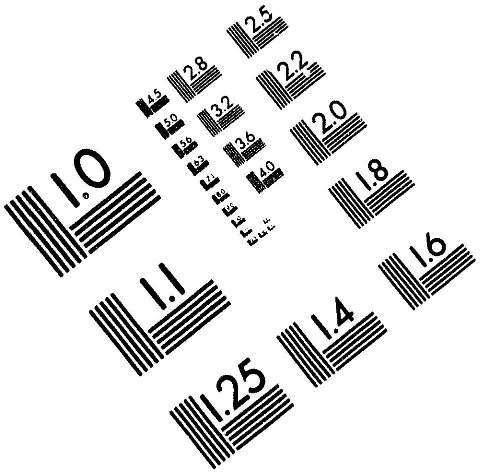

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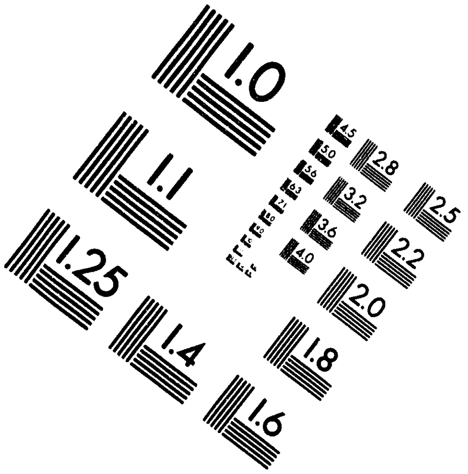

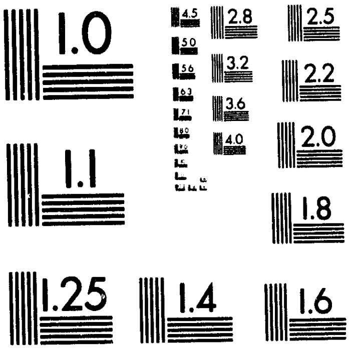

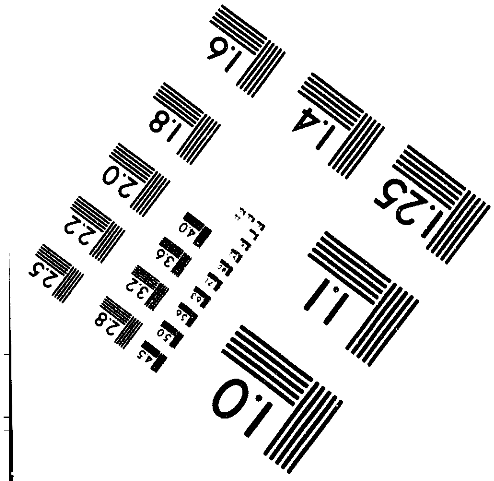

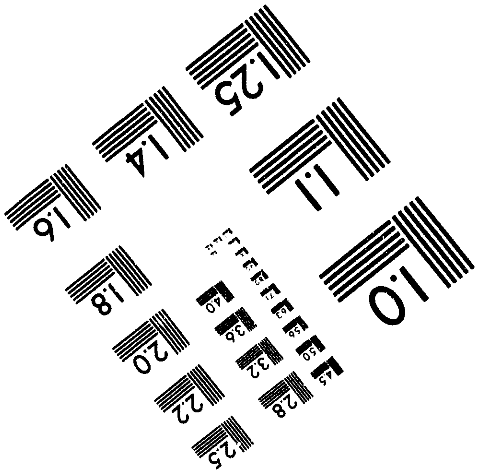

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INFRARED SIGNATURES FOR REMOTE SENSING

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INFRARED SIGNATURES FOR REMOTE SENSING

