Pressure-dependent terahertz optical characterization of heptafluoropropane*

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(Received 11 July 2014; published online 20 August 2014)

Heptafluoropropane (HFP), as the best alternative to halon fire-suppression agents, is now a widely used fire extinguishing agent. The current studies of HFP, concentrating on the extinguishing mechanisms of flames and decomposition products, in general deal with the destructive and high temperature cases. In this paper, terahertz time-domain spectra are used to characterize HFP at different pressures. Optical parameters of HFP, such as absorption coefficient, refractive index, and relative permittivity, and their relationship with concentration of samples, are discussed. The absorption peak of HFP at 0.3 THz depends strongly on the applied pressure, and the corresponding parameters increase almost linearly with increasing HFP concentration. The present study lays a foundation for future extensive applications.

Keywords: optical constant, heptafluoropropane, terahertz, pressure

PACS: 78.47.D–, 42.87.–d, 78.20.Ci **DOI:** 10.1088/1674-1056/23/10/107804

1. Introduction

In recent years, perfluorinated hydrocarbon and hydrofluorocarbon compounds have been developed as the best alternative to halon fire-suppression agents such as Halon 1301 (CF_3Br), which is prohibited to be produced by international treaty. 2H-heptafluoropropane (having a chemical structure of CF_3CFHCF_3, commonly referred to as HFP or HFC-227ea), as a new type of fire suppression agent,[1] is promising to widely substitute for halon agents because of its remarkable strong points, such as a zero potential of ozone depletion, low global warming potential, high efficiency of suppressing a flame, and so on. Due to the practical importance of heptafluoropropane (HFP) in fire protection, as well as its somewhat lower suppression efficiency than Halon 1301,[2,3] it is desirable to understand the chemical behavior of this compound in flame environments.

HFP is a colorless and odorless gas at normal temperature and pressure, but it is stored in liquid state at a certain pressure. Besides serving as an extinguishing agent, it can also be used as a refrigerant and propellant for medical use.[4,5] So far, many thermophysics properties of HFP have been studied, such as the saturated liquid viscosity and gas phase thermal conductivity,[6] specific heat at constant pressure (C_p) and Joule–Thomson coefficient (μ_{J-T}),[7] P–ρ–T properties,[8] liquid phase PVT properties, saturated vapor pressure,[9] and formation heat.[10]

Furthermore, the fire-extinguishing mechanisms and properties of HFP turning into gas flames, including the physical extinguishing mechanism and chemical extinguishing mechanism, have also been studied.[11–13] Traditional research methods for HFP, e.g. the fast pyrolysis method, Fourier transform infrared spectroscopy (FTIR), and gas chromatography/mass spectrometry (GC/MS), aim to analyze thermal decomposition products. All these studies are related to thermodecomposition of HFP under high temperature, so it is inevitable to damage the HFP's structure through the thermodecomposition: HFP will produce HF and COF_2 under condition of high temperature. HF and COF_2 are highly corrosive gases and will bring great hazard to humans and equipment when the volume fraction reaches a certain level.

Terahertz time-domain spectroscopy (THz-TDS) is a new technique based on femtosecond laser technology. It relies on synchronous and coherent detection and possesses an extremely high signal-to-noise ratio (SNR) (up to 10000:1). More importantly, THz-TDS is capable of obtaining the refractive index in addition to the absorption coefficient without using the Kramers–Kronig relation.[14] Therefore, THz-TDS has shown important applicability in research in different fields.[15–19] In the THz range (0.1 THz–10 THz, 3.33 cm^{-1}–333 cm^{-1}, or λ = 3 mm–0.03 mm), many polar molecules

*Project supported by the National Key Basic Research Program of China (Grant No. 2014CB744300), the Specially Funded Program on National Key Scientific Instruments and Equipment Development, China (Grant No. 2012YQ140005), and the Beijing Natural Science Foundation (Grant No. 4122064).

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have unique spectral fingerprints, which are from the rotational transitions of the molecules. Therefore, many gases may be detected more efficiently or accurately by their relatively simple rotational spectra, rather than their more complex vibrational or rovibrational signatures. In addition, for more extensive applications, the optical properties which relate to atomic states of HFP have rarely been reported; THz-TDS signals could achieve optical constants directly.

In this paper, we perform a pulsed THz spectroscopic investigation between 0.2 THz and 2.0 THz. The transmission spectra of HFP are measured at different pressures, and the optical parameters, such as absorption coefficient, extinction coefficient, refractive index, and dielectric constants, are obtained. Moreover, we investigate the relationship between HFP concentration and these optical constants. The absorption peak of HFP at 0.3 THz depends strongly on the applied pressure and the corresponding parameters increase almost linearly with the increase of HFP concentration.

