Synergistic use of different atmospheric instruments: What about the spectral parameters?

J.-M. Flaud, B. Picquet-Varrault, A. Gratien, J. Orphal and J.-F. Doussin

Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris 12&7 and CNRS, 61 av. du Général de Gaulle, 94010 Créteil Cédex, France

Abstract- Optical measurements of atmospheric minor constituents are performed using spectrometers working in the UV-visible, infrared and microwave spectral ranges. In particular recently the satellite ENVISAT has been launched with three spectrometers on board, SCIAMACHY and GOMOS working in the UV-visible spectral region and MIPAS working in the thermal infrared. In the future, the combined use of Nadir-viewing UV-visible and thermal infrared spectrometers (onboard remote-sensing satellites such as OMI and TES onboard EOS-AURA, or GOME-2 and IASI onboard MetOP) will provide an important improvement of vertical trace gas concentration profiles. The analysis and interpretation of the atmospheric spectra require good knowledge of the molecular parameters of the species of interest as well as of the interfering species. This is true not only in the spectral domain used to retrieve the species (thermal infrared for MIPAS for example) but also in the other spectral domains used by other instruments: Meaningful comparisons of profiles retrieved by various instruments using different spectral domains require indeed that the spectral parameters are consistent in these spectral domains. To illustrate these points we will concentrate on two molecules namely ozone and formaldehyde.

In the mid-infrared range, the 10 µm ozone band is very strong and is the most widely used to derive concentration profiles. In the UV region, the Huggins and/or Hartley bands are currently used for spectroscopic remote-sensing of ozone. In this paper we will present two sets of results:
- First a careful comparison of four sets of ozone line intensities measured independently in the 10 µm region has been achieved. From them new and more accurate transition moment constants for the \( \nu_1 \) and \( \nu_3 \) bands of \(^{16}\text{O}_3\) were derived and used to generate new line positions and intensities. These new spectroscopic parameters allowed one to simulate atmospheric spectra better than the previous spectroscopic parameters showing that on a relative basis the new spectral parameters are of better quality (J. M. Flaud, G. Wagner, M. Birk, C. Camy-Peyret, C. Claveau, M. R. De Backer-Barilley, A. Barbe, and C. Piccolo, Ozone absorption around 10 µm, J. Geophys. Res., Vol. 108, NO. D9, 4269, doi:10.1029/2002JD002755, 2003)
- Second, there have been rather few intercomparisons of ozone absorption cross sections in the UV and mid-infrared regions. We will present the results of such comparisons either between the 10 µm region and the absorption of ozone at 254 nm or between the 10 µm and the Huggins bands showing that still some inconsistencies at the level of 4-5% exist.

For the measurement of atmospheric formaldehyde concentrations, mid-infrared and ultraviolet absorptions are both used by ground, air or satellite instruments. It is then of the utmost importance to have consistent spectral parameters in these various spectral domains. Consequently the aim of the study performed at LISA was to intercalibrate formaldehyde spectra in the infrared and ultraviolet regions. The experiments were performed by acquiring simultaneously UV and IR spectra at room temperature and atmospheric pressure using a common optical cell. The reactor contains two multiple reflection optical systems interfaced to a Fourier transform infrared spectrometer and to an UV-visible absorption spectrometer. The results of the work will be presented allowing one to point out a much better agreement with one of the various UV absorption cross sections available in the literature.

1. INTRODUCTION

Molecular spectroscopy, besides its own research themes, represents a powerful tool in a number of fields (Atmospheric physics, astrophysics, atmospheres of the planets, combustions, leakage and process control …) to probe the medium of interest. It allows one indeed to measure in a non-intrusive way numerous properties of the medium (Temperature, pressure, abundance of constituents…). As far as atmospheric physics is concerned the past years have seen a noticeable increase of studies aiming at (1) a better understanding of the different phenomena driving the atmospheric system and (2) the prediction of its evolution in the future. In particular human activities, important since the beginning of the industrial period, are strongly changing the atmospheric composition. One can quote for example the enhanced greenhouse effect due to the emission of gases such as carbon dioxide or methane, or the loss of ozone
in the stratosphere clearly observed over the poles (ozone hole), or even pollution for which issues such as air quality, free tropospheric ozone levels, acidic deposition, natural versus anthropogenic emissions are still open.

