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Assessment of Infrared Remote Chemical Sensing Systems with Numeric Simulations

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Abstract

A general approach to the evaluation of remote chemical sensors is described that can be used to provide evaluation of the chemical detection in a particular chemical scenario. It will be used to make comparisons of a CO₂ laser differential absorption lidar sensor and a passive thermal FTIR sensor. The focus of the study will be to evaluate the advantage of the FTIR sensor’s increased spectral coverage and number of frequency channels.

Keyword: CO₂ DIAL, chemical detectivity, active sensors, passive sensors, numeric simulation, remote sensing, FTIR, chemical prediction error

1. INTRODUCTION

The evaluation of remote chemical sensing systems for potential application to the detection of chemical and biological weapons related activities is of particular importance in the current global political environment. Since implementation of comprehensive field testing to validate the applicability of detection systems is prohibitively expensive, numerical simulations are likely to play a major role in the evaluation process of developing sensors. In this paper we will provide some examples in which a simple noise model is used to compare the chemical detection capabilities of CO₂ Differential absorption lidar system with a broad band 8 to 12 micron infrared passive sensor. While the noise model may be overly simple for quantitative evaluation of the complicated technology, the numerical experiments can be used to derive some useful insight into the tradeoffs between the two specific remote sensing technologies. In addition, the general framework for the description of the process can be used to discuss the development of more accurate simulations which can be benchmarked with data obtained from prototype sensors.

Figure 1 provides a conceptual schematic of the general approach of numerical simulations. The main components are a spectral database, the sensor parameters, the chemical detection parameters, the noise model and the chemical prediction algorithm. The spectral database consists of a set of spectra which contains relevant chemical species including those to be detected and those that might interfere. The sensor parameters define the operation of the sensor which will include the number of frequency channels, the effective resolution of each channel, the sensor standoff range, detector performance, the target being investigated, the specific procedures used to normalize background variations, etc. The chemical detection parameters will define which species are to be detected and those that interfere along with the their concentration ranges. The noise model will allow for the calculation of realizations of the anticipated spectra which will simulate the operation of the sensor. The prediction algorithm is the process used to produce chemical concentration predictions from realistic spectra from the sensor.
General Approach to Simulation of Sensor Performance

Figure 1. This flow chart shows the components of a numeric simulation of sensor performance.

The different components in this general approach must interact in a complicated manner if the simulations are to faithfully represent the capability of the sensor. The noise model will be dependent on the sensor parameters. For instance, the number of frequency channels and their resolution will affect the noise on each channel in a complicated manner that depends on the atmospheric conditions, range and target conditions. The noise model will also be dependent on the definition of the chemical problem. If the concentrations are large enough to saturate the signal on certain channels, those channels will have a higher effective noise level. The noise model used in the simulations, which assumes an equal absorption sensitivity per channel, will ignore most of these interactions. Since passive sensors detect changes in spectral radiance and not directly spectral absorption as in the DIAL sensor, any difference in the sensors absorption sensitivity must be factored into the results of this analysis.

2. DEFINITION OF SENSORS PARAMETERS AND THE CHEMICAL DATABASE

In the studies described below an active sensor using CO₂ DIAL and a passive technique based on a Fourier Transform Infrared spectrometer will be evaluated. The DIAL technology is described elsewhere. The DIAL frequency channels are determined by the wavelengths of the CO₂ molecular transitions which are located in the 900 to 1100 cm⁻¹ range, well within a convenient atmospheric window. The FTIR spectrometer has evenly spaced frequency channels with a frequency range determined by the atmospheric transmission window from 800 and 1200 wavenumbers. In practice the range could be a little wider but some regions with in the 800 to 1200 range may be marginal due to atmospheric absorption features. In addition, the passive FTIR will have limited resolution - assumed to be one cm⁻¹ in this study-relative to the natural linewidth of atmospheric transitions and the natural line widths of the gases being detected.
The advantage of the CO$_2$ DIAL technique over the passive FTIR is that it could, in principle, provide a better single channel signal-to-noise ratio. In addition it has high frequency resolution with laser line widths as narrow as a few thousandths of a wavenumber. This will allow for the transitions of species with sharp spectral features not to be averaged out as will be the case with the passive FTIR sensor. In figure 2 this effect is demonstrated for ammonia where a .05 cm$^{-1}$ resolution spectrum (calculated from the HITRAN database parameters) and 1 cm$^{-1}$ spectrum (from the Infrared Analysis database) are compared. The lower resolution spectrum has an effectively weaker signature. In addition, a non-linear dependence of absorption strength with concentration can result from the limited resolution of the FTIR.

![Comparison of Cross Sections for Ammonia With Different Spectral Resolution](image)

Figure 2. The figure compares the cross section spectrum of ammonia at two different spectral resolutions. The continuous line represents the .05 cm$^{-1}$ spectrum calculated from the HITRAN database parameters. The square points is the one cm$^{-1}$ spectrum obtained from the Infrared Analysis QASOFT database. It shows the cross section is effectively reduced due to the limited resolution of the FTIR sensor.