2. Experimental technique

We employed THz-TDS to characterize the spectral features of HFP in the range of 0.2 THz–2.0 THz.[20–24] Figure 1(a) shows a schematic diagram of the THz spectrometer. THz pulses were generated by an 800-nm femtosecond laser (Mai Tai laser, Spectra Physics). The laser beam was split into pump and probe beams. The pump beam ($\sim$ 300 mW) was focused onto the photo-conductive antenna to generate the THz pulses. The generated THz pulses propagated through two off-axis parabolic mirrors and were focused on a ZnTe crystal, which was used to detect the THz field by the probe beam through electro-optic sampling. Figure 1(b) shows a schematic diagram of the chamber which was used to store the HFP samples, each with a length of 500 mm. One side of the cell was equipped with 7 mm thick quartz glass, and the other side was equipped with a gilded corner reflector, which ensured that the reflected THz wave was parallel to the incident wave. The reflex mechanism is illustrated in the lower left corner of Fig. 1(b). Quartz is an optimal window material due to its almost complete transparency and lack of dispersion in the THz frequency range.[25] The entire THz system was located in an airtight enclosure filled with nitrogen to mitigate the effects of water vapor on the THz beams.[26] HFP gas samples were 10% HFP and 90% nitrogen: the resulting nitrogen has no permanent dipole moment, nor does it show the THz absorption.

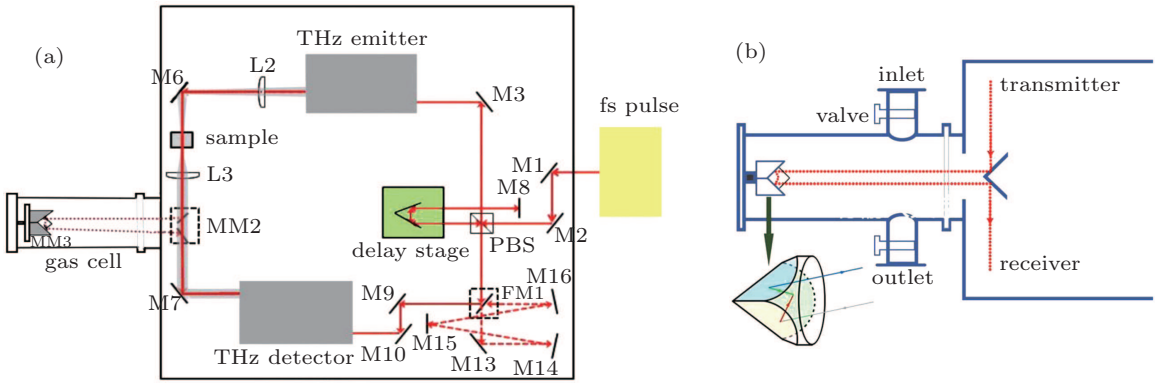


Fig. 1. (color online) (a) Schematic diagram of the THz spectrometer; (b) detail of the chamber with the reflex mechanism of the corner reflector in the lower left corner.

The measurement sequence is as follows. Firstly, system operation and stability are checked by measuring the performance of the THz-TDS system. Secondly, the air tight box is filled with high-purity (99.9%) nitrogen. And the vacuum chamber is evacuated to 5 mbar (1 bar = 10^5 Pa) with a roughing pump, then to 3×10^{-3} mbar with a molecular pump. After that, the THz reference pulses transmitted through the entire system are measured. Thirdly, the THz wave, passed through the chamber filled with the HFP gas sample, is detected. At the same time, the corresponding pressure is obtained by vacuum gauge at room temperature. Then, the check valve on the chamber is opened and the gas sample is released. The third step is repeated several times during the complete transmission measurement.

3. Results and discussion

Figures 2(a) and 2(b) present the time domain spectra measured by scanning the chamber and the Fourier transformed spectra which are calculated by fast Fourier transform of HFP at different pressures and recorded in vacuum in 0.1 THz–1.6 THz. It can be seen that the sample signals are attenuated in comparison with the reference signals due to the absorption of the HFP. Besides, the attenuation increases with increasing pressure. Moreover, there exists a time delay between the sample signals and reference because of the larger refractive index of the THz wave in the sample than in nitrogen.[27] Here the time delay δt is the difference between the time of the peak of the sample signals and that of the reference. As shown in Fig. 2(c), the amplitude peak $V_{\rm P}$ decreases

and δt increases linearly with increasing pressure. The correlation coefficients of these two fitting lines are 0.98718 and 0.9895, respectively.

