TUNABLE FAR INFRARED STUDIES IN SUPPORT OF STRATOSPHERIC MEASUREMENTS

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The Smithsonian Astrophysical Observatory is a member of the
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1 Introduction

This report summarizes research done under NASA Grant NAG5-4653. The research performed under this grant has been a collaboration between institutions including the Smithsonian Astrophysical Observatory, the National Institute of Standards and Technology, the University of Oregon, and the NASA Langley Research Center.

The program has included fully line-resolved measurements of submillimeter and far infrared spectroscopic line parameters (pressure broadening coefficients and their temperature dependences, and line positions) for the analysis of field measurements of stratospheric constituents, far infrared database improvements, and studies for improved satellite measurements of the Earth's atmosphere. This research program is designed to enable the full utilization of spectra obtained in far infrared/submillimeter field measurements, such as FIRS-2, FILOS, IBEX, SLS, EosMLS, and proposed European Space Agency measurements of OH (e.g., PIRAMHYD and SFINX) for the retrieval of accurate stratospheric altitude profiles of key trace gases involved in ozone layer photochemistry.

For the analysis of the spectra obtained in the stratosphere from far infrared measurements it is necessary to have accurate values of the molecular parameters (line positions, strengths, and pressure broadening coefficients) for the measured molecules and for possible interfering species.
Knowledge of line positions is in increasingly good shape, with some notable exceptions. The increase in position information includes research that has been performed in the present program of research on HO2, H2O, H2O2, O3, HCl, HF, HBr, HI, CO, OH, and ClO. Examples where further line position studies are necessary include hot band and minor isotopomer lines of some of the major trace species (H2O, O3) and normal lines of some triatomic and larger molecules (NO2). Knowledge of strengths is in generally good shape, since most of the lines are from electric dipole transitions whose intensities are well determined from Stark effect measurements; exceptions include some molecules with large vibration-rotation interactions (NO2) and internal motions (H2O2 above the lowest torsional state). The line parameters that are still the least well determined are pressure broadening coefficients, and their temperature coefficients. These are strongly dependent on the quantum states involved in the transitions, in a way that is much more complex than the simple projection by directional cosine matrix elements involved in determination of rotational line strengths from static dipole moments.

The following molecules have now been measured or detected in the atmosphere using far infrared and millimeter-wave emission spectroscopy from balloon- and satellite-borne spectrometers: OH, HO2, H2O (including minor isotopomers and hot band lines), H2O2, O3P, O2 (including minor isotopomers), O3 (including minor isotopomers and hot band lines), HOCl, HCl, HF, HBr, ClO, CO, CO2, N2O, NO2, N2O5, HNO3, ClNO3, and HCN. Many of these species have spectral lines that are saturated in stratospheric spectra. In these cases, the measured line equivalent widths are proportional to (line strength × Lorentz width)\(^{1/2}\) so that the pressure broadening coefficients are as important as the line intensities in determining concentration profiles. Interpretation of field measurements for these species have required ongoing measurement programs of pressure broadening measurements. Other species (HO2, HOCl, H2O2, HBr, and NO2, as examples) have required further line position studies in order to fully analyze the field measurements.

### 2 Developmental Work

In the TuFIR technique, tunable far infrared radiation is generated by means of CO2 laser difference frequencies in a metal-insulator-metal (MIM) diode [1, 2, 3]. This NIST-developed technique has been demonstrated to be an excellent source of coherent radiation for spectroscopy. As summarized in reference 2, the technique has been used to measure highly accurate far infrared frequencies of stable molecules to serve as frequency and wavelength calibration standards, and to measure frequencies of transient species for astronomical searches. The general features of the TuFIR technique are summarized here. In the usual two-wave mixing mode of TuFIR operation, radiation from two CO2 lasers is combined on a beam splitter and then focussed on a MIM diode, where the difference frequency (far infrared) radiation is generated. One laser is a CO2 waveguide laser, frequency-offset locked to a saturated fluorescence stabilized CO2 laser.
The second laser is a frequency modulated, saturated fluorescence stabilized CO₂ laser. The FIR radiation is thus also frequency modulated. Phase sensitive detection is used to measure the modulation-broadened first derivative of the sample absorption. The waveguide CO₂ laser provides a tunability of up to ±200 MHz. Acousto-optic modulators operating at 90 MHz are used to isolate the lasers from the MIM diode and to provide additional wavelength coverage. By changing pairs of CO₂ laser lines we can cover about 80% of the spectrum between 0.3 and 6 THz. The FIR frequency is known absolutely to ±10 KHz \[4\] and has a spectral purity of \(\sim 10\) KHz. An alternative method of TuFIR operation, three-wave mixing, trades off some of the FIR power for increased tunability. It is effected by directly mixing two saturated fluorescence stabilized CO₂ laser, along with a tunable microwave source, on the MIM diode. Either TuFIR mode is capable of providing fully-resolved measurements at the Doppler widths of far infrared lines, which range from about 0.5 to 20 MHz. The three-wave mixing method is now normally the preferable method of operation, since the choice of CO₂ lasing lines is much less constrained and since the power curve for the tuned FIR radiation is much flatter. Measurements with this method can now be made up to frequencies at least as high as 9 THz \[5\]. Since lines can be fully resolved by the TuFIR method, linewidths can be measured directly, rather than being inferred from a curve of growth. The curve of growth method, necessary when the instrument resolution is coarser than the linewidth, requires that the amount of absorber gas be kept constant. This is a major difficulty when performing measurements on unstable species such as OH, or on strongly surface absorbing species such as HCl or HF.

