LABORATORY MID-INFRARED ABSORPTION CROSS-SECTION SPECTRA OF LARGE VOLATILE MOLECULES FOR ATMOSPHERIC REMOTE SENSING

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Remote sensing techniques of terrestrial and astrophysical atmospheres rely heavily on our knowledge of the spectral signatures of molecules. The mid-infrared spectral region is particularly useful as most molecules are radiatively active in that range i.e. they are able to absorb photons of energy corresponding to transitions between rotational and vibrational (ro-vibrational) energy levels.

The 8-14 μm range presents the additional interest to correspond to an atmospheric spectral window i.e. a part of the electromagnetic spectrum that allows radiation to partially pass through the atmosphere. Molecules absorbing or emitting in that spectral range can be detected by a sensitive instrument if their spectral signature is known.

The spectral signature depends on the probability for a molecule to absorb a photon at a given energy. Because this probability is determined by the geometry and composition of the molecule, each absorption profile is unique for a given species. The spectral signature of molecules in the mid-infrared is usually represented by their absorption cross-section (in cm^2 $molecule^{-1}$) as a function of the wavenumber (in cm^{-1}).

Large molecules (typically six and more atoms) are found in weak abundance in the atmosphere. The pressure mixing ratio of these constituents typically ranges from a few hundreds to a fraction of a ppt (part-per-trillion). However, many of those compounds, particularly those containing C-Cl, C-F and C-Br bonds, have large absorption cross-sections ($>10^{-18}$ cm^2 $molecule^{-1}$) in the mid-infrared atmospheric spectral window. This make these molecules extremely potent greenhouse gases. Hence, most halocarbons have a global warming potential over a horizon of 100 years (GWP_{100}) three to four orders of magnitude larger than CO_2 [1].

SUMMARY

The acquisition of accurate experimental reference cross-sections on large atmospheric volatile molecules, and particularly halocarbons, is discussed.

Many large polyatomic molecules are now detectable through remote sensing either by ground-based (e.g. Mahieu *et al*. [2]) or satellite missions (e.g. Brown *et al*. [3]). The trend of halocarbons such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) is particularly followed due to their contribution to both climate change and ozone depletion. The processing of remote sensing signals relies heavily on the availability and accuracy of the molecular absorption cross-section reference data. This article will review the method used to acquire and validate these data.

MOLECULAR DATA FOR ATMOSPHERIC REMOTE SENSING

The molecular spectroscopic data used in remote sensing retrieval are usually obtained by laboratory experiments or ab-initio calculations. The line-by-line spectroscopic parameters of small molecules such as CO_2, H_2O, O_3 or CH_4 are included in database like HITRAN [4] or GEISA [5]. From their spectroscopic parameters, synthetic absorption spectra can be generated over a large range of temperature and pressure conditions and compared with remote sensing data to extract the pressure-missing ratio profiles of these atmospheric gases.

Large molecules do not fit into this model. As the number of atoms increases, so does the number of ro-vibrational transitions, making line-by-line ab-initio calculations impractical. Heavier molecules such as halocarbons also have large moment of inertia, which bring the ro-vibrational lines close together. Experimentally, the infrared absorption spectra of such molecules typically appear as broad bands, each of these bands corresponding to the overlapping of multiple individual transitions. An illustration of a heavy molecule broad band can be seen in Fig. 1 with the ozone-depleting compound CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane). The main features of those spectra correspond to transitions between fundamental modes of vibrations i.e. absorption from the ground vibrational state to a higher vibrational state ($v = 0 \rightarrow v' > 0$). But spectra are complicated even further by the presence of hot bands — temperature-dependent transitions from thermally populated excited vibrational states ($v > 0 \rightarrow v' > v$) — and combination bands resulting from the coupling of fundamental modes. A line-by-line description of each ro-vibrational transition of those molecules is therefore still impossible. This situation is dealt with by providing as reference the absorption cross-section spectra of the large polyatomic molecules, in a range of temperature and pressure suitable for atmospheric simulations.

Theoretical calculation on large molecules is usually limited to the estimation of the spectral position and integrated strength of the absorption bands. Several methods and basis sets are available depending on the complexity of the molecule. Among them, the density functional theory (DFT) method provide results competitive with ab-initio calculations such as 2nd-order Møller-Plesset at a reduced computational cost [7]. The radiative efficiency of a molecule, an essential parameter to determine their impact on the radiative forcing, can be estimated from computational methods when no experimental data are available [1 and references therein]. Theoretical calculations can also nicely complete an experimental investigation by verifying the lack of impurity and by facilitating the detection of conformers (e.g. Le Bris *et al.* [8]). However, it still cannot reasonably be used alone to simulate an absorption cross-section spectrum of a large molecule with an accuracy high enough for remote sensing.