These questions are studied both theoretically and experimentally. From the experimental point of view atmospheric measurements are performed using various platforms (ground networks, balloons, planes, satellites) and different techniques. Among them optical remote sensing methods are widely used. In particular, measurements from space are the only ones able to provide a continental or global view of the atmosphere. This is why a number of satellite experiments using various optical techniques (radiometers, grating spectrometers, Fourier transform interferometers ...) have been launched. Recently, high quality optical remote sensing instruments working either in the middle and thermal infrared such as MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) or in the visible-ultraviolet such as SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY), have been launched on the ESA’s Environmental Satellite (ENVISAT). In all cases the analysis of the measurements requires the best possible knowledge of the spectral parameters (line positions, intensities, widths, absorption cross sections ...) of the measured species and of their variations with temperatures and pressures. This is particularly true for the recent instruments which cover wide spectral ranges at rather high spectral resolutions with excellent signal to noise ratios. The spectral parameters are derived from experimental and/or theoretical spectroscopy and, since obviously the accuracy of the retrieved profiles depends highly on the quality of the spectroscopic parameters, given the improved capabilities (higher spectral resolution, better signal to noise ratio ...) of the new instruments, it is clear that new laboratory studies using the best experimental techniques and/or sophisticated theoretical models are required. This is true in the various spectral domains used to retrieve a given species: Meaningful comparisons of profiles retrieved by various instruments using different spectral domains require indeed that the spectral parameters are consistent in these spectral domains. To illustrate these points we will concentrate on two molecules, namely ozone and formaldehyde. The paper is organized as follows: The case of the ozone molecule for which it will be shown that despite a number of studies there is still a problem of consistency between the mid-infrared and ultraviolet cross sections will be discussed first. Then we will describe the case of the formaldehyde molecule showing that some measurements are not consistent both in the infrared and visible spectral domains.

2. THE OZONE (O₃) MOLECULE

Ozone plays an important role as far as the chemistry and the radiative properties of the atmosphere are concerned. Consequently its atmospheric concentration has been and is the subject of a number of measurements. Among the various techniques used to measure atmospheric ozone, optical remote sensing techniques are widely used. They cover large parts of the electromagnetic range (MW, IR, UV) and this is why a number of studies have been devoted to the measurements of line intensities and/or absorption cross sections in these various spectral domains; for example for a list of references see (Flaud et al., 2003a; Orphal, 2003). As also for many other molecules the quantitative measurements were usually made only in a given spectral domain, and therefore there exist rather few intercomparisons of absorption cross sections. In the following we present a summary of the various recent measurements performed in the infrared followed by a discussion of problems arising from recent intercomparison experiments.

2.1. Ozone line intensities at 10 microns

In the infrared the 10 µm region is of particular interest since it corresponds to an atmospheric window and to the strongest infrared absorption of this molecule. Accordingly a large number of atmospheric ozone measurements are performed in this spectral domain. This is why a number of laboratory line intensities measurements have been performed at 10 µm. When dealing with O₃ line intensity measurements, the main difficulty is to determine precisely the ozone concentration in the cell. To do so, two main methods are used: making direct pressure measurements or employing, as a reference standard, the UV absorption of O₃ at 254 nm. This determination of the amount of O₃ in the cell is critical to all measurements. The direct pressure measurements rely upon the purity and stability of the O₃ concentration while using the UV method may lead to some dissociation of ozone. A recent paper (Flaud et al., 2003a) has made an analysis and a synthesis of the various infrared measurements showing that three sets of independent
measurements (De Backer Barilly and Barbe, 2001; Wagner et al., 2002; Claveau et al., 2001) are highly consistent (dispersion of ~0.8 % and standard deviation of ~1.9 %) whereas the fourth set of data (Smith et al, 2001) gives intensities which are 4.4 % higher (see Table 1). As a consequence new calculations based on the three sets of consistent data were performed and the corresponding spectral parameters were introduced in the MIPAS and the HITRAN04 databases (Flaud et al., 2003b; Rothman et al., 2005).

Table 1. Comparison of experimental intensities

<table>
<thead>
<tr>
<th>Numbers of lines in common</th>
<th>Ratio</th>
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<tr>
<td>CLA/WAG\textsuperscript{a}</td>
<td>262</td>
</tr>
<tr>
<td>DEB/WAG</td>
<td>257</td>
</tr>
<tr>
<td>SMI/WAG</td>
<td>350</td>
</tr>
<tr>
<td>SMI/DEB</td>
<td>101</td>
</tr>
<tr>
<td>SMI/CLA</td>
<td>61</td>
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\textsuperscript{a} CLA, DEB, SMI and WAG stand for the sets of line intensities measured in [Claveau et al., 2001], [De Backer-Barilly and Barbe, 2001], [Smith et al., 2001] and [Wagner et al., 2002] respectively.