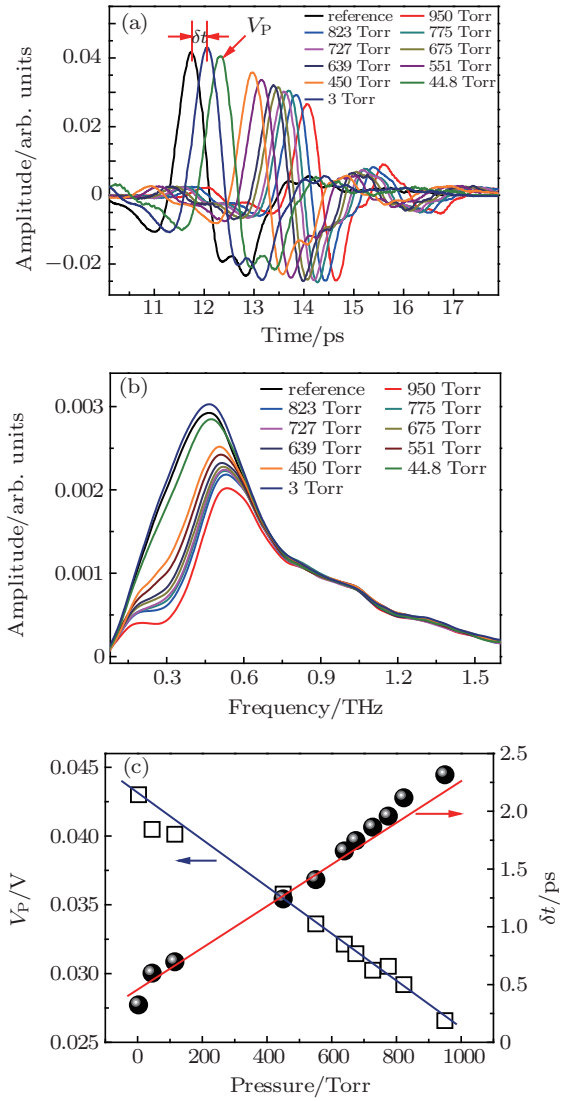


Fig. 2. (color online) (a) THz time-domain spectra for different pressures; (b) Fourier transformed spectra for different pressures; (c) linear fittings of peak amplitude and time delay versus pressure of HFP.

According to the Beer–Lambert law, the transmitted THz amplitudes at absorption centers decay exponentially with the increase of gas concentration and can be given as

$$E = E_0 \exp(-\alpha L/2) = E_0 \exp(-\rho\sigma L/2), \tag{1}$$

or

$$\ln(E/E_0) = -\rho\sigma L/2, \tag{2}$$

where E is the transmitted THz field of HFP, E_0 the reference THz field, which is usually obtained from THz spectra under low pressure conditions (< 20 mTorr), α the power absorption coefficient, ρ the concentration of gas molecules, σ the absorption cross section, and L the transmitted distance. From the equation of state for an ideal gas

$$PV = nRT, \tag{3}$$

we can obtain

$$\rho = n \times 6.02 \times 10^{23}/V = P \times 6.02 \times 10^{23}/RT, \tag{4}$$

where R is the gas constant and is equal to 8.314 J/(mol·K), T the temperature, P the pressure, n the mole number of gas, and V the volume of gas. Finally, we can obtain the amplitude absorption coefficient as

$$\alpha L/2 = \ln(E_0/E) = (\sigma L \times 6.02 \times 10^{23}/2RT) \times P. \tag{5}$$

So the absorption coefficient is proportional to pressure, $\alpha \propto P$. On the basis of Avogadro's hypothesis, for two samples, the ratio of their concentrations ρ is equal to that of their pressures at a given temperature and volume, that is, $\alpha \propto \rho$.

The absorption coefficient spectra of HFP samples at different pressures are calculated and the results are shown in Fig. 3(a). The intensity of the absorption coefficient increases in a frequency range of 0.1 THz–0.5 THz and decreases in a frequency range of 0.5 THz–1.6 THz as the pressure of the sample increases. It is clear that there is an observable absorption peak in each of these HFP spectra at 0.3 THz. To investigate the dependence of the absorption coefficient on HFP pressure and concentration at a certain frequency, we extract the data α_1 at 0.3 THz as shown in the inset, where the linear relationship can be directly observed with a slope of 2.88×10^{-3} and correlation coefficient of 0.98636.

