric quadrupole hyperfine structure is absent. And due to the symmetry mentioned above, the acetylene has no permanent electric dipole moment. Consequently, the first and second-order Stark shifts are also absent.

6. Power shift

A frequency shift in saturated absorption with the intensity of the laser was early found by Barger and Hall.[21] However, to our knowledge, an explicit physical model of the power shift has not yet been available. The effect of power shift was considered to be associated with the dispersive character of the laser output line profile,[22] which is related to diffraction losses of the cavity,[23] collisions of molecules[24] and some possible effects from resonant-light pressure.[25] The contribution of second-order Doppler effect and recoil effect mentioned above also cannot be neglected.

A theoretical calculation of the power shift is very

difficult because of the lack of precise knowledge of the mechanism. Edwards gave an experimental result of $-1.5\,\mathrm{kHz/Wmm^{-2}}$. According to this value, the frequency shifts versus the power variation in the cavity, ΔP, and the length variation of the confocal cavity, L, are shown in Fig.4. It seems that a long cavity can also effectively reduce the power shift like the result in section 2. However, the decrease is because the long cavity has a larger beam radius, which results in a lower light intensity in the cavity, leading to a smaller shift, which is disadvantageous to saturated absorption. So the design of long cavity here is not a good way to reduce the influence of the power shift. In order to reproduce the stability of 5.7×10^{-14}, the intensity in the cavity must be stable within $0.0076\,\mathrm{W/mm^2}$. For a 10 cm confocal cavity, the power in the cavity is just allowed to vary 1.14 mW. In the acetylene-saturated absorption, the saturation intensity has been estimated for the line P13 of $^{13}C_2H_2$ as[4]

$$I_\mathrm{s}(\mathrm{W/m^2}) = 15\times10^2(10+7.52\times p)^2, \qquad (13)$$

where p is the pressure in Pa. For the typical pressure 2.7 Pa of saturated absorption, this gives a saturation intensity of $1.35\,\mathrm{W/mm^2}$. So the fluctuation of the power in the cavity is limited to within 0.6%.

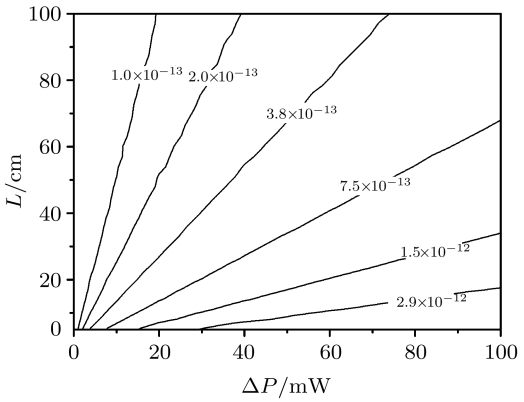


Fig.4. The frequency shift caused by power shift as a function of L and ΔP.

7. Conclusion

Various effects on frequency shifts in the acetylene saturated absorption line have been discussed in detail. Since a constant and stable shift in frequency can be a matter of definition, the magnitudes of uncertainties of frequency shift are considered. The typical values of stability in frequency are listed in Table 1.

Table 1. Magnitudes of uncertainties in frequency shifts of the acetylene saturated absorption caused by various effects discussed in this paper.

effect	condition	frequency shifts of saturation absorption (T = 298 K, p = 2.7 Pa, L = 10 cm)
second-order Doppler	$\Delta Q = \pm1$ mW	$\mp1.63\times10^{-14}$
recoil	dependent on pressure, temperature and power	10^{-13} to 10^{-12}
pressure shift	$\Delta p = \pm0.133$ Pa	$\pm3.2\times10^{-13}$
	$\Delta T = \pm3$°C	$\pm3\times10^{-14}$
zeeman effect	$\Delta B = \pm10^{-4}$ T	$\pm5\times10^{-12}$
power shift	$\Delta P = \pm2$ mW	$\mp1\times10^{-13}$

