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An infrared spectral database for detection of gases emitted by biomass burning

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ABSTRACT

We report the construction of a database of infrared spectra aimed at detecting the gases emitted by biomass burning. The project uses many of the methods of the Pacific Northwest National Laboratory (PNNL) infrared database, but the selection of the species and special experimental considerations are optimized. Each spectrum is a weighted average derived from 10 or more individual measurements. Each composite has a spectral range from ≤600 to ≥6500 cm^{-1} with an instrumental apodized resolution of 0.11 cm^{-1}. The resolution was chosen to bring out all spectral features, but recognizing that pressure broadening at 760 Torr results in essentially all ro-vibrational lines having these or greater linewidths.

1. Introduction

The Pacific Northwest National Laboratory (PNNL) has constructed a database of broadband infrared reference spectra as sponsored by the U.S. Department of Energy (DOE) [1,2]. The data are for broadband sensors, either passive or active, that detect gas emissions associated with many types of energy production (coal, gas, nuclear) along with numerous environmental pollutants and toxic industrial chemicals (TICs). Three important characteristics of the data are: (1) the spectra are quantitative corresponding to 1 ppm-m at 1 atmosphere and 296 K; (2) their large frequency range (minimum span of 600–6500 cm^{-1}); and (3) the spectral resolution is high, 0.11 cm^{-1}, effectively the narrowest linewidths that would be encountered when monitoring near the surface of the earth due to the ~760 Torr pressure broadening. Since any measurement is likely to involve a multitude of both biogenic (NH_3, CO_2, H_2O, CH_4) and anthropogenic (CO, SO_x, NO_y, freons, mineral acids, etc.) interferents, the list of molecules contained in that database has grown large (>500 compounds). The database has applications beyond passive and active broadband monitoring: For example, since the data are quantitative, the integrated band strengths can be used to quantify absolute line intensities in high resolution low-pressure gas studies. The spectra are also useful for instructional purposes, e.g. in courses teaching spectroscopy.

One category of molecules that was not specifically targeted in the PNNL database is gases emitted by vegetation fires. Biomass burning has been used for land management and many other purposes for most of human history, but over the last half century the impact has likely increased largely due to tropical deforestation fires [3]. Biomass burning has only been studied by atmospheric chemists since ~1979 [4] but interest has increased greatly since that time. Biomass burning includes several types of fires: Landscape fires consist of large acreages, but small (indoor) cooking fires are also a significant source due to their prevalence in developing countries [5]. Recent estimates [3] of the total amount of biomass burned globally are approximately 5–7 Pg C/year. In the United States and other countries prescribed fire is used as a land management tool (e.g. on military installations and timber production lands) to minimize the impact of wildfires, and promote desirable stand characteristics; many stands are burned on a 3- to 4-year rotation. Thus, quantitative information is needed to study the impact of the trace gas and particle emissions on human health and atmospheric chemistry.

Many techniques have proven useful for quantifying the gases emitted by biomass burning. Examples include whole air sampling in canisters followed by GC analysis for hydrocarbons and FT-IR and mass spectrometry for on-line measurements of the hydrocarbons, other volatile organic compounds (VOCs), and inorganic species [6]. These studies have shown that typically 60–80% of the non-methane organic compound (NMOC) emissions from biomass burning are in the form of the more reactive oxygenated VOCs (OVOCs) [3].

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Table 1
List of compounds planned to be measured as part of the biomass burning database.