There are therefore strong needs for accurate experimental cross-section spectra of large molecules. Ideally the reference data should be at a resolution high enough so that no feature is missed. This aspect is particularly important on the *Q*-branch of the absorption bands, which can become very sharp as the temperature decreases.

EXPERIMENTAL ACQUISITION TECHNIQUE

Semi-conductor lasers are now able to reach the 8-14 μm portion of the electromagnetic spectrum using technology such as quantum cascade laser. However, a compromise still needs to be made between the spectral range and the resolution of the laser. Therefore, acquisitions of high-resolution experimental absorption cross-sections covering the whole mid-infrared atmospheric spectral window are still dependent on Fourier transform infrared spectroscopy (FTIR).

A Fourier transform spectrometer (FTS) is based on Michelson interferometry. A lightsource is divided by a beamsplitter into two signals of equal intensity. The two beams travel separate paths before being reflected by mirrors and recombined at the beamsplitter. A change in the optical path difference between the two beams is created by moving one of the mirrors. The intensity

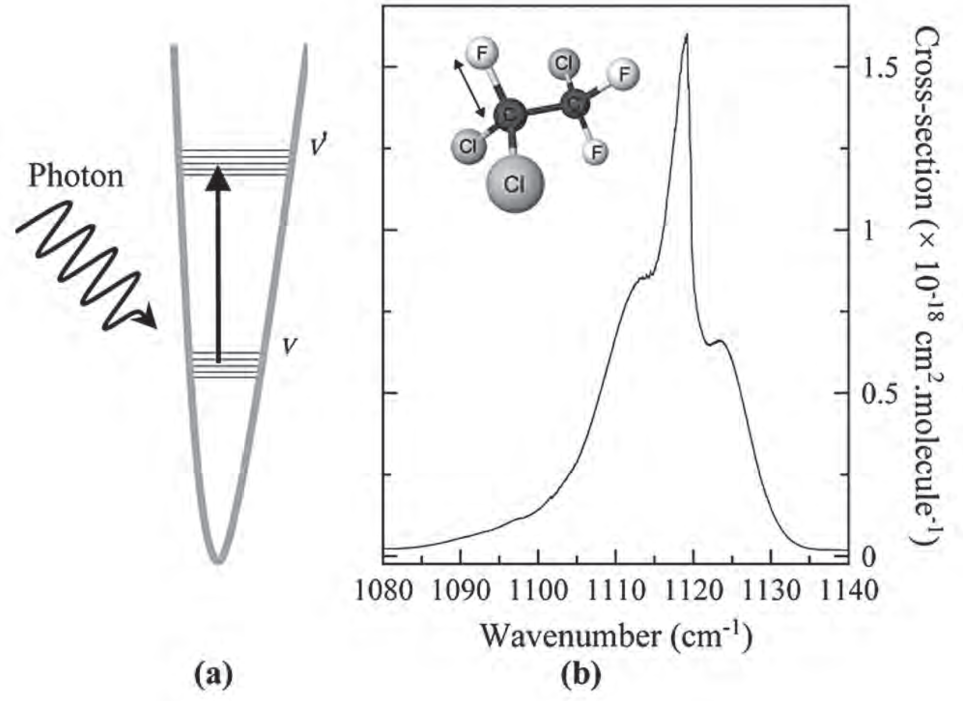

Fig. 1 Absorption of light in the mid-infrared by a large molecule in gaseous phase. (a) The molecule is excited by photo-absorption. Since vibrational energy states are orders of magnitude greater than rotational energy states, the transitions from the rotational levels in the ground vibrational state ($v = 0$) to the rotational levels in an excited vibrational state ($v' > 0$) form a band. (b) C–F stretching vibration on the C_1 conformer of CFC-113 and the broadband associated with this fundamental vibration mode. (Data from Le Bris *et al.* [6])

of the recombined beam is detected as the mirror is moving, which create an interferogram. After a phase correction, the signal output is switched to the frequency domain by a Fourier transform. In a typical mid-infrared configuration, the FTS operates with a thermal source (Globar) and a KBr beamsplitter. The recombined beam is sent to a liquid nitrogen-cooled mercury (MCT) detector. This configuration typically allows to cover a spectral range from the 500’s cm^{-1} to the 6000’s cm^{-1}.

The gas sample can be either pure or mixed with dry air or nitrogen. Mixed samples broaden the band shapes and give spectra similar to those acquired by remote sensing. Pure vapours allow a better control of the pressure and thus a better accuracy. However, the cross-section spectra need to be processed through a pseudo-line method such as the one developed by Toon *et al*. [9] before being used for atmospheric retrieval.