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ABSTRACT

PNL's capabilities for infrared and near-infrared spectroscopy include tunable-diode-laser (TDL) systems covering 300–3000 cm^{-1} at <10-MHz bandwidth; a Bruker Fourier-transform infrared (FTIR) spectrometer for the near- to far-infrared at 50-MHz resolution; and a stable line-tunable, 12-w cw CO_2 laser. We also have a beam expansion source with a 12-cm slit, which provides a 3-m effective path for gases at ~10 K, giving a Doppler width of typically 10 MHz; and long-path static gas cells (to 100 m). In applying this equipment to signatures work, we emphasize the importance of high spectral resolution for detecting and identifying atmospheric interferences; for identifying the optimum analytical frequencies; for deriving, by spectroscopic analysis, the molecular parameters needed for modeling; and for obtaining data on species and/or bands that are not in existing databases. As an example of such spectroscopy, we have assigned and analyzed the C–Cl stretching region of CCl_4 at 770–800 cm^{-1}. This is an important potential signature species whose IR absorption has remained puzzling because of the natural isotopic mix, extensive hot-band structure, and a Fermi resonance involving a nearby combination band. Instrument development projects include the IR sniffer, a small high-sensitivity, high-discrimination (Doppler-limited) device for fence-line or downwind monitoring that is effective even in regions of atmospheric absorption; preliminary work has achieved sensitivities at the low-ppb level. Other work covers trace species detection with TDLs, and FM-modulated CO_2 laser LIDAR. We are planning a field experiment to interrogate the Hanford tank farm for signature species from Rattlesnake Mountain, a standoff of ca. 15 km, to be accompanied by simultaneous ground-truthing at the tanks.

INTRODUCTION

The contributions of Battelle Pacific Northwest Laboratory (PNL) to the CALIOPE program involve separate projects in frequency-modulation techniques, infrared spectroscopy for signatures detection, and instrumentation for remote sensing. This paper will discuss our spectroscopic capabilities and signatures work, and certain aspects of instrument development; the other topics will be addressed by J. F. Kelly in a separate paper at this meeting.

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INFRARED SPECTROSCOPY LABORATORY

Over the past few years, PNL has developed a state-of-the-art high-resolution infrared spectroscopy laboratory covering the near- to far-infrared region. Instrumentation includes:

- A Bruker IFS 120HR Fourier-transform infrared (FTIR) spectrometer, configured to operate from 10,000 to 10 cm^{-1} (1–1000 μm) with a resolution of better than 0.0017 cm^{-1} (50 MHz).
- Two tunable diode laser (TDL) systems covering 3000 to 300 cm^{-1} (3.3–33 μm) with bandwidths of better than 0.0003 cm^{-1} (10 MHz).
- An ultrastable line-tunable 12-w CW CO_2 laser.

Appropriate gas sampling equipment is also available. In addition to the usual types of gas cells, we have a 100-m fixed-path cell for the TDL sources, and a 40-m adjustable-path cell for use with the FTIR. These are filled on an ultraclean precision gas manifold with pressures monitored by Baratron gauges that are traceable to NIST.

Of particular interest is a beam expansion source in which seeded species attain temperatures of ~10 K without condensation. The expansion slit has a length of 12 cm, which affords (with multiple reflections) a 3-m effective path through the expanding gas. With this arrangement, linewidths of ~10 MHz (0.0003 cm^{-1}) are routinely obtained. This source has been used for the past two years to record TDL spectra[1,2]; the necessary pumps and sample chamber are now being obtained to couple a second such source to the FTIR instrument.

Full data reduction, analysis, and fitting capabilities are available, as is spectral simulation using HITRAN or other databases.

WHY HIGH RESOLUTION?

Is a *high*-resolution facility of the type described above necessary, or even useful, to the CALIOPE project? CALIOPE requires spectroscopic information on species that will be observed, for the most part, at atmospheric pressure, and thus will have linewidths of 0.01 to 1 cm^{-1}, assuming pressure-broadening coefficients typical of most molecules. Clearly resolution of this order or better is required to study such transitions. But how much better? We will present arguments that significantly higher resolution is important.

<u>1. Spectroscopic Parameters.</u> Many of the molecules and infrared absorption features of potential interest to CALIOPE are not in existing databases such as HITRAN. The spectroscopic and molecular parameters needed to properly model such bands can only be obtained usefully from fully-resolved and accurately-calibrated spectra: in fact, it is just such data that comprise the HITRAN compilation in the first place.