1,2-Dimethylimidazole	p-Cymene	Limonene	Pinic acid
1-Butene	Diacetone alcohol	Limono-aldehyde	Pinoic acid
2-Methyltetrol	Dimethyl mercury	Malonic acid	Propionic acid
2-Pentanone	Eucalyptol	Menthol	α-Pinene (±)
3-Methoxyphenol	Farnesol	Methyl vinyl ether (MVE)	β-Pinene (±)
3-Methylfuran	Fluoranthene	Methyl-2-methylbutyrate	Pyrene
3-Nonanol	Glycolaldehyde	Methylhydroperoxide	Resin
4-Methoxyphenol	Glycolaldehyde	Myrcene	Retene
4-Pentene-1-ol	Guaiacol	Myrtenal	Succinic acid
5-Nonanol	Hepatenedioic acid	Nonanedioic acid	Syringaldehyde
Acetol	Hexadecanoic acid	Pentanedioic acid	Terpineol
Acrylamide	Hexanedioic acid	peroxyacetyl nitrate (PAN)	Tetramethylpyrazine
Camphor	Hopane	Peroxyacetyl acid	Vanillin
ε-Caprolactam	Levoglucosan	Phenol	Vinyl phenol

2. SERDP biomass burning infrared database

These considerations borne in mind, we have begun a program to advance the IR-based identification and quantification of gases in biomass plumes for the Strategic Environmental Research and Development Program (SERDP). The IR method can be used both to verify results from other methods (e.g. mass spectrometry) as well as to detect new species. The technique is versatile enough to be used on laboratory fires, on the ground, and from aircraft [7]. It has even been deployed from space on passive IR sensors such as ACE [8] or SCIAMACHY [9]. Many of the molecules found in biomass burning plumes already have spectra in the PNNL [2], HITRAN [10] or GEISA [11] databases. For example, many common biomass burning gases such as CO, CO_2, H_2O, NO and NO_2 are in most IR databases due to their ubiquitous occurrence in the atmosphere. Other species are already in the PNNL database due to their role as pollutants (e.g. SO_2, H_2SO_4, and HNO_3) or as biogenic emissions that could interfere in the analysis of pollutants (e.g. isoprene, methacrolein, and formaldehyde). We estimate that there already exist reference spectra for 40–50 biomass burning emissions that can be quantified by IR spectroscopy. It is anticipated, however, that there are at least an equal number (particularly OVOCs) that might be observed if reference spectra were available. Step 1 of our program is to identify what compounds need to be added to the database, the main criterion being that they are known or suspected biomass burning emissions or smoke plume photochemistry products. Ultimately, by IR or other methods, it is necessary to derive as many emission factors (EF, that is grams emitted compound per kilogram biomass burned) for different types of fuels, conditions, etc. as possible. This should enhance *a priori* predictions of the fire impacts. The reference spectra are a means towards that end.

The identification of candidates for the database initially relied on a literature search. In more detail, the four selection criteria were: (1) The species has been seen in a biomass burning plume by non-IR methods or is expected to occur based on known chemistry; (2) The species is expected to have reasonably strong IR absorption in the 1300–700 cm^{-1} fingerprint region (e.g. species such as elemental Hg or CBr_4 would be ruled out); (3) The species has a vapor pressure >∼0.01 Torr or a boiling point of <250–300 °C, so that it is both amenable to laboratory measurement and would not immediately condense in a biomass burning plume; (4) The species can be reactive in the atmosphere, but it must be sufficiently stable in an N_2 bath gas in the lab (many minutes to hours) so that the measurement can be completed. Subject to revision, the initial proposed list of species is shown in Tables 1 and 3. Table 1 contains those species that are planned to be measured and Table 3 lists the species already completed with some experimental details. The tables do not include the biomass burning gases that are already included in the PNNL reference database such as alkanes, alkenes, aromatics etc. The contents of that database can be found at http://nwir.pnl.gov.

3. Experimental

3.1. Acquisition parameters and objectives

The methodologies used to collect the data for these libraries have been previously described [1,2,12–14]. Many of the salient features of the IR database are summarized in Table 2. The most important aspects are that the data are in fact quantitative, with each resultant spectrum derived from 10 or more individual quantitative measurements, the resolution is quite high, and that the data are carefully calibrated on both the wavelength and absorbance axes.