A stainless steel gas cell equipped with ZnSe windows is positioned along the recombined beam path between the FTS and the detector. For highly absorbing molecules, a very short cell is preferred to prevent nonlinear saturation effects while keeping the gas pressure at a reasonable level for accurate readouts. For atmospheric remote sensing applications, it is often necessary to obtain the absorption cross-sections of gases at low temperature. To avoid condensation on the cell windows, prevent absorption of the source radiation outside of the cell, and protect the hygroscopic KBr beamsplitter, all the elements of the optical paths from the source to the detector must remain under vacuum.

DATA ANALYSIS AND COMPOSITE SPECTRA

In a typical experiment, a baseline spectrum is first obtained from a series of scans taken with an empty cell at a temperature T. The gas sample is then allowed to fill the cell at a controlled pressure P and a second series of scans is taken. The optical depth $\chi_{P,T}$ for each wavenumber is obtained from the experimental data using the Beer-Lambert law:

$$\chi_{P,T}(\upsilon) = \ln\left[\frac{I_{0,T}(\upsilon)}{I_{P,T}(\upsilon)}\right]$$

where υ is the wavenumber in cm^{-1}; $I_{0,T}$ is the light intensity passing through the empty cell (baseline) and $I_{P,T}$ is the light intensity passing through the cell filled with the sample at the pressure P.

The absorption cross section σ_T at a wavenumber υ can then be extracted using the following equation:

$$\sigma_T(\upsilon) = \chi_{P,T}(\upsilon)\frac{T}{T_0}\frac{P_0}{P}\frac{1}{N_L L}$$

where T_0 and P_0 are the standard conditions for temperature and pressure; N_L is the Loschmidt’s constant ($N_L = 2.651 \times 10^{22}$ cm^{-3}) and L the length of the cell in cm.

Molecular spectra have usually a large dynamic range. Thus, a set of different gas pressures must be used to get a good signal to noise ratio on the smallest structures while keeping the signal from the strongest bands unsaturated. Thus, the cross-section spectrum of a compound at a given temperature is ideally a composite spectrum retrieved from multiple pressure-dependent scan series.

The optical depths corresponding to excessively optically thin (i.e. noisy) or optically thick (i.e. saturated) environments are eliminated (see Fig. 2). The thresholds on the optical depth are determined empirically. Pressure-induced self-broadening can play a role when working on a pure vapour as sharp features are usually pressure-dependent. In such case, the optical depth no longer varies linearly with the pressure even in the absence of saturation. However, it has been observed [11] that, in that event, a quadratic fit on the optical depth still allows the retrieval of the cross-section at the zero-Torr limit.

SOURCES OF ERRORS AND DATA VALIDATION

FTIR spectra, particularly in the atmospheric spectral range, can be affected by an array of artifacts and practical issues. The

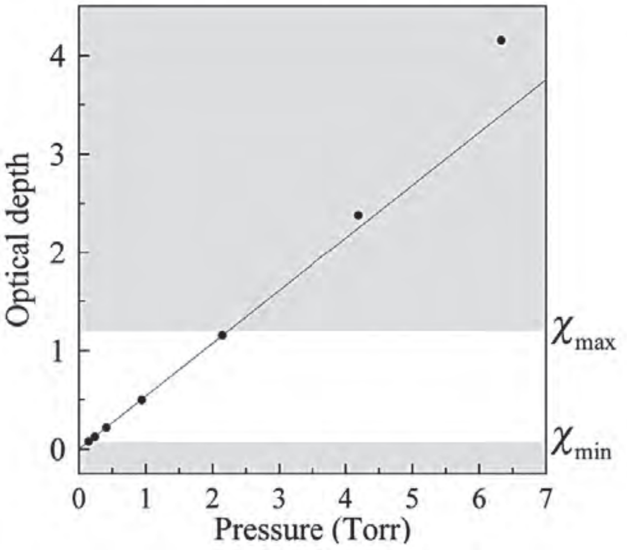

Fig. 2 Calculation of the effective cross-section $\sigma_{T,v}$ of perfluorodecalin ($C_{10}F_{18}$) for $\upsilon =$ 1079.3 cm^{-1}. In this example, the optical depth $\chi_{P,T}$ varies linearly with the pressure between the threshold values χ_{min} and χ_{max} (white area). The two points in the upper grey area correspond to saturated environments and are eliminated from the calculation. (Data from Le Bris *et al.* [10])

following section presents the most common sources of errors and the methods used to minimize them[1].

One of the main source of uncertainties comes from the variation of the luminance of the thermal source during the scans. As high-resolution FTIR acquisitions can take a considerable amount of time, a drift between the primary baseline and the gas spectra is not uncommon. Left untreated, the drift leads to an improper zeroing of the absorption cross-sections. It is therefore important to adjust the primary baseline (typically built from hundreds of scans) with control baselines of a few dozens of scans taken before and after each cell filling. Depending on the compound being studied, adjustment of the primary baseline can also be done using area of the molecular spectra where no absorption occurs.