The values of refractive index $n(\nu)$ of HFP at different values of frequency ν are determined by the phase difference according to $n(\nu) = 1 + c\Delta\Phi/2\pi\nu L$, where $L = 1000$ mm in our setup and $\Delta\Phi$ is the relative phase difference of the sample and reference spectra. Figure 3(b) shows the refractive index (here we use n_1 to present the refractive index at a specific frequency) spectra of HFP with different pressures at $\nu = 0.3$ THz, which depend slightly on THz frequency. The plot located in the top right corner is the linear fitting of $n_1 \propto P$ & ρ, with a slope of 6.0×10^{-7}. Figure 3(c) shows the frequency dependence of extinction coefficient κ, which is determined by $\kappa(\nu) = c\alpha(\nu)/4\pi\nu$ for each frequency component ν. The experimental data reach maximum values at 0.3 THz, and the higher the pressure, the larger the maximum value is. It has been reported that the gas extinction coefficient changes proportionally with concentration.[28] For the experiment in this paper, gas concentration is in proportion to pressure; therefore, the extinction coefficient increases with increasing pressure since $\kappa \propto \alpha$ at the selected frequency.

The monotonic variations of the real part ε'' and imaginary part ε' of dielectric constant ε of HFP samples with pressure are obtained at the selected frequency of 0.3 THz, as $\varepsilon' = n^2 - \kappa^2$ and $\varepsilon'' = 2n\kappa$ as presented in Fig. 3(d). Generally, the magnitude of dielectric constant represents the strength of

polarization. For various gaseous dielectrics, because of the large distance between gas molecules, they are difficult to polarize, thus the relative dielectric constants are close to that of vacuum. The experimental data with a maximum of 1.0017 and minimum of 1.0002 accord well with the theoretical results.