3.2. Instrumental characteristics

The spectrometers used are two Bruker IFS 66v/S vacuum benches that eliminate spectral interference from H_2O and CO_2 lines, as well as providing more intensity stability. We have documented all relevant parameters associated with both data acquisition and data processing in earlier papers; the reader is directed to these references for greater detail [1,2,13]. Briefly, however, each system uses a glow bar source, a germanium-on-KBr beamsplitter, a mid-band photoconductive mercury cadmium telluride (MCT) detector, and a second aperture system (*vide infra*). For species of moderate to high volatility, a fixed 19.96 cm cell is used in the standard sample compartment and the vapor-phase mixtures are generated by passive vaporization followed by filling with N_2 ballast gas. For low volatility liquids whereby only small gas-phase mixing ratios can be achieved, a long-path White cell (set to 8.05 m) is used to increase the path length and an active disseminator is used to quantitatively and actively generate the gas mixtures [15]. The disseminator dispenses the liquid at a fixed volume rate from a syringe pump onto a heated surface where it is flash vaporized on a stainless steel surface, and eluted with N_2 gas from a calibrated mass flow controller.

We note that the PNNL spectrometers have been modified to redress two artifacts that give rise to photometric errors; both phe-

Table 2
Experimental and acquisition parameters associated with the PNNL SERDP database of infrared reference spectra.

Parameter	Value
Resolution (≡0.9/optical path)	0.112 cm^{-1}
Digital point spacing	0.060 cm^{-1}
Wavelength range	≤600 to ≥6500 cm^{-1}
Wavelength accuracy	≤0.003 cm^{-1}
Nr. spectra in composite	≥10 individual pressure burdens
Normalized amount of absorber in spectrum	1.0 ppm-m (at 1.0 atm, 296 K)
Intensity accuracy	3.0% (well behaved species—static) 7.0% (well behaved species—flow) n/a (best effort basis)

nomena arise at the aperture [1]. One of these is the "warm aperture" problem [1,16], whereby at high resolution the cooled (MCT) detector sees not only source radiation through the aperture hole, but also the aperture annulus, which is near or above room temperature. The metal annulus therefore effectively serves as a warm blackbody source. These blackbody rays do not satisfy the resolution condition since they enter the interferometer as off-axis rays; the effect in spectral space is a distorted absorption line shape that shows a "tailing" to red frequencies. The second artifact [1] is caused by light that has already been modulated by the interferometer returning towards the source and being reflected by the reflective polished metal surface on the back of the aperture (wheel) to re-enter the interferometer and be modulated again. This "double modulation" produces an optical 2*f* alias that can add spurious signals and distort intensities at all wavelengths. The PNNL spectrometers have both been modified to remove these two effects by adding a second focal plane with aperture after the interferometer that mimics the optical speed of the original system. The light seen by the detector from the back of the second aperture is not modulated, and as a DC signal is filtered away by the Fourier transform.

To minimize well-known MCT nonlinearity problems we have used a software correction [17] from the spectrometer manufacturer that functions independently of the electronic bandwidth to compensate for the MCT's nonlinear conversion of photons to signal, especially near the interferogram centerburst. Moreover, our data averaging scheme uses a weighting mechanism that corrects for nonlinearity deviations from the Beer–Lambert law. The absorbance is scaled to a calibrated value (1.0 ppm-m at 296 K, 1 atm) by using careful methods for measuring the optical path length, as well as periodic intensity calibrations using known absorbers, commonly isopropyl alcohol (2-propanol). The wavelength axis is routinely calibrated [2] using 165 individual rotational–vibrational lines of CO and N_2O gases at low pressure to achieve a wavenumber accuracy of better than 0.003 cm^{-1}.

4. Results

Table 3 summarizes the current status of the biomass burning infrared database in terms of those species completed, whereas Table 1 lists those species still to be measured. Also tallied in Table 3 are related physical data and parameters associated with the IR measurements. This includes whether the species was measured using the static system with passive evaporation or the flow system with the active disseminator. All measured IR spectra are digitally available at http://nwir.pnl.gov including the metadata associated with each file. Also listed in Table 3 are integrated band intensities and wavenumber positions for the strongest band observed in each spectrum. The data are recorded on either of two systems, with the lower volatility samples being reserved for the flow disseminator—White cell system.