We have now developed an expertise in ultra-high resolution spectroscopy using the TuFIR method that includes:

- The development of radical source chemistries, allowing us to measure pressure broadening and line positions of OH, HO₂ and ClO;

- Development of 3-wave mixing, which trades off some of the power available in the tunable far infrared beam for much wider tunability. For a particular measurement, either 2-wave or 3-wave mixing can be chosen according to experimental need;

- Design and fabrication of spectroscopy cells, a flow-metering system for radical chemistry, and other laboratory apparatus;

- Development of instrument control and data acquisition software, allowing for precise control of the TuFIR instrument parameters and long integration times for weak spectral lines and;

- Development of software for nonlinear least-squares fitting of measured spectra to obtain pressure broadening coefficients and/or line positions, based upon the algorithm of
Spectra which have the typical modulation-broadened Voigt derivative line shape (other line shape options are available as well, including normal Voigt and Voigt second derivative) are calculated using a complete radiative transfer model, including the effects of line saturation and modulation broadening. Voigt line profiles and their derivatives are calculated, with the capability of varying Doppler and Lorentz widths, line positions, absorber amounts, and baseline and laser power curve variations modeled with polynomials up to cubic order.

- Development of software to perform multiple linear regressions to obtained line broadening and/or shifting information from studies employing complex source chemistries.
- Development of Hamiltonian fitting capability that includes asymmetric top molecules with electron spin-rotation interactions, up to high degree in centrifugal distortion, and nuclear hyperfine (spin-spin dipolar, Fermi contact, and nuclear quadrupole) interactions.

3 Molecule Studies

We have developed a capability for performing spectroscopic measurements on radical species and on weak lines that is unique. Our laboratory measurements under this program include:

**Spectral Standards** TuFIR line position measurements of CO, HCl, and HF for use as spectral standards in the far infrared from 10-200 cm\(^{-1}\) (0.3-6 THz) have been determined. Additional measurements of HCl and HF have been made up to 9 THz.

**OH** Studies of the pressure broadening of the hyperfine-resolved lines at 118.455 cm\(^{-1}\) and 83.869 cm\(^{-1}\) by N\(_2\), O\(_2\), H\(_2\) and He, and their temperature dependences have been completed and published. These studies include re-determination of the OH line positions to higher accuracy. It should be noted that the studies of the 83.869 and 118.455 cm\(^{-1}\) lines provide all of the necessary quantitative spectroscopic parameters needed for the analysis of OH data from the satellite-based OH measurements currently being proposed by NASA and ESA. The 118 cm\(^{-1}\) line is the best line of the 13 lines measured by FIRS-2 for stratospheric OH measurements. The 83 cm\(^{-1}\) line is the one usually considered for heterodyne measurements of OH because of the somewhat lower frequency and the availability of a suitable far infrared laser line of CH\(_3\)OH to use as a local oscillator. The studies of OH have also led to the development of OHIO (OH Interferometer Observations), a proposed satellite-based instrument that could measure stratospheric OH using a combination of a single Fabry-Perot resonator and a diffraction grating, with a detector operated at 80 K. This concept is being pursued in collaboration with the Space Research Organization of
the Netherlands as a potential OH measurement device for both NASA and ESA satellite platforms, and was a component of the ESA PIRAMHYD study (OH profiling by far infrared limb sounding).