<u>2. Intensities.</u> The intensity of a given transition, important in any analytical scheme, is a parameter whose determination is known to be fraught with numerous potential pitfalls. It is generally accepted that reliable quantitative intensity work can only be accomplished using

spectral resolution much narrower than the width of the feature under consideration. The only exception might be when *band* intensities are measured by an extrapolation technique such as Wilson-Wells; but such results would be of use to CALIOPE only if they could be reduced to individual transition strengths, and this again requires full knowledge of the spectroscopic constants, and hence a high-resolution band analysis.

3. Identification of Interferences. No database contains *all* bands of *all* species that might affect a remote measurement at a specific frequency; none ever will. Such data must be obtained as needed, and at high resolution. Figure 1 shows an absorption feature of N_2O at 4.5 μm that we had been using to detect and analyze this species. After we observed nonlinear Beers-law plots, we looked at this line more closely and discovered an unsuspected transition 0.029 cm^{-1} to the red, probably due to water vapor. This absorption is very weak but sufficient to cause the anomalous results noted in long-path, atmospheric-pressure analyses. It is undocumented in HITRAN, and obviously can be detected only at high resolution.

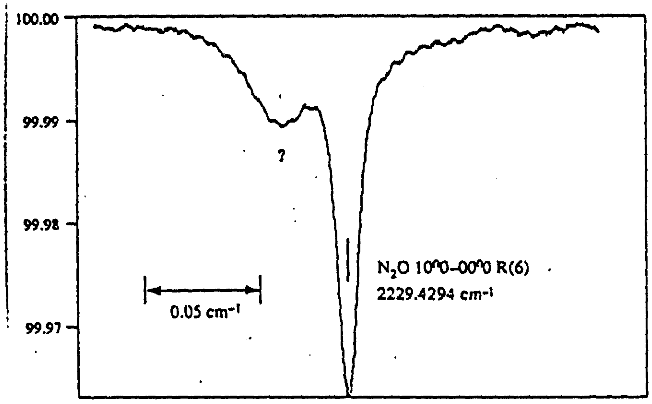

Figure 1. A potential analytical line of N_2O with an adjoining absorption, probably from water, that makes it useless for quantitative work.

4. Selection of Analytical Frequencies. For the relatively heavy molecules of interest to CALIOPE, the best analytical frequency might correspond to a Q branch or other dense grouping of individual transitions that provide high sensitivity. In such features the absorbance can change sharply over very narrow frequency regions (~0.01 cm^{-1}), offering ideal conditions for on-off–resonance or derivative techniques. Such regions can of course be identified only at very high resolution.

5. Low-Pressure Applications. It is quite possible that remote sensing applications may require knowledge of band structures at pressures well below atmospheric. Possible examples are for downwind sensing in the upper atmosphere, and for applications involving the sniffer technology described below. At lower pressures the linewidths will be reduced proportionally, requiring better resolution.

SIGNATURES WORK

Carbon Tetrachloride

A molecule of considerable potential interest in monitoring industrial activity is carbon tetrachloride. CCl_4 has a strong infrared-active stretching fundamental, ν_3, in the 12.5–13 μm region. This band, a logical one for remote sensing and monitoring of this species in the atmosphere, has never been resolved and analyzed properly because of hot-band structure, overlapping due to the natural chlorine isotopic mix, and a Fermi resonance with the combination band $\nu_1 + \nu_4$. To give an idea of the complexity of this region, in the natural isotopic mix of CCl_4 at 300 K, the most abundant species and vibrational states $(\nu_1\nu_2\nu_3\nu_4)$ are

$C^{35}Cl_3{}^{37}Cl$	0000	6.9%	$C^{35}Cl_4$	0100	3.8%
$C^{35}Cl_4$	0000	5.4	$C^{35}Cl_4$	0001	3.6
$C^{35}Cl_3{}^{37}Cl$	0100	4.9	$C^{35}Cl_2{}^{37}Cl_2$	0000	3.3
$C^{35}Cl_3{}^{37}Cl$	0001	4.6	$C^{35}Cl_3{}^{37}Cl$	0101	3.2

Many dozens of others will make significant contributions to the absorption at ambient temperatures. Furthermore, each of the three abundant isotopic species has a basically different type of band, since each belongs to a different rotational class: $C^{35}Cl_4$ is a spherical top, $C^{35}Cl_3{}^{37}Cl$ a symmetric top, and $C^{35}Cl_2{}^{37}Cl_2$ an asymmetric top. Such a region can be disentangled only with the high-resolution and molecular-cooling techniques discussed above.

