Detailed infrared spectra of refrigerant gases

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Introduction

Climate change is a serious problem caused primarily by the use of fossil fuels, although greenhouse gas (GHG) emissions are also regarded as a major contributor. Globally, greenhouse gas emissions cause an increase in average temperature, a decrease in ice mass, which causes sea level rise, and extreme climate events. Surface temperature has risen by 1.4 °C since the 1900s, with an exceptional increase of 0.18 °C predicted for June 2023 (Rohde 2023).

Fluorinated greenhouse gases (FGGs) are categorized as global pollutants. Most fluorinated greenhouse gases have an extremely high global warming potential (GWP) when compared to other greenhouse gases (Hansen et al., 2010). Historically, chlorofluorocarbons (CFCs) have been utilized as propellants for packaging materials, aerosol solvents, and refrigerants, and they have been identified as potential contributors to ozone depletion (Wallington et al., 1994). The Montreal Protocol of 1987 agreed to eliminate the use of CFCs. This led to the replacement of CFCs with hydrofluorocarbons (HFCs) (Sheraz et al., 2021). As a result of recent changes in environmental legislation, new refrigerant categories have evolved, with the goal of making refrigerant gases "greener" in terms of their impact on the ozone layer.

Aim of the study

It is critical to be able to detect the existence and concentration of these new gases, as well as older gases, in order to evaluate if the systems are operational and whether they can be recycled or destroyed. Additional reasons why quantitative measurements of the presence of such gases are required include: Leak detection during the manufacturing of air conditioning components to ensure that they are leak-free, as well as testing newer systems to ensure that they are running at maximum efficiency and mixing ratios. Fast Fourier transform spectroscopy can be utilized for detection and quantification. However, detailed infrared spectra of currently used refrigerants are scarce or even not available in the literature. In the present work, we report on a detailed study on infrared spectroscopy of refrigerant gases. These were achieved utilizing an in-house 3D-printed tubular reactor with two BaF_2 windows, which can be integrated into the beamline of a Bruker IR-Spectrometer.

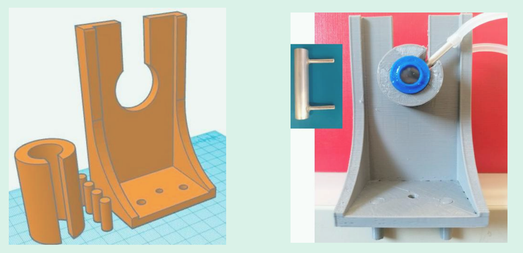
Materials and Methods

The refrigerant gases examined in the present study were R32, R134a, R410a and R404a. Below the chemical structure for each one is given:

No	Refrigerant gas	Description
1	R-32	Difluoromethane (CH_2F_2), aka HCF-32
2	R-134a	1,1,1,2-Tetrafluoroethane (CF_3CH_2F), aka HFC-134a
3	R-410a	Azeotrope mixture of R32 and R125 (Pentafluoroethane, CHF_2CF_3), aka HFC-125
4	R-404a	R125:R143a (1,1,1-trifluoroethane):R134a = 44:52:4

The FTIR spectra of the refrigerant gases were achieved utilizing an in-house 3D-printed tubular reactor with two BaF_2 windows, which can be integrated into the beamline of a Bruker (Billerica, MA, USA) FTIR Spectrometer. The BaF_2 windows (purchased by Crystran Ltd., Poole, UK) have a thickness of 1 mm and 8 mm diameter. The transmission range of the BaF_2 windows is from 0.15 μm to 12 μm, and the refractive index 1.45 at 5 μm, with a reflection loss of 6.5% at 5 μm (2 surfaces), which qualifies it a suitable candidate for an IR Sensor.

The examined gases were diluted first in air and then in nitrogen at concentrations 5%, 10% and 15% v/v using gastight bags guaranteeing zero contamination and losses. Then, the IR sensor was exposed to the gas mixtures by fixing the two BaF_2 windows on the aluminum reactor using the blue caps (Scheme 1).