\textsuperscript{b} Uncertainties are one standard deviation.

The problem here is that, while the data of Smith et al. (2001) are in very good agreement with the HITRAN2K line intensities (Rothman et al., 2003) which were derived from the calculation of Flaud et al. (1990), there is a 4 % discrepancy with the three other sets of infrared data and consequently with the new calculation of Flaud et al. (2003a) based on the three sets of measurements in agreement.

2.2. Intercomparison of ozone line intensities in the 10 microns infrared and the ultraviolet (300-350 and 253.7 nm) spectral regions

Two papers dealing with the intercomparison of ozone absorption at 10 µm and in the ultraviolet have been recently published. The first one (Dufour et al., 2004) has remeasured using a diode laser system a few ozone lines at 10 µm and, using the corresponding measured values, have determined the ozone absorption at 253.7 nm. The main findings of this paper are that (1) the newly measured infrared lines are in excellent agreement with the recent line intensity calculation (Flaud et al., 2003a) and (2) are highly consistent with the ozone UV absorption coefficient at 253.7 nm as measured by Hearn (1961). Such results suggest that the new calculation, based, as already said, on three independent infrared measurements, is valid and is consistent with the ozone absorption at 253.7 nm. The second paper (Picquet-Varrault et al., 2005) has compared the ozone absorptions at 10 µm and in the Huggins bands between 300 and 350 nm. The results shows that there is a good agreement between the IR HITRAN2K data and the UV cross sections of various authors (Bass and Paur, 1985; Malicet et al., 1995; Burrows et al., 1999, Bogumil et al., 2001) whereas there is a discrepancy of about 5 % with the calculation of Flaud et al. (2003a).

2.3. Discussion

If one tries to summarize the situation one can say:
- There exist three sets of infrared data in good agreement.
- These three sets are consistent with the ozone UV absorption cross sections at 253.7 nm.
- They are not consistent with a fourth set of infrared data and with the HITRAN2K line intensities.
- The fourth set of infrared data is in good agreement with the HITRAN2K line intensities and with ozone UV absorption cross sections in the Huggins bands (300-350 nm).

It is then clear that all these experiments do not provide consistent results and that more experimental work is needed. In fact this example shows that quantitative spectroscopy is difficult and that extreme care is needed when accuracies of the order of the percent are to be reached.
3. THE FORMALDEHYDE (H\textsubscript{2}CO) MOLECULE

Formaldehyde which is a product of most of the atmospheric VOC (Volatile organic compounds) oxidation processes and which is involved in many photochemical processes, especially in the production of HO\textsubscript{x} radicals in the troposphere (Carlier et al., 1986), is an atmospheric key species. To have a good understanding of the physical and chemical processes in which it is involved, very accurate atmospheric concentration profiles are required. For this reason, many ground-based, air-borne, and balloon-borne or satellite measurements of formaldehyde are performed routinely using spectrometers working in the UV-visible and mid-infrared spectral ranges. Consequently, the knowledge of the formaldehyde absorption cross-sections and of their consistency is of the utmost importance. Hence a large number of experimental determinations of its UV and mid-infrared cross sections have been performed. However experimental studies which have ever verified the consistency between the cross-sections in the two spectral ranges are to our knowledge absent, preventing meaningful comparisons of formaldehyde concentration profiles obtained by spectrometric measurements in the mid-infrared and UV spectral regions. Therefore a study aiming at intercomparing infrared and UV absorption cross-sections for this molecule has been undertaken at LISA (Gratien et al., 2006).

3.1. Experimental details

In order to get rid of the overarching problem of measuring the abundance of the species in the cell experiments were performed by acquiring simultaneously UV and IR spectra at room temperature and atmospheric pressure using a common optical cell. This cell is made of a Pyrex reactor which contains two multiple reflection optical systems interfaced to a Fourier transform infrared (FTIR) spectrometer and to an UV-visible absorption spectrometer. Details concerning spectrometric devices are presented in Fig. 1.

Fig. 1: General setup of the reactor and spectrometers (Picquet-Varrault et al., 2005). Note that the infrared and UV path lengths can be set up independently allowing one to obtain the best recording conditions in both spectral domains.
Several spectra were recorded simultaneously in the mid IR and in the UV spectral regions. Fig. 2 shows examples of such spectra acquired with UV and IR path lengths of 72 m and 12 m, respectively.