Songlin Xu of PNL has recorded spectra of 1% CCl_4 in argon, expanded through the 12-cm slit, with a tunable diode laser and an effective path of ~3 m through the expansion. At the resulting effective temperature of ~10 K, we observe fully-resolved rovibrational structure of the fundamentals originating in the ground vibrational state, 0000, for both ν_3 and $\nu_1 + \nu_4$. Most of these bands have been analyzed, and the spectroscopic and molecular constants obtained.[3]

The analysis of the highest-frequency band in the group, assigned to $C^{35}Cl_4$, is illustrative. For a spherical-top molecule, the line frequencies in the P and R branches are given by

$$\nu(J,p) = m + nM + pM^2 + qM^3 + \ldots + (g - hM + \ldots)F_4(p) + \ldots,$$

where J and p are the total angular momentum quantum number and the sublevel designation; $M = -J,(J+1)$ for P,R-branch transitions; and $F_4(p)$ is a symmetry-adapted fourth-rank tensor operator that describes the angular momentum coupling in the molecule. From a preliminary fit of 71 P- and R-branch lines covering P(20) to R(23), we obtain the following constants, with an overall standard deviation of fit of 0.00034 cm^{-1}:

Parameter	Fitted value, cm^{-1}	Approximate significance
m	798.67766 ± 0.00007	band origin (ν_0)
n	0.043782 ± 0.000007	$B' + B'' - 2(B\zeta)$
p	$(2.47 \pm 0.03) \times 10^{-5}$	$B' - B''$
q	$(7.77 \pm 0.20) \times 10^{-7}$	$-2(D' + D'')$
g	$(7.93 \pm 0.07) \times 10^{-6}$	tensor splitting
h	$(-1.64 \pm 0.12) \times 10^{-8}$	constants

This is a typical spherical-top band, exhibiting PQR rovibrational structure, with the higher-J transitions in all three branches split by angular-momentum coupling effects (tensor terms in the

Hamiltonian). The central portion is illustrated in Fig. 2, showing the Q branch and lower P- and R-branch lines. At room temperature, where the most-populated rotational state is J ≈ 60, this band will consist of many thousands of individual (J,p) transitions. When one considers the many hot bands that become important at higher temperatures, the isotopic mix, and the accompanying Fermi-resonant combination band, we conclude that the "ν_3" region of CCl_4 may comprise the order of 10^6 lines.

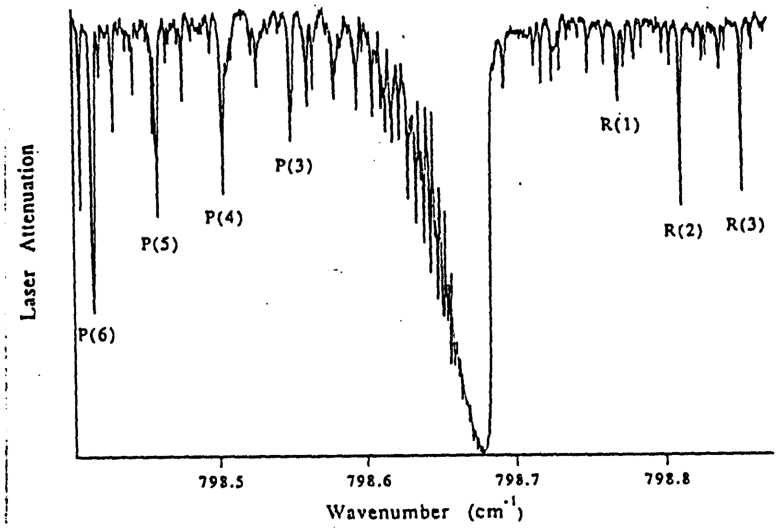

Figure 2. The Q-branch region of the 12.5-μm CCl_4 band, as recorded in a jet expansion with a TDL.