Scheme 1. 3D-printed reactor for FTIR measurements of gaseous samples: (left) scheme and (right) photo of the aluminum reactor (insert) mounted on the holder.

Results

FTIR spectra of refrigerant gases

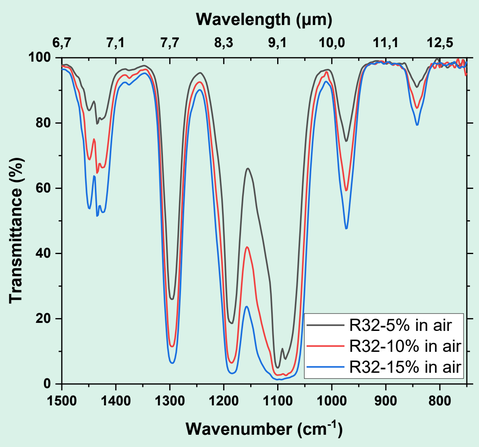


***Fig. 1**. FTIR spectra of R-32 @ 5, 10 and 15% v/v diluted in air.*

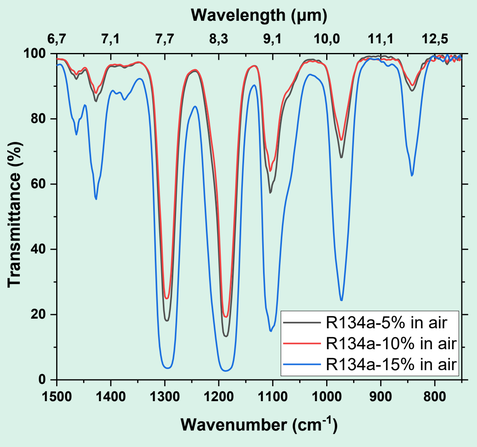


***Fig. 2**. FTIR spectra of R-134a @ 5, 10 and 15% v/v diluted in air.*

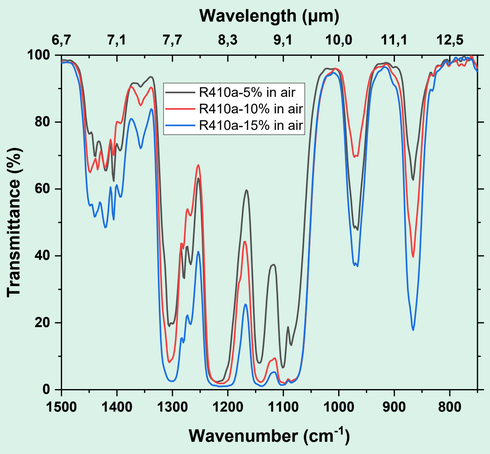


***Fig. 3**. FTIR spectra of R-410a @ 5, 10 and 15% v/v diluted in air.*

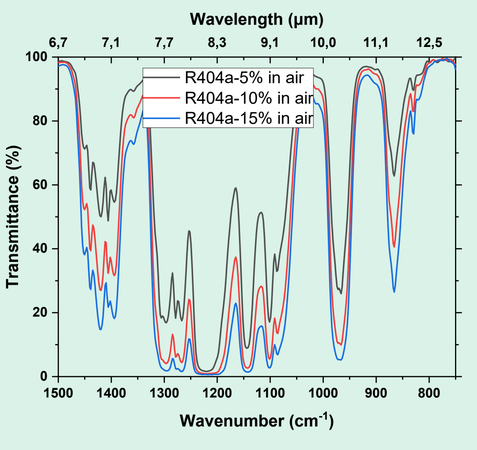


***Fig. 4**. FTIR spectra of R-404a @ 5, 10 and 15% v/v diluted in air.*

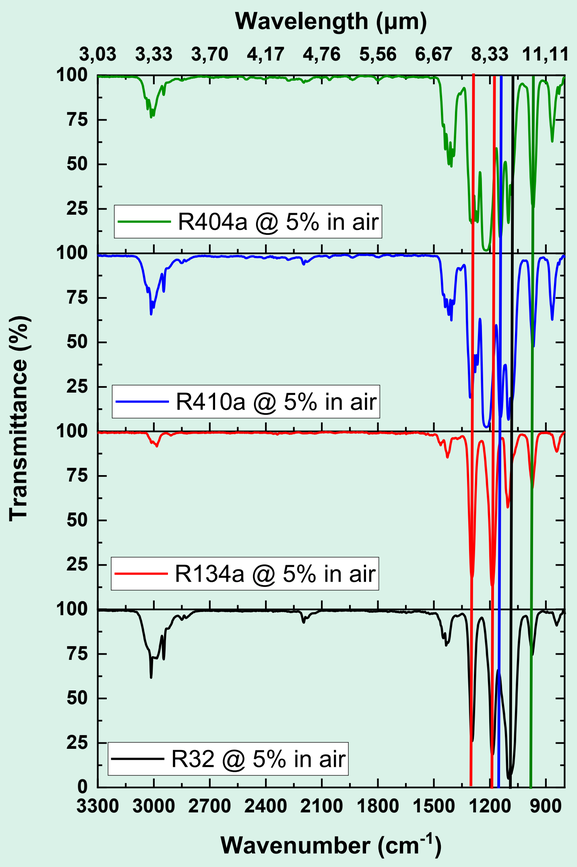


***Fig. 5**. FTIR spectra of R-32, R-134a, R-404a % R-410a @ 5, 10 and 15% v/v diluted in air.*

The FT-IR spectra of the refrigerants R-32, R-134a, R-410a and R-404a for the footprint area and for different concentrations (5%, 10% and 15% in air) are shown in Fig. 1-4. Fig. 5 presents the full range transmittance spectra for these gases for the case of 5% concentration in air, where the characteristic wavelengths for the identification of each refrigerant are also distinguished. Namely, for R-32, it is 9.213 μm, and for R-134a, it is 7.71 μm and/or 8.42 μm, for R-410a it is 8.756 and for R-404a it is 11.561.