Fig. 2: Example of UV and IR spectra of formaldehyde acquired simultaneously. Note the excellent signal to noise ratios obtained in both spectral domains.

3.2. Results and discussion

From these experiments, the IR quantities \( \frac{\int (A.d\sigma)/l}{l} \) where \( A \) is the absorbance and \( l \) is the optical path length were plotted versus the UV quantities \( \frac{\int (A.d\lambda/l)}{l} \) leading to a straight line whose slope (Fig. 3) corresponds to the ratio of the integrated band intensities \( I_{BI}^{IR}/I_{BI}^{UV} \). In the infrared and ultraviolet regions, the measured absorbances were integrated between 1660 and 1820 cm\(^{-1}\) and between 300 and 360 nm respectively.

Fig. 3: IR/UV calibration plots. \( P = I_{BI}^{IR}/I_{BI}^{UV} \) (in nm\(^{-1}\)×cm\(^{-1}\))

This ratio was then compared to the various ratios that can be obtained when using IR and UV integrated band intensities published in the literature (see Table 2).
Table 2: Comparison of measured H$_2$ CO integrated band intensities in the IR (1660-1820 cm$^{-1}$) and in the UV (300-360 nm) spectral regions.

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<tbody>
<tr>
<td>IB$<em>{IR}$ / IB$</em>{UV}$ *</td>
<td>11.04</td>
<td>8.45</td>
<td>10.78</td>
<td>11.27</td>
<td>11.07</td>
<td>10.95</td>
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<tr>
<td>Deviation</td>
<td>-</td>
<td>27%</td>
<td>2%</td>
<td>-2%</td>
<td>-0.3%</td>
<td>1%</td>
<td></td>
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<tr>
<td>IB$<em>{IR}$ / IB$</em>{UV}$ *</td>
<td>11.04</td>
<td>9.93</td>
<td>12.67</td>
<td>13.24</td>
<td>13.02</td>
<td>12.87</td>
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<tr>
<td>Deviation</td>
<td>-</td>
<td>11%</td>
<td>-14%</td>
<td>-18%</td>
<td>-16%</td>
<td>-15%</td>
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</tr>
<tr>
<td>IB$<em>{IR}$ / IB$</em>{UV}$ *</td>
<td>11.04</td>
<td>10.07</td>
<td>12.84</td>
<td>13.42</td>
<td>13.19</td>
<td>13.04</td>
<td></td>
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<tr>
<td>Deviation</td>
<td>-</td>
<td>9%</td>
<td>-15%</td>
<td>-19%</td>
<td>-18%</td>
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* in nm$^{-1}$×cm$^{-1}$

From the results presented in Table 2, one can observe that a good consistency (better than about 5%) exists between the UV data of Meller and Moortgat (2000) and four out of the five infrared data, i.e. Nakanaga et al. (1982); Sharpe et al. (2004); Herndon et al. (2005), and Klotz et al. (2004). The fifth one published by Hisatsune et al. (1955) is about 20% lower than the others leading to a disagreement of 27% with the UV absorption coefficients published by Meller and Moortgat (2000). On the other hand systematic differences of about 16% are observed between the LISA ratio and those obtained when using the UV data published by Rogers (1990) and Cantrell et al. (1990) and the four infrared data sets which are in good agreement. Hence, if one assumes that the infrared data which are in good agreement are correct, these results suggest that the cross-sections published by Rogers (1990) and Cantrell et al. (1990) could be overestimated by about 15%. This is a serious problem since the cross-sections measured by Cantrell et al. (1990) are included in the HITRAN database. As a consequence the formaldehyde concentrations retrieved from remote-sensing experiments using the HITRAN cross-sections would be underestimated by about 15%. Nevertheless, before making definite conclusions, we think that additional cross-sections determinations in both spectral ranges are needed.

4. CONCLUSION

It was not the goal of this paper to give a complete overview of the infrared spectroscopy applied to atmospheric and or astrophysical measurements but rather to show on a two selected examples recent progress, both experimental and theoretical, achieved by modern molecular spectroscopy. For example it was shown that it is necessary to use in the laboratory the best experimental techniques if one wants to get accurate measurements and even when doing so it appears that discrepancies of a few percents exist between different authors demonstrating that extreme care is required when dealing with high accuracy (~one percent) quantitative spectroscopy.

References