Clearly, adding this information to an atmospheric database is impractical. But it is also unnecessary: this molecule can be covered adequately for the purposes of CALIOPE by combining the spectroscopic analyses of the ground-state transitions, which allow many thousands of transitions to be calculated to experimental accuracy using only a few constants, with judicious semi-empirical modeling of the hot-band structure. We emphasize that the ground-state transitions will be the most intense even at ambient temperatures, and spectroscopy such as that of Fig. 2 therefore provides immediately useful analytical information. Spherical-top bands can exhibit several types of Q branches, including some in which the lines diverge rapidly from the band origin and disperse the total branch absorption over a broad region.[4] But this is a compact Q branch with all transitions on one side (the red) of the band origin, and with the tensor splittings tightly clustered, resulting in a sharp branch edge at 798.68 cm^{-1}. This edge persists even at normal temperatures and pressures, and provides the type of analytical frequency mentioned earlier, in which there is a steep absorption change in a very narrow region. For analytical purposes, this is the ideal situation. There are, in fact, several such regions near 12.5–13 μm that are promising for the sensitive analysis of CCl_4.

Other Signature Species

We are investigating the status of the spectroscopic database for other chemicals that might be signatures for certain industrial processes. Examples are the chlorinated hydrocarbons such as CH_2Cl_2 (methylene chloride), CHF_2Cl (Freon 22), and CF_2Cl_2 (Freon 12). For some of these (*e.g.*, CHF_2Cl) the bands of potential analytical interest have been pretty thoroughly analyzed,[5] though it is not clear that in all cases are the spectroscopic constants accurately enough known for satisfactory modeling over a broad temperature range—this tends to be especially true in dense Q-branch regions. In such cases the literature values of the spectroscopic constants can be used, with perhaps minor adjustments based on limited additional high-resolution spectroscopy. For other species (*e.g.*, CF_2Cl_2) new data at high resolution and low temperature are clearly needed, and we have begun to acquire such data.

INSTRUMENTATION DEVELOPMENT

We have evaluated various approaches to the problem of remote sensing.[6] PNL's work on frequency-modulated IR DIAL will be covered by J. F. Kelly in another paper at this meeting. Here we will discuss the Sniffer, a unique point-detection device, and consider the possible usefulness of Rattlesnake Mountain as a test range for the interrogation of the Hanford Reservation for signature species.

Herriot-Cell Sniffer

The Herriot-cell Sniffer developed at PNL can be used for quantitative detection of atmospheric effluents such as those associated with chemical and nuclear-weapons production. Although the Sniffer is highly specific to a particular effluent, it can be configured for detection of almost *any* infrared-active molecular species (*i.e.*, any molecule, except homonuclear diatomics such as N_2, O_2, Cl_2). Extremely high sensitivity (*i.e.*, sub-ppb) and excellent speciation are obtained by combining a highly-monochromatic laser source with a long optical path length, low-pressure, Doppler-limited sampling system. Reduced-pressure sampling and high resolution also enable operation with analytes whose transitions fall well within regions of strong atmospheric absorption by H_2O and CO_2, where more conventional remote-sensing techniques are useless.

The device consists of a mid-infrared tunable diode laser that is actively locked to a specific rotational-vibrational transition of the target effluent. Sample is continuously admitted to the Sniffer absorption cell, which is maintained at a pressure of 30 Torr or less to remove pressure-broadening effects on the transition linewidth. While one might expect lowered sensitivity as the pressure, and hence the number density of the absorbers, is reduced, this is in fact compensated by the fact that the peak absorption cross section for any radiative process varies inversely with the resolved linewidth of the transition. As a result, at the high resolution provided by TDLs, the peak absorption of any line remains constant as pressure is lowered, until the natural linewidth is reached. This is demonstrated by the experimental data of Fig. 3. Ultimate spectral resolution is limited by Doppler broadening, and will depend upon the temperature and molecular weight of the effluent molecule, but will typically be on the order of 150 MHz (0.005 cm^{-1}).