Another issue of FTIR spectroscopy is the relative weakness of the optical signal. The source being a black body, the radiation power is constrained by its temperature. This available power is further limited by the iris controlling the spatial coherence. Individual high-resolution acquisitions are therefore often noisy and a large number of scans must be added to obtain a satisfying signal-to-noise ratio. However, because high-resolution data also requires a lengthy displacement of the FTS arm, a compromise must be reach between resolution and acquisition time. Fortunately, for many large molecules, a resolution of 0.02 cm^{-1} does not significantly alter the line shape and is comparable to the resolution used in satellite remote sensing mission such as SCISAT ACE-FTS [12].

The iris itself creates an artifact. To maximize the transmitted power, the iris has to be set close to the source. The warmed-up annulus around the aperture creates an off-axis secondary thermal radiation superimposing to the main source. This leads to distortion of the signal as the aperture size decreases. Fortunately, the warm aperture artifact can be strongly reduced by inserting a second aperture at the focal point of the beam between the FTS and the detector [13].

MCT detectors have a notorious non-linear response to the photon flux. The effect is particularly noticeable on the central peak of the interferogram, which create a baseline offset on the spectrum. The raw interferograms may require corrections before the phase correction and the Fourier transformation. Other errors such as the uncertainty on the pressure and temperature measurements, the sample purity, and the optical path length can usually be easily evaluated and minimized.

The validations of experimental data are performed either by comparison with independent studies when they exist, or as mentioned earlier, with the line positions and integrated band strengths of the theoretical calculations. Another method to verify the quality of the data is to survey the variation of the integrated band strengths with temperature. Although the band shapes are temperature-dependent due to the change of population in the rotational levels of the ground vibrational state, the overall integrated intensities should remain constant. Taking into account all sources of errors, the uncertainties on the experimental total integrated intensity of strongly absorbent gases such as halocarbons at the 95% confidence limit are often below 5%.

PRESENT AND FUTURE NEEDS FOR REMOTE SENSING

The phase-out of ozone depleting substances has led to the production and emission of substitute compounds. Among them, hydrofluorocarbons (HFCs) have become the major replacements in many applications. However, their important global warming potential may offset the benefit on the climate of the bans of CFCs and HCFCs [14]. So far, the majority of detections of HFCs have been made either by *in-situ* experiments through the AGAGE (Advanced Global Atmospheric Gases Experiment) network or using flask sampling like the NOAA (National Oceanic and Atmospheric Administration) network. However, molecules such as HFC-134a [15] and HFC-23 [16] are now detectable by satellite measurements. It is likely that, in the near future, more molecules will be added to the list, which will require precise absorption cross-section reference data over a wide range of atmospheric temperatures and pressures.

The study of exoplanet atmospheres, and in particular the search for biosignature gases, represent another exciting new field of investigation. The next generation of ground-based and space-based telescopes, such as NASA's James Webb Space Telescope, will have the capacity to probe the atmosphere of Earth-like planets. The potential for an exoplanet to host life could therefore be assessed by analyzing the presence of gases that are exclusively (or mostly) produced by life on Earth. The standard biosignature gases are small molecules such as O_2, CH_4, N_2O, O_3, which are substantial in the Earth atmosphere. However, it has recently been shown [17] that larger molecules such as ethyl mercaptan, ethanol, isoprene, thioglycol, dimethyl sulfide, toluene, benzene, dimethyl disulfide, dimethyl sulfoxide, fluoroacetone, methyl ethyl ketone, acetone, acetaldehyde, methyl mercaptan, and methyl vinyl ketone can provide similar detectability. A more extended list of potential stable volatile biomarkers has recently been published [18]. The availability of the spectral signature of those large molecules in a relevant range of temperatures and pressures will be essential to assess their utilities as biomarkers and to interpret the atmospheric spectra of exoplanets.

CONCLUSION

Despite their weak abundance in the atmosphere, large volatile molecules and particularly halocarbons, can strongly affect the climate due to their high absorption cross-sections within the

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[1] Some typical issues of Fourier transform spectroscopy such as spectral aliasing or dynamic alignment errors are usually corrected by commercial spectrometers and will therefore not be discussed here.

mid-infrared spectral window. Large molecules are also very interesting candidates as biosignature tracers in the study of Earth-like exoplanet atmospheres. The new generation of remote sensing instruments will likely allow more and more compounds to be detected. To make the most of these instruments, it will become increasingly necessary to have excellent reference molecules at an appropriate resolution and in a wide range of temperatures and pressures.

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