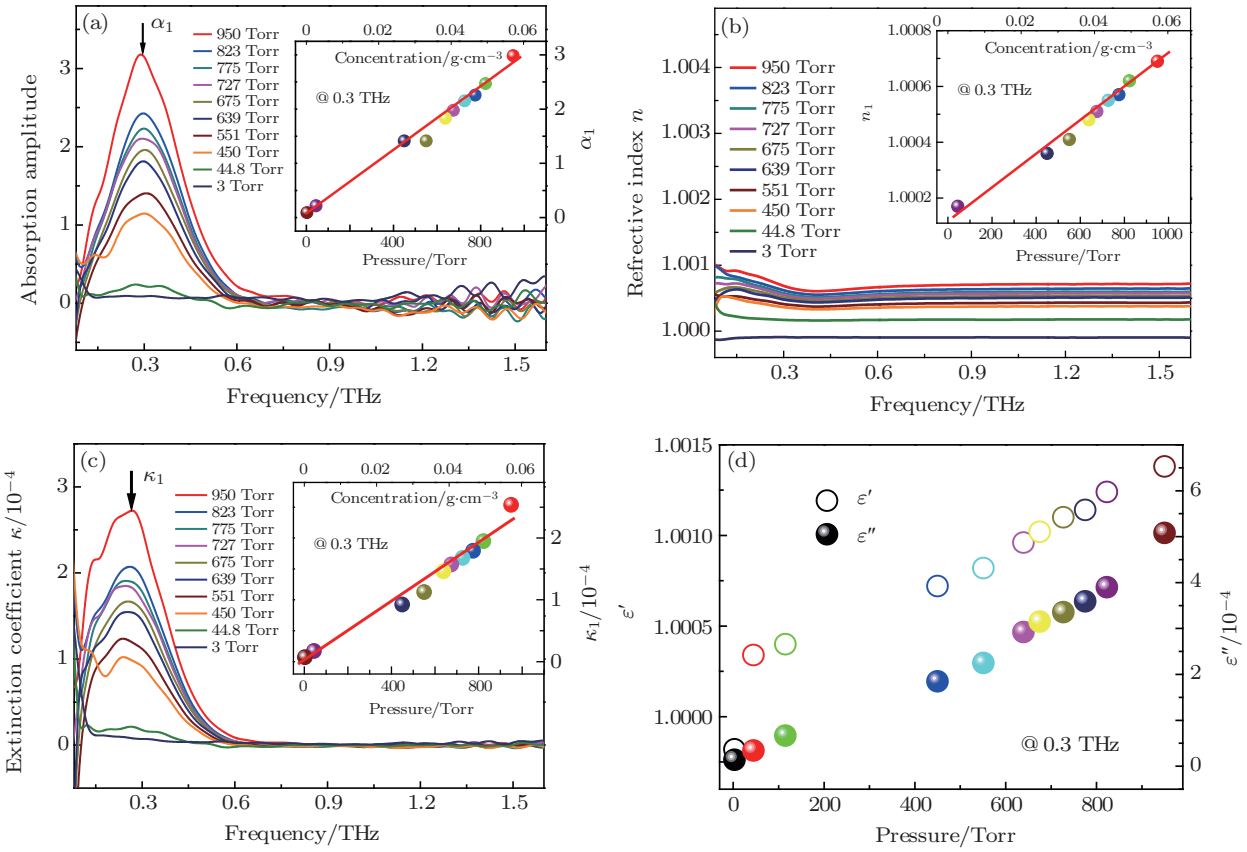


Fig. 3. (color online) (a) Absorption spectra of HFP and the inset of linear fitting of the peak absorption amplitude at 0.3 THz versus pressure and concentration; (b) the values of refractive index n for different pressures (the inset in the upper right corner shows the linear fitting of the data at 0.3 THz versus pressure and concentration); (c) extinction coefficient spectra and the linear fitting of κ versus pressure and concentration of HFP samples, (d) the real part and imaginary part of dielectric constant of HFP for different pressures at 0.3 THz.

Each of the above-mentioned optical constants is actually a function of the frequency of the incident light, reflecting the aggregation state and symmetric properties of atoms and molecules inside substance. Compared with other methods which extract optical properties from the basic spectral measurements, THz-TDS has advantages such as nondestructive examination of the sample, easy manipulation and less requirement for experimental equipment. In addition, optical characterization of HFP may be useful to study the extinguishing mechanics.

4. Conclusion

In this work, we studied heptafluoropropane samples (10% HFP and 90% nitrogen) at different pressures using THz-TDS. We measured the absorption coefficient, extinction coefficient, refractive index, and dielectric constant of HFP at different pressures and investigated the relationship of these optical constants to sample concentration. The results show that there exists a characteristic absorption peak at 0.3 THz and the corresponding parameters at 0.3 THz increase almost linearly as HFP pressure and concentration increase, which is in good consistence with the Beer–Lambert law.

References

[1] Miziolek A W and Tsang W 1995 *ACS Symposium Series* (Washington DC: American Chemical Society) p. 388
[2] Sheinson R S and Penner-Hahn J E 1989 *Fire Safety J.* **15** 437
[3] Nyden M R and Linteris G T 1994 *J. Res. Natl. Inst. Stan.* **861** 467
[4] Durlka S K and Biswas P 1998 *Environ. Sci. Technol.* **32** 2301
[5] Wang J, Levendis Y A and Riegter H 2001 *Environ. Sci. Technol.* **35** 3541
[6] Rossi M, Camino G and Luda M 2001 *Polym. Degrad. Stabil.* **74** 507
[7] Wirbser H, Bräuning G, Gürtner J and Ernst G 1992 *J. Chem. Thermodyn.* **24** 761
[8] Scalabrin G, Piazza L and Richon D 2002 *Fluid Phase Equilibr.* **199** 33
[9] Defibaugh D R and Moldover M R 1997 *J. Chem. Eng. Data* **42** 160
[10] Lee C, Yang W and Parr R G 1988 *Phys. Rev. B* **37** 785
[11] Westmoreland P R 1994 *Twenty-Fifth Symposium (International) on Combustion* 1505

[12] Burgess Jr 1996 *Prog. Energy Combust. Sci.* **21** 453
[13] The current NIST HFC mechanism may be downloaded from http://fluid.nist.gov/ ckmech.html.
[14] Lucarini V and Saarinen J J 2005 *Kramers–Kronig Relations in Optical Materials Research* (Berlin: Springer)
[15] Zhao H, Zhao K and Bao R M 2012 *J. Infrared Milli. Terahz Waves* **33** 522
[16] Watanabe Y 2004 *Opt. Commun.* **234** 125
[17] Chen Y 2011 *J. Appl. Phys.* **110** 044902
[18] Choi D H 2012 *J. Chem. Phys.* **137** 175101
[19] Fukunaga K and Picollo M 2010 *Appl. Phys. A* **100** 591
[20] Jiang C 2014 *Energ. Fuels* **28** 483
[21] Jin W J 2013 *Appl. Geophys.* **10** 496
[22] Bao R M 2013 *Sci. China: Phys. Mech. Astron.* **56** 1603
[23] Zhao H 2012 *Sci. China: Phys. Mech. Astron.* **55** 195
[24] Tian L 2009 *Sci. China: Series G: Phys. Mech. Astron.* **39** 1938
[25] Naftaly M 2007 *Proc. IEEE* **95** 1658
[26] Exter M V 1989 *Opt. Lett.* **14** 1128
[27] Wang H and Zhao G Z 2010 *Acta Photonica Sinica* **39** 1185
[28] Liu X M and Shao M 2004 *Acta Scientiae Circumstantiae* **24** 185