Conditions described in Table 1 are somewhat arbitrary, and some values of corresponding fluctuations, such as those of the recoil and Zeeman effects, are obtained by rough approximations. The fluctuation in frequency shift caused by the Zeeman effect is the largest among those effects. So when there is a large external magnetic field during frequency stabilization, some measures like shielding must be taken to avoid its disturbance. In practice, a long cavity can effectively reduce the influence of the second-order Doppler effect. For example, when the change of the absorbed power, ΔQ, is 1 mW, a 10 cm confocal cavity will yield a frequency shift of -1.63×10^{-14}; nevertheless a 20 cm confocal cavity only produce a frequency shift of -7.4×10^{-15}. Moreover, it is a better choice to stabilize the temperature of the cavity within at least ±2.5°C. This will effectively avoid the temperature-induced shift related to recoil effect and pressure shift, and further improve the laser frequency stability. Such an analysis may be attractive when establishing high-resolution calibration standard at 1.5 μm using cavity-enhanced technique. Our analysis may provide the theoretical guidance for an optimum design of the cavity.

References

[1] Li X F, Pan W, Ma D, Luo B, Zhang W L and Xiong Y 2006 *Acta Phys. Sin.* **55** 5094 (in Chinese)

[2] Tan Z W, Cao J H, Chen Y, Lin Y, Ning T G and Jian S S 2007 *Acta Phys. Sin.* **56** 274 (in Chinese)

[3] Tan Z W, Ning T G, Liu Y, Chen Y, Cao J H, Dong X W, Ma L N and Jian S S 2006 *Acta Phys. Sin.* **55** 2799 (in Chinese)

[4] Labachelerie M, Nakagawa K and Ohtsu M 1994 *Opt. Lett.* **19** 840

[5] Ma W G, Dong L, Yin W B and Jia S T 2005 *Chin. Phys.* **14** 709

[6] Labachelerie M, Nakagawa K, Awaji Y and Ohtsu M 1995 *Opt. Lett.* **20** 572

[7] Nakagawa K, Labachelerie M, Awaji Y, Kourogi M, Enami T and Ohtsu M 1995 *Opt. Lett.* **20** 410

[8] Nakagawa K, Labachelerie M, Awaji Y and Kourogi M 1996 *J. Opt. Soc. Am.* B **13** 2708

[9] Awaji Y, Nakagawa K, Labachelerie M and Ohtsu M 1995 *Opt. Lett.* **20** 2024

[10] Edwards C S, Margolis H S, Barwood G P, Lea S N, Gill P and Rowley W R C 2005 *Appl. Phys.* B **80** 977

[11] Demtroder W 1981 *Laser Spectroscopy* (Berlin: Springer) p620

[12] Bagayev S N, Chebotayev V P, Dmitriyev A K, Om A E and Nekrasov Y V 1991 *Appl. Phys.* B **52** 63

[13] Yaws C L 1980 *Matheson Gas Data Book* (Lyndhurst, NJ: Matheson Gas Products) Appendix 23

[14] Kol'chenko A P, Rautian S G and Sokolovskii R S 1969 *Sov. Phys. JETP* **28** 986

[15] Stenholm S 1974 *J. Phys.* B: *Atom. Molec. Phys.* **7** 1235

[16] Borde Ch J 1977 *Laser Spectroscopy* III (Berlin: Springer) p121

[17] Hall J L, Borde C J and Uehara K 1976 *Phys. Rev. Lett.* **37** 1339

[18] Riehle F, Ishikawa J and Helmcke J 1988 *Phys. Rev. Lett.* **61** 2092

[19] BordeéC J, Camy G and Decomps B 1979 *Phys. Rev.* A **20** 254

[20] Swann W C and Gilbert S L 2000 *J. Opt. Soc. Am.* B **17** 1263

[21] Barger R L and Hall J L 1969 *Phys. Rev. Lett.* **22** 4

[22] Ghosh Roy D N, Bertinetto F, Rebaglia B I and Cresto P C 1983 *J. Appl. Phys.* **54** 531

[23] Floch A L, Naour R L, Lenormand J M and Tachee J P 1980 *Phys. Rev. Lett.* **45** 544

[24] Mironov A V, Privalov V E and Sinitsa S A 1988 *Opt. Spectrosc.* **64** 386

[25] Grimm R and Mlynek J 1989 *Appl. Phys.* B **49** 179