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INFRARED EMISSION FROM INORGANIC COMBUSTION PRODUCTS IN A FLAME ENVIRONMENT

PREPARED BY

RESEARCH AND DEVELOPMENT DEPARTMENT

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INFRARED EMISSION FROM
INORGANIC COMBUSTION PRODUCTS
IN A FLAME ENVIRONMENT

By

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PURPOSE

The purpose of this article is to describe a research problem
and to discuss some of the scientific and technological problems
associated with the work. In the most general sense, I will describe
a problem which deals with the radiant energy output in the infrared
region from selected inorganic substances in a flame environment.

BACKGROUND

In a manner analogous to illuminating flames,[1] 25% of whose radiant
energy is released in the visible region, let us imagine that we are
interested in the infrared region from about 700 cm^{-1} to 1400 cm^{-1}
instead of the visible and that we want to create emitters in a flame
which radiate intensily in this region in preference to other regions.
In our problem, the radiation will not originate from electronic
transitions of inorganic flame species as it does in the illuminating
flame but instead will come from some other transition.

Energy associated with electronic transitions is observed in the
ultraviolet and visible regions, that from vibrational transitions is
in the infrared, and that from rotation (pure) of a molecule is found
in the microwave region.[2] It is clear that, if we wish to create a
flame whose radiation consists mainly of energy from vibrational
transitions, we need to suppress radiation from electronic and rotational
transitions and enhance those from vibrational transitions which fall
within the proper energy range. This is easier to say than do in a
flame environment. Because pure rotational transitions are of very low
energy, we neglect these as unimportant to our problem. By control of
the combustion rate and proper fuel-oxidant selection, we can minimize

electronic transitions by keeping the effective flame temperature low.
In this way, we provide energy sufficient to excite the vibrational
energy modes while electronic excitation is kept at a minimum. These
descriptions apply to our effort to create a flame with the desired
emission features. To approach this problem systematically, it is
beneficial to know the vibrational characteristics of a possible flame
species so that the potential of a molecule (as an emitter) may be
determined in advance. For those flame species for which the data are
not known, it is the goal of this work to acquire that information.

STATEMENT OF THE PROBLEM

Our problem is to identify and characterize the vibrational
features of selected flame combustion products which radiate intensily
in the 700 to 1400 cm^{-1} region and which preferably do not radiate
intensily in other regions. In this problem, we arbitrarily will limit
our consideration to inorganic flame species which might be found in
the flame.

APPROACH

From classical theory of the harmonic oscillator,[3] the vibrational
frequency of the oscillator is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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where k is the force constant between the vibrating masses and μ is
the reduced mass of the bonded atoms;

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

where m_A and m_B are the mass of atoms A and B respectively. Because
we are interested in a flame environment (or the non-incandescent but
vibrationally excited exhaust), we need to consider mainly molecular
species composed of only a few atoms. For simplicity, we ignore large
molecules since most will have decomposed in the flame. We, therefore,
will concentrate on diatomic and triatomic molecular species. Knowing
that k is in the order of 2×10^5 to 2×10^6 dynes/cm,[4] we can immediately
compute the range of reduced mass μ associated with vibrational frequencies
between 700 and 1400 cm^{-1}. At this point one might be tempted to make
this calculation to find the candidate species and conclude that the
problem is almost solved. Unfortunately, it is not this simple.

First, we are not dealing with a perfect harmonic oscillator.
Secondly, there most likely will also be radiation in this region which
is not due to vibrational transitions; such as continua due to flame
processes of decomposition, association, ionization and the like. Next,
if we consider triatomic and larger species, there is more than one
vibrational mode possible; unlike diatomic species which have one
fundamental vibrational mode. Also, there are the allowed vibrational
overtones, binary combination bands, difference bands, and possibly
even ternary combination bands which can account for radiation in the
desired region. Finally, we cannot ignore completely the possible

presence of organic molecules or radicals which are decomposition products of organo-metallic fuels used or which originate from other ingredients added for reasons which are not important to our problem.

A search of the literature and completion of the suggested computation for metal oxide, halide and other flame stable species will yield a large number of molecules which will vibrate in the desired energy range. A convenient summary is Drago's Fig. 7-15 reproduced on the next page.[5] Herzberg[6] gives a vibrational frequency summary for molecules with 3 to 12 atoms. Conley[7] summarizes vibrational data pertaining to organo-silicon, organo-sulfur, organo-phosphorus and other organo-metallic compounds. From these summaries it is clear that we can expect strong emissions in the desired range from the organo - Si, S, and P compounds. Many of the diatomic metal-oxygen and halogen vibrations such as MnO, BO, and BF also fall between 700 and 1400 cm^{-1}.