While this paper cannot discuss all results, Fig. 1 presents a typical result of the IR spectra for species associated with burning effluents, namely the quantitative broadband IR spectrum of 3-methyl-1-butanal (commonly called isovaleraldehyde). Isovaleraldehyde is a flavoring agent and occurs naturally in oils (lavender, peppermint) and coffee extract. It is also suspected to be in biomass burning plumes as it has been observed as a (photo-)oxidation product of isoprene and other terpenes via methacrolein [18,19]. The spectrum is seen to contain multiple bands in the longwave infrared (LWIR), as well as the C–H stretching region (midwave IR) that can all be used for identification.

As is typical of ketones and aldehydes [20], the most intense band in the spectrum arises from the carbonyl stretching frequency in the 1700–1750 cm^{-1} domain, in this case 1746.07 cm^{-1} for isovaleraldehyde. For atmospheric remote sensing applications, however, such bands are sometimes of limited utility due to interference from the ro-vibrational lines of the water ν_2 bending mode. However, the spectrum is seen to contain multiple relatively strong bands in the longwave infrared, as well as the C–H stretching region (midwave IR) that can all be used for identification. As is typical for hydrocarbons and moderately substituted hydrocarbons, the C–H stretching region provides many strong bands in the 2800–3100 cm^{-1} domain. While such broad C–H bands can provide good sensitivity and can thus be useful for gas-phase monitoring, in the absence of any rotational structure they provide little specificity: Essentially every hydrocarbon, including most substituted species, has the typical broad C–H stretching features at these wavelengths, though for isovaleraldehyde the peak at 2967.37 cm^{-1} is sharp (pseudo-Q-branch width ~2.9 cm^{-1}) providing some specificity. Of greater utility, however, is the sharp doublet at 2712.69 and 2704.26 cm^{-1}. This is a somewhat unusual region for such a strong absorption; it corresponds to one of the two fundamental C–H stretching modes involving the aldehyde carbon, and this mode is in Fermi resonance with the first overtone of the C–H bending vibration [20,21]. The other aldehyde C–H stretching mode occurs at a characteristic value [20] of 2818.16 cm^{-1}. The 2712 and

Table 3
List of compounds presently measured as part of the biomass burning database along with relevant physical and measurement parameters.

Common name	CAS#	MW(g/mol)	VP-25(Torr)	BP-C (°C)	Flow vs. static	Msmt's at 25 °C (or 50 °C)	Strongest band pos'n (cm^{-1})	Strongest band int'y (∫ Limits)	Strongest band int'y (cm^{-2} atm^{-1})
1-Penten-3-ol	616-25-1	86.1	13.00	115	Static	10	2971.89	2800–3050	659.9
2-Amyl furan	3777-69-3	138.2	1.2 @ 50 °C	153	Flow	12	2940.32	2808–3024	1214.0
2-Carene	4497-92-1	136.2	10 @ 50 °C	167	Flow	11	2927.48	2798–3075	1883.3
2-Nonanone	821-55-6	142.2	2.0 @ 50 °C	195	Flow	13	2934.94	2798–3048	1735.9
2-Vinylpyridine	100-69-6	105.1	12 @ 50 °C	159	Flow	11	741.20	712–770	94.3
3-Carene	498-15-7	136.2	10 @ 50 °C	171	Flow	12	2876.33	2798–3051	1869.2
Amyl-alcohol	584-02-1	88.2	8.80	116	Static	10	2971.71	2798–3023	1190.7
Diacetyl, biacetyl	431-03-8	86.1	72 @ 30 °C	88	Static	10	1729.28	1668–1790	762.3
Ethyl benzoate	93-89-0	150.2	0.30	213	Flow	12 @ 50 °C	1277.48	1224–1329	1814.0
Furfural	98-01-1	96.08	1.3	162	Flow	15	756.08	708–790	549.2
Geraniol	106-24-1	154.2	0.05	229	Flow	10 @ 50 °C	2931.27	2798–3100	1616.8
Glyoxal	107-22-2	58.0	220.00	50	Static	12	1731.15	1678–1780	579.9
Hydrogen peroxide	7722-84-1	34.0	1.40	102	Flow	9	1250.74	1135–1393	432.9
Isobutyric acid	79-31-2	88.1	2.00	154	Flow	9 @ 67 °C	1778.48	1698–1839	1075.6
Isocaproic acid	646-07-1	116.1	0.06	200	Flow	11 @ 50 °C	1781.62	1697–1850	1039.8
Isovaleraldehyde	590-86-3	86.1	50.00	92	Static	10	1746.10	1688–1800	516.1
Methyl glyoxal	78-98-8	72.1	>40	72	Static	10	1733.29	1668–1799	689.9
α-Methylfuran	534-22-5	82.1	139.00	62	Static	10	726.91	688–760	237.2
Valeraldehyde	110-62-3	86.1	26 @ 20 °C	103	Static	10	1746.10	1673–1824	526.8
Valeric acid	109-52-4	102.1	0.25	184	Flow	11 @ 67 °C	1780.74	1698–1839	1054.9