**HO₂** The positions of a number of HO₂ lines have been determined, including all but one of the lines used for remote sensing in the far infrared by the SAO, and three of the six lines used by IROE. The measured lines have been included in the 1992 SAO line parameter database. A new program has been written to fit the measured lines to a Hamiltonian expression including spin-rotation and hyperfine interactions by full diagonalization in a parity-conserving basis set. The analysis of the measured spectrum, simultaneously fitted with previous microwave, millimeter and submillimeter spectra [7, 8], has been completed and published. The pressure broadening of the HO₂ doublet \( 132_{12} \leftarrow 121_{11}, J = 27/2 \leftarrow 25/2 \) at 83.32 cm\(^{-1}\) by N\(_2\) and O\(_2\) at room temperature was measured in collaboration with the European Laboratory for Nonlinear Spectroscopy (LENS), in support of potential future heterodyne measurements in the atmosphere. The results from this investigation have now been published. Further work to extend the Hamiltonian fitting to higher values of \( K_a \) (up to 9) and \( N \) (up to 31) by combining the simultaneous fitting with combination differences from near infrared measurements of the lowest electronic transition has been completed and published. This research was done in collaboration with the Steacie Institute for Molecular Sciences, National Research Council of Canada, and the University of Ulm. Similar fitting has now been done with DO₂, combining previous microwave measurements and combination differences for rotational levels up to \( N = 31, K_a = 9 \) from the \( \tilde{A}^2A' \rightarrow \tilde{X}^2A'' \) band. The result is that we now have extensive descriptions for both isotopomers, including off-diagonal components for both nuclear hyperfine and spin-rotation tensors. This allows us to determine the absolute signs of these components, which will further elucidate the electronic structure of HO₂.

**HCl** Measurements of pressure broadening of the 83.39 cm\(^{-1}\) R\(_3\) line of H\(^{35}\)Cl, including its temperature dependence, have been published.

**HI** We have measured and analyzed the quadrupole-resolved rotational spectrum of HI up to the R\(_{11}\) lines. HI is of general spectroscopic interest, particularly since it provides a good example of the rotational dependence of the nuclear quadrupole coupling. In combination with measurements of the vibrational dependence, the data are used to determine the electric field gradient at the \(^{127}\)I nucleus and its first two derivatives with respect to the internuclear distance. The measurements also provide an accurate value of the \(^{127}\)I nuclear spin-rotation interaction.

**O₂** Pressure broadening of the 50.87, 60.46, and 83.47 cm\(^{-1}\) lines of O₂ has been published. We have published a critical study on the use of O₂ magnetic dipole-allowed rotation lines for
the calibration of far infrared atmospheric measurements.

H$_2$O The N$_2$ and O$_2$ broadening coefficients, and their temperature dependences over the 200-300 K range, of the H$_2$O line at 88.650 cm$^{-1}$ have been determined.

O$_3$ The N$_2$ and O$_2$ broadening coefficients, and their temperature dependences over the 200-300 K range, of the O$_3$ line at 114.469 cm$^{-1}$ have been determined.

H$_2$O$_2$ Detailed positions have been determined for most of lines which are major contributors to the $^2Q_4$ and $^2Q_5$ branches of the lowest torsional band, i.e., the structures which are currently used for atmospheric H$_2$O$_2$ measurements.

HF Temperature-dependent studies of the N$_2$ and O$_2$ broadening of the HF R$_3$ line at 164 cm$^{-1}$, used by FIRS-2 and other instruments for stratospheric HF monitoring, have been completed. The data have been analyzed and a publication is currently in preparation. The study also includes a more accurate determination of the line position.

NO Measurements of $^{14}$NO and $^{15}$NO in the X$^2\Pi$ ($v = 0$) state have been made up to 3.9 THz. The analysis of the measurements includes re-determination of rotational, fine- and hyperfine parameters of these two isotopomers, including the spin-orbit coupling constant.

1992 Smithsonian Astrophysical Observatory Line Parameter Database

The Smithsonian Astrophysical Observatory maintains a line parameter listing for analysis of atmospheric thermal emission measurements in the far- and mid-infrared which is updated at frequent intervals. The current version of the listing extends from 10-800 cm$^{-1}$, and contains more than 150,000 lines. The listing is modeled on the HITRAN line parameter listing [9], and contains the best currently available parameters from the HITRAN listing, the JPL Microwave and Submillimeter Line Listing [10], laboratory measurements (including those made under the present research program), and extensive library research and calculations. The SAO line parameter listing reflects the fact that we have thoroughly researched every line of every molecule used in SAO atmospheric measurements and continue to improve the database as atmospheric measurements require. SAO92 contains, in particular, the line parameters that have enabled recent stratospheric measurements of HO$_2$ [11, 12, 13], H$_2$O$_2$ [12, 13, 14], HOCl [13, 15], and the first measurement of stratospheric HBr [15] to be made. A publication on the database has appeared in the Journal of Quantitative Spectroscopy and Radiative Transfer [17]. The database is updated regularly, and is available at http://cfa-www.harvard.edu/firs/sao92.html. The SAO far infrared database is now included in the regular updates of HITRAN [18].
4 Publications from this Research Program


Improved Molecular Constants for the Ground State of DO$_2$, K.V. Chance, D.A. Ramsay, and

5 References


7 Microwave Spectrum of the HO_2 Radical, S. Saito, *J. Molec. Spectrosc.* 65, 229-238 (1977)


10 Submillimeter, Millimeter, and Microwave Spectral Line Catalog, R. L. Poynter and H. M. Pickett, *Publ. 80-23, revision 2*, Jet Propulsion Laboratory, Pasadena, CA, 1984; current values obtained by FTP.