The passive FTIR with limited resolution but broad spectral coverage has many advantages from a spectroscopic standpoint. It has many more channels than a practical CO$_2$ DIAL system that typically is limited to less than 50 lines (i.e., frequency channels) for each isotopic laser system used in the sensor. In this study the FTIR will have 801 uniform frequency channels between 800 and 1200 cm$^{-1}$. The increased number of frequency channels will likely result in better diagnosis of complicated mixtures of chemicals and can be used to reduce the chemical prediction error. The fact that a broader frequency range can be covered will result in more chemicals being detected by the FTIR system. It is these advantages of the passive FTIR sensor that will be investigated in the simulations presented in this paper.

The chemical database used to provide spectra for the simulation was the QASOFT data base available commercially from Infrared Analysis. Included in this data base are 151 spectra of chemicals with .125 cm$^{-1}$ resolution spectra obtained under known concentration, pathlength and pressure. These spectra are provided in the digital format used by the GRAMS Spectral Notebase software system, which was used to perform most of the manipulations of the spectra using ARRAY BASIC.

The first study addressed the advantage of spectral coverage provided by the FTIR sensor. To accomplish this, an ARRAY BASIC program was written to convert all the database spectra to absolute cross section spectra using the concentration-pathlength documentation provided in the spectral files. Four sets of absolute cross section spectra were generated with different frequency scales: (1) For the passive case the
frequency scale spanned 800 to 1200 cm\(^{-1}\) in increments of .5 cm\(^{-1}\) to represent 1 cm\(^{-1}\) resolution; (2) 100 \(^{12}\)C\(^{16}\)O\(_2\) laser lines frequencies; (3) 100 \(^{13}\)C\(^{16}\)O\(_2\) laser line frequencies; and (4) 100 \(^{13}\)C\(^{18}\)O\(_2\) laser line frequencies. These spectra were then used to assess the number of species that had cross sections above a threshold varying from 10 to 1 cm\(^{-1}\) atm\(^{-1}\).

The results of this study are provide in figure 3. In this plot, the percentage of species with cross sections greater than a certain threshold is plotted versus the threshold value for the passive FTIR spectral band and that encompassed by all three of the CO\(_2\) isotopes. 48\% of the species in the database have a maximum cross section greater than 10 cm\(^{-1}\) atm\(^{-1}\) between the 800 and 1200 cm\(^{-1}\), while only 23\% of the species in the database have a maximum cross section above this for any of the three different isotopic CO\(_2\) laser lines. If the cross section is reduced to 3 cm\(^{-1}\) atm\(^{-1}\) then the numbers become respectively 63\% and 50\% and at 1 cm\(^{-1}\) atm\(^{-1}\) 87\% and 69\%. At the highest cross section threshold the passive FTIR has roughly twice as many species as for the laser frequencies which is near to the ratio of the total band coverages. However, as the cross section threshold is lowered, the ratio becomes less than two. This results from the fact that at most chemicals will have a number of weak bands which likely will overlap with CO\(_2\) laser lines.

![Percent of Species in QASOFT Master Database with Cross Section larger than a given threshold](image)

**Figure 3.** This plot shows the percentage of chemicals which have a cross section greater than a certain threshold versus the threshold value. The FTIR sensor as defined in this paper has a twice the frequency range of the CO\(_2\) DIAL sensor thus a larger number of species.

To gain some insight into what types of chemicals would be assessable with the FTIR band and not the CO\(_2\) laser lines, a sort on the database was performed in which the species that had a cross section less than 1 for CO\(_2\) laser line and greater than 5 cm\(^{-1}\) atm\(^{-1}\) for the FTIR band. This resulted in 19 species out of 151 total species. Of these 15 were either a substituted benzene, a small chlorinated or brominated hydrocarbon without double bonds, or a small ketone. The remainder were inorganic gases. Thus the relative advantage provided by the extended frequency span of the FTIR will be dependent on the types of chemicals that are being detected.
3. CHEMICAL PREDICTION ERROR STUDIES

In order to investigate the advantage of an increased number of frequency channels on the ability to detect chemicals, several numerical simulations were performed using spectra from the database. In these simulations the chemical prediction errors were estimated for detecting a species with a sharp line absorption spectrum and one with broad absorption features as a function of the number of laser lines used and the presence of known interfering absorbers.

The chemical problem was defined as trying to detect simultaneously ammonia (the sharp absorber) and Freon 12 (the broadband absorber). The spectra are provided in figure 4 along with eight additional spectra that will be used to simulate interfering species. The interfering species were chosen from the species with the highest cross sections for the CO$_2$ laser lines in the database.

![Figure 4. This figure shows the spectra used for the study. All spectra were obtained from the QASOFT database.](image)

The sensor parameters are defined without a direct relation to a specific configuration of sensor standoff range, atmospheric conditions, or operational parameters. They are defined purely by the frequency channels. For the FTIR there will be 801 frequency channels with $0.5 \text{ cm}^{-1}$ spacing between the 800 and 1200 cm$^{-1}$. For the DIAL system the frequency channels will be restricted to the strongest 48 lines for the $^{12}$C$^{16}$O$_2$ and $^{13}$C$^{16}$O$_2$ isotopic species. In the study the number of lines used was varied in increments of eight. The smallest number of lines was eight, consisting of one line from each of the 10R, 10P, 9R, and...
9P bands of each isotopic laser. For each increment of eight lines added, one for each band, the lines were chosen to match one of the strongest remaining absorption lines for both ammonia and freon 12. Because of the limited number of strong absorbing lines for ammonia, only the first few iterations provided significant absorption.