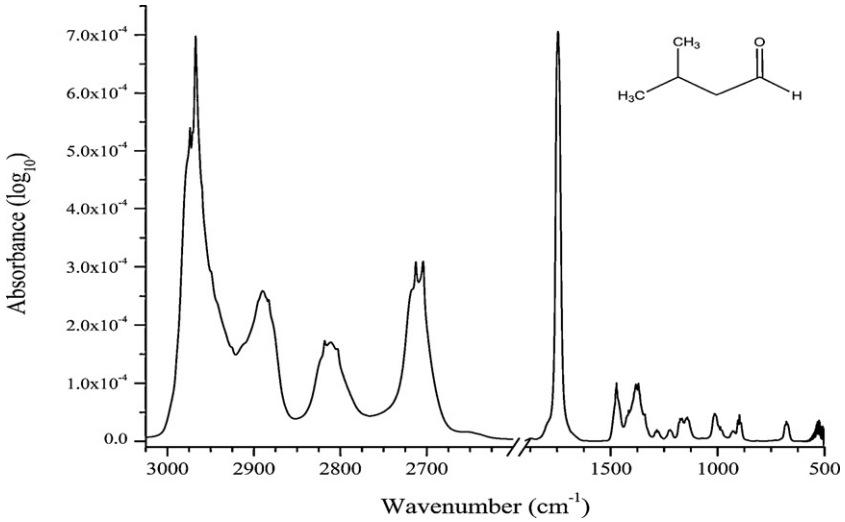

Fig. 1. Composite 298 K infrared spectrum of isovaleraldehyde (3-methyl-1-butanal) from 10 individual measurements. The *y*-axis is quantitative and corresponds to an optical depth of 1 ppm-m. The complete spectrum spans to 6500 cm^{-1}.

2704 peaks occur at frequencies low enough to avoid interference from the water ν_1 and ν_3 O–H stretching modes, but at frequencies greater than the R-branch lines of the CO_2 ν_3 asymmetric stretch in the 2400 cm^{-1} region. The so-called midwave infrared window (3–5 μm) is not frequently used with passive monitoring due to the lack of blackbody radiation from the earth's surface, but this spectroscopic window is especially useful for extractive *in situ* [22] methods as well as active and semi-active [23] remote sensing.

As an example of a different class of compounds, Fig. 2 presents a typical result for the broadband IR spectrum of 2-vinylpyridine (also known as α-vinylpyridine). In terms of sources, 2-vinylpyridine is known primarily as an industrial compound, mostly used in tire manufacturing as a tire cord and belt additive. It is also a known component of tobacco smoke [24] and is thus suspected to be emitted in biomass burning. Its reactions with the common atmospheric oxidants either O_3 or OH radical are known to produce 2-pyridinecarboxaldehyde and formaldehyde [25]. The IR spectrum is seen to contain multiple strong bands in the longwave infrared between 700 and 1300 cm^{-1}, and many of these bands (or all in combination) are well suited for atmospheric monitoring.