The Sniffer cell is based on a Herriot multipass design and contains a pair of spherical mirrors

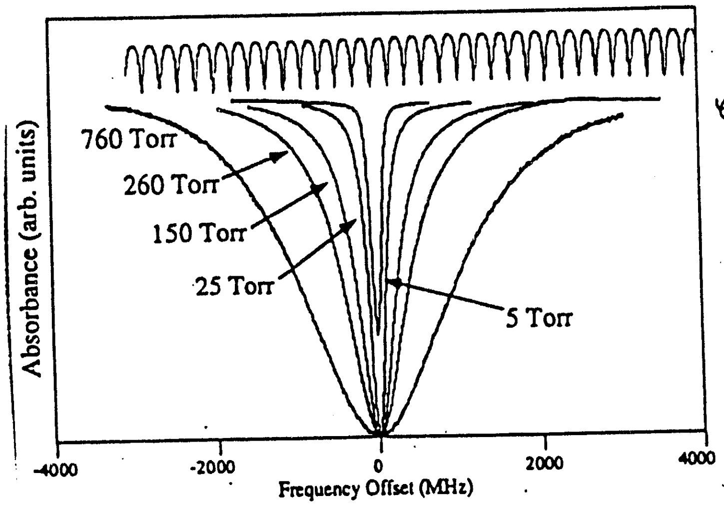

Figure 3. Absorption of the 1–0 R(6) line of CO at 2169 cm^{-1}, demonstrating that with a narrow-line source (a TDL) the peak absorption cross section is independent of pressure in the high-pressure limit.

separated by 55 cm, which create a 100-m folded optical path. ~~for increased optical path.~~ The detection system consists of two detectors and two lock-in amplifiers. The first detector/lock-in is configured for first-derivative detection of the reference gas, and the second for second-derivative detection of the Sniffer cell absorption. The instrument produces a DC voltage that is directly proportional to the absolute concentration of the effluent being monitored. Preliminary experiments using a 1-m absorption cell have detected CO and N_2O at 5 ppb. Using the multipass configuration with other improvements will easily improve the detectivity to the ppt level. Such a device can easily be transported and operated from the trunk of a car or on an aircraft. Alternatively, the Sniffer can be placed several miles downwind of a suspected effluent source and operated as a long-term monitoring unit. Depending upon the chemical identity of the target effluents, the sniffer can be configured to detect multiple effluents simultaneously.

The infrared spectroscopic detection scheme that the instrument is based on is ideally suited for detection of airborne effluents such as volatile organics (VOCs) and rare isotopes due to fissile by-products. These species might include solvents used in the separation or synthesis of nuclear materials (*e.g.*, CCl_4, toluene, trichloroethylene), or rare isotopes due to fissile by-products such as $H^{129}I$ and $N_2{}^{17}O$.

A Realistic Test Range: Rattlesnake Mountain Observatory

The Hanford Reservation presents a unique opportunity for testing remote-sensing instrumentation, since it is an actual (former) production facility that still has large inventories of processing chemicals, some of which have leaked or are leaking into the environment. Along the southern edge of the reservation is Rattlesnake Mountain, a ridge running northwest-southeast with a commanding view of the reservation. There is an observatory at the summit (3524′) with adequate utilities. From the observatory one has an unobstructed view over the waste tank farms at the 200 Area (200 West and 200 East), located ~~3200~~′ 2900 below the observatory at slant distances of ca. 15 km.

We plan to install a 12-w stabilized line-tunable CW CO_2 laser at the observatory and probe the atmosphere over the waste tanks, initially with a detector at the tank farm, later to be substituted with a retroreflector, in both cases with simultaneous ground-truthing using the Sniffer or other analytical instrumentation. Such an experiment will provide valuable basic data on the usefulness of infrared FM DIAL under realistic conditions.

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