The noise model assumed that the systems both will provide absorbance spectra. It will be assumed that the noise on each frequency channel will be .01 absorbance units with a uniform distribution with no correlation among the channels. With this noise model the concentration prediction error will be independent of the concentration of the species involved in the study. To implement the noise model, an ARRAY BASIC program was written which would take as input a spectrum of ammonia and freon 12 at a concentration-path-length of 100 ppm-m and generate 200 realizations in which the random .01 noise was added to this original spectrum.

Generalized least squares routine from Numerical Recipes in C was used to provide concentration-pathlength estimates for the species which spectra were included in the least squares analysis. The standard deviation of the 200 estimated concentration-pathlengths was used as the concentration prediction error. Figure 5. Shows calculated prediction error for ammonia and freon 12 using different numbers of CO2 laser lines when only ammonia and freon 12 are included in the analysis.

Figure 5 shows the dependence of concentration prediction error as a function of the number of laser lines when only ammonia and freon 12 are included in the analysis. Shown as a straight line are the concentration prediction errors for the passive FTIR. The graphic demonstrates that the large number of additional channels for the FTIR instrument will provide a significant reduction in the concentration prediction error. However the effect is less for ammonia than freon 12. For freon 12, the prediction error using eight lines is 17 time that of the passive FTIR and for ammonia the factor is 4.5. This is the result of two factors: (1) The effective ammonia cross sections are higher for the laser because of the effect shown in figure 2; and (2) The fact that spectrum of ammonia consists of sparse sharp lines results in most of the frequency channels defining the baseline which provides less benefit to the concentration prediction than channels which have absorption. When the number of lines is 48, the respective factors become 4.2 and 1.7 for freon 12 and ammonia indicating that increasing the number of lines result in a reduction in
prediction error that is more dramatic for freon 12. When 96 lines are used the factor is 3.2 for freon 12 which is near to being the square root of the ratio of the number of channels.

Figure 6. Compares prediction error dependence on number of laser lines for CO2 DIAL for case where only the two species of interest are analyzed and where eight additional species are included in the analysis.

Figure 6 shows a study in which the effect of interfering species is investigated. In this study the generalized least squares algorithm included all the species that are shown in figure 4 which makes the total number of species 10. The procedure of evaluating the concentration prediction error versus number of laser lines was repeated. However, in this case the number of species required that the eight laser line configuration be omitted. For this particular choice of interfering species, the effect on prediction is much more dramatic for freon 12 than ammonia. In the case of where 16 laser lines are used, addition of the eight species in the fit results in the prediction error increase by 400 percent for freon 12 and only 10 % for ammonia. For 96 lines the effect is diminished with the error increasing by 80 % for freon 12 and 5 % for ammonia. This is the result of the fact that some linear dependency is introduced into the normal
equations of the least squares problem involving the freon 12 spectrum and the spectra of the additional species. By adding more lines, the effect of the linear dependency effect is reduced. This effect is minimal in the case of ammonia with its sharp and unique spectrum.

4. Summary

The numerical simulations described here, while overly simple and not tied directly to the real sensor noise, allow for an evaluation of the relative advantage of the many spectral channels in a passive FTIR sensor compared to a CO₂ DIAL system as the number of laser lines increases. For a broad absorber the advantage is more evident and results in much higher prediction errors for the smaller number of frequency channels afforded by CO₂ DIAL. As the number of laser lines used increases it appears that the prediction error decreases roughly by the square root of the number of channels. For sharp absorbers increasing of number of laser lines has less of an effect. The simulations also showed that the effect of interfering species is larger for the broadband absorber than for chemicals with sharp absorption features. This was especially evident when the number of laser lines used approached the number of species included in the analysis. However, once the number of laser lines is three to four times the number of species, the prediction error begins to decrease much more slowly with the number of laser lines used.

It should be emphasized that in this study the single-channel noise level was the same regardless of the number of channels available. In practice the active CO₂ DIAL system could attain much higher single channel signal-to-noise levels resulting in a limited number of laser lines giving lower concentration prediction errors. To accomplish this type of quantitative evaluation will require detailed noise models which include noise different in each frequency channel. The models will have to include noise sources which are correlated among the frequency channels that can result from varying target albedo, target temperature, instrumental imperfections, and atmospheric radiance and absorption effects. These effect are extremely difficult to model and most likely will have to be evaluated from actual chemical detection experiments performed with prototype sensors. Once a noise model has been benchmarked, numerical evaluations in the general framework described in this paper can be used to extrapolate sensor performance to the multitude of chemical detection problems including those related to chemical and biological weapons.

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6. REFERENCES


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