For each gas, we obtained calibration lines as presented in Figures 6-9. These lines represent the relative transmittance of the peak at the characteristic wavelength for the different concentrations of each refrigerant gas. It is evident that relative transmittance is adversely proportional to the gas concentration increase. As a result, these fittings constitute a tool on one hand for the detection of the corresponding refrigerant gas and on the other hand for the evaluation of their concentration.

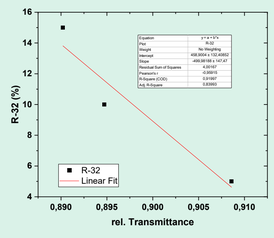


***Fig. 6**. Calibration line for R-32 at 9.213 μm.*

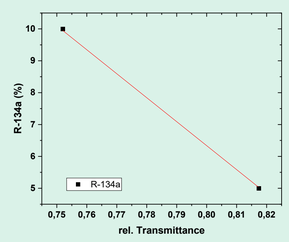


***Fig. 7**. Calibration line for R-134a at 7.71 μm.*

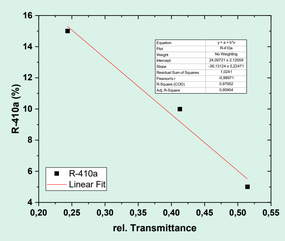


***Fig. 8**. Calibration line for R410a at 8.756 μm.*

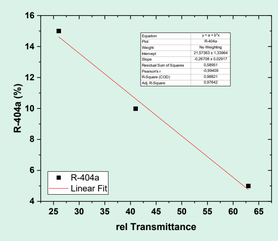


***Fig. 9**. Calibration line for R404a at 11.561 μm.*

Conclusions

Detailed FTIR spectra were measured for the refrigerant gases R-32, R-134a, R-410a and R-404a using an in-house 3D-printed reactor and the methodology developed in previous works of the authors. Via this protocol, all the afore mentioned gases can be successfully identified and their purity can be determined aiming to the early detection and classification of any corresponding refrigerant gases emissions.

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