The 2-vinylpyridine spectrum is seen to contain multiple longwave IR bands, as well as in the midwave infrared C–H stretching region, all of which can all be used for identification. One feature of the 2-vinylpyridine spectrum of note, however, is common to dozens of species in the PNNL gas-phase database, especially for the aromatic molecules, namely that the compound has (multiple) very sharp Q-branches, often associated with ring or conjugated bond modes. These are seen in the inset of Fig. 2. While 2-vinylpyridine is of no or low symmetry (C_s point group due to the mirror symmetry in the plane of the molecule, assuming no free torsion motion about the ring-vinyl C–C bond), the spectrum still exhibits several very sharp, well-resolved Q-branches. For example, the peaks at 938.93 and 741.20 cm^{-1} exhibit Q-branch linewidths of only 0.50 and 0.60 cm^{-1} FWHM, respectively. Such peaks are clearly useful for broadband (FT) infrared monitoring. Equally important, such sharp Q-branches are especially amenable to infrared laser monitoring. External cavity quantum cascade lasers (QCLs) can now frequency tune as much as 200 cm^{-1}. Even without external cavity tuning, modern QCLs can readily tune 5 cm^{-1} by varying the temperature or current [26]. This implies that modern IR laser systems together with the observed sharp features can provide ultrasensitive (ppt-level) detection of such species even in open-path systems with the species pressure-broadened to atmospheric pressure. Due to the intrinsically sharp absorption lines, the resulting specificity is

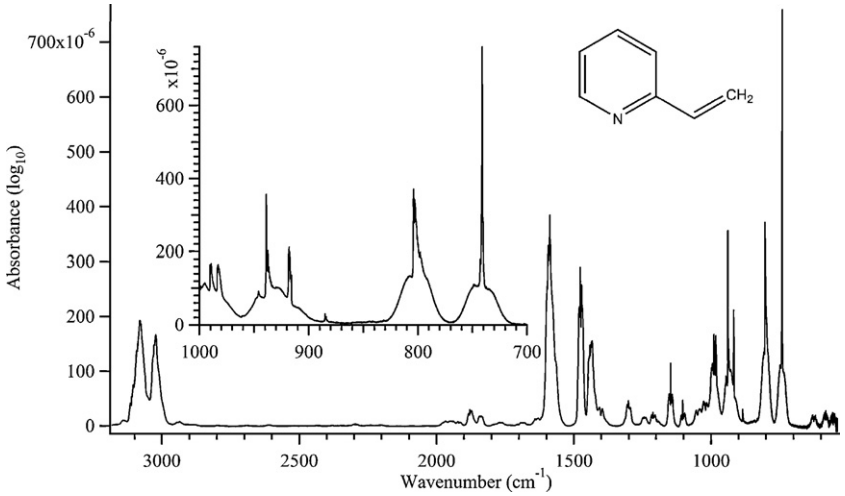

Fig. 2. Composite 298 K IR spectrum of 2-vinylpyridine from 10 individual measurements. The *y*-axis is quantitative and corresponds to an optical depth of 1 ppm-m. The complete spetrum spans to 6500 cm^{-1}.

very high, and due to the inherent brightness of the lasers systems (*vis-à-vis* thermal sources) the sensitivity can be orders of magnitude higher, though only over a limited spectral range. Because such systems can be constructed as open-path systems, greater path lengths can be achieved without extractive degradation of the compounds.

5. Discussion

As discussed above, existing gas-phase IR databases of necessity include a host of mostly small molecules that must be accounted for in any ambient atmospheric sensing scenario including common gases (O_3, CO_2, H_2O, etc.), anthropogenic pollutants (CO, SO_x, NO_y, H_2SO_4, etc.) [27], and species that are primarily biogenic in origin (NH_3, CH_4, C_2H_4, isoprene, methacrolein, formaldehyde, H_2O_2, CH_2I_2) [28,29]. The goal of the present program is to apply the advanced technology used in creating the DOE/PNNL database to produce a supplemental data set specifically for the gas-phase molecules emitted by biomass burning. The fires include many types: prescribed fire, wild fire, food cooking fires, and they could burn fuels from many types of ecosystems. The PNNL and other databases already contain many VOCs and other compounds of relevance (alkanes, alkenes, aromatics, amines, etc.). However, for biomass burning, certain classes of molecules are missing. We estimate that reference spectra are already available for about 40–50 species that occur in biomass burning plumes, but that there are perhaps 50–100 more species that could potentially be observed via IR methods were reference spectra available. Part of our program is thus to identify what new compounds are likely to be present in biomass burning plumes, which then suggests that they should be added to the IR database, specifically aimed at those species likely to be, or at least suspected to be, present and playing a role as burning effluents or transformation products, e.g. OVOCs. As IR spectrometers (both laser and broadband) continue to increase in sensitivity, it is anticipated that the number of IR-observable species should continue to grow.

Tables 1 and 3 show compounds that are known or expected to occur in biomass burning plumes and whose spectra should prove useful. One can recognize certain classes of compounds: A first set of compounds is singly- and doubly-nitrogen-substituted aromatic compounds. Relatively new techniques such as PILS (particle into liquid sampler) and NIPT-CIMS (negative ion proton transfer chemical ionization mass spectrometry) [30] have observed several such compounds that might be detected by IR methods. Specifically, Laskin et al. [31] have recently reported measurements of species such as 1,2-dimethylimidazole, tetramethylpyrazine, and ε-caprolactam. While larger species in this family have also been reported, only those mentioned above are likely to have sufficient vapor pressure to enable measurement of their IR spectra.

A second, more obvious, class of compounds includes additional terpenes, hemi-terpenes, retenes and other pyrolysis biomarker compounds: While isoprene is currently in the PNNL database, we plan to add species such as limonene, the carenes, pinenes, pyrene, and myrcene. Along with isoprene, such unsaturated compounds are well known to be emitted directly by plants, but also produced by the heating of vegetation [3,7]. Related compounds whose IR spectra should be included are oxidation products of these species, namely alcohols, aldehydes, ketones and ethers. The oxidation of terpenes and hemi-terpenes (such as isoprene) is a dominant process known to create a wide variety of carbonyl compounds, some of which continue on to react with OH radical or further oxidize in the atmosphere [32]. Isoprene has a median concentration of ~2 ppb in wooded areas of the southeastern US, and those levels rise as isoprene is released during biomass burning, thereby increasing the number of reactive carbonyl compounds subsequently created in the atmosphere. While methacrolein and MVK spectra are already available, specific examples of needed additions include: (iso-)pentanal, (iso-)butanal, glyoxal, methyl glyoxal, diacetyl, 1-penten-3-ol, 2-pentanone, and guaiacol. The relevance of such compounds, including their role as potential precursors in the formation of secondary organic aerosols (SOA) is discussed for example by Yokelson et al. [3].

We also plan to record the spectra of second and third order oxidation products. Inspection of Tables 1 and 3 shows that the planned species list also include several carboxylic acids and dicarboxylic acids. While such species are logically biomass burning products, there are relatively few measurements of these compounds using infrared methods. Part of the problem is limited volatility, and specifically that many of the larger species are solids. For this class of compounds, as well other OVOCs that exist as solids (e.g. phenol and 4-vinylphenol) it is difficult to quantitatively generate reference spectra. The vapor pressures are intrinsically low; the requisite long-path cells typically are of large volume and surface area and any "cold spots" can lead to condensation, rendering an inaccurate pressure reading. We are currently developing methods to reliably generated quantitative vapor-phase measurements of low concentrations of such compounds, and details of the method will be presented in a forthcoming paper.

6. Summary

Recent experimental evidence indicates that there are numerous compounds likely to be present in biomass burning plumes that might be quantified by IR-based methods if reference spectra were available. Several of these compounds exhibit very sharp spectral features making them amenable to both broadband FT-IR measurements as well as infrared laser-based techniques. We report construction of a new database of high resolution, high accuracy broadband infrared spectra of gas-phase compounds specifically associated with biomass burning.

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