Up to this point we have tacitly assumed that if an absorption is listed in the literature, the molecule, by Kirchoff's law, would also emit at this frequency. We must note that a molecule can emit even though no IR absorption is listed. This results from the fact that the infrared absorption selection rules require a dipole change in the molecule during vibration. Thus, a molecule such as F_2 would not absorb in the infrared since there is no dipole change during vibration but, if excited thermally or by other means, can radiate energy at its fundamental vibrational frequency (892 cm^{-1}).
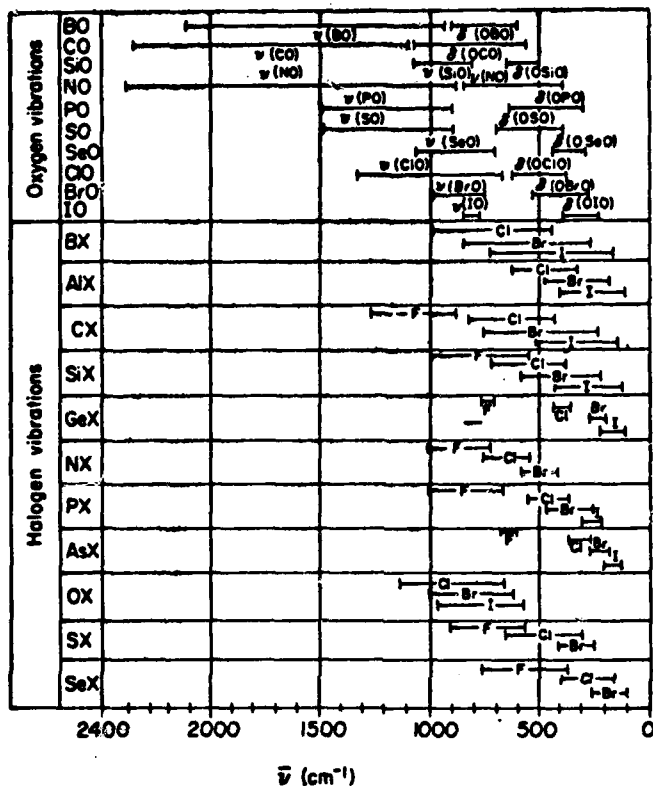
Fig. 7-15 from Drago, reference 5.

$\bar{\nu}$ (cm^{-1})

Fig. 7-15. Range of Infrared Group Frequencies for Some Inorganic Materials. The symbol ν_{M-X}, where M and X are general symbols for the atoms involved, corresponds to a stretching vibration. The symbols, ν_1, ν_2, etc., were previously defined. δ corresponds to an in-plane bending vibration (δ, the symmetric bend, δ_a the asymmetric bend), π to an out-of-plane bend. ρ to rocking and wagging vibrations.

Table 2-1

Vibrational frequencies (cm^{-1}) of alkali halides in the gas phase (1, 2)

	F	Cl	Br	I
Li	906	641	563	498
Na		366	302	258
K		281	213	(173)
Rb		228	(166)	(128)
Cs		209	(139)	(101)

( )=estimated value

Table 2-27B

Infrared absorption frequencies (cm^{-1}) of solid alkali halides ($\mathcal{S}$)

	Cl	Br	I
Na	174	139	123
K	149·5	121	105·5
Rb	124	91·5	79·0
Cs	106·5	77·5	64·5

Tables from Adams, reference 8.

From the discussion so far, the reader has already undoubtedly concluded that we should not expect to see a few sharp bands in the 700-1400 cm^{-1} range from a flame resulting from combustion of a metal or organo-metallic compound with oxygen or halogen compounds as the oxidant. On the other hand, one can expect many overlapping intense bands in this region (assuming proper formulation of the ingredients) which will make identification and characterization of the emitting species difficult. Hence, the problem becomes quite complex.

EMITTER CANDIDATES

Of the oxygen vibrations listed in Drago Fig. 7-15, possible emitters might be BO, SiO, PO, and SO. An emitter not listed but of interest in MnO. We should notice that Drago gives group frequencies which are applicable to molecule segments and which should not be confused with fundamental frequencies of diatomic species.

Of the halogen vibrations, possible emitters might be BCl, BF (not listed), SiF, SiCl, PF, and SF. As in the case of the oxygen vibrations, the frequency of the group depends on the composition of the remainder of the molecule to which the group is attached. We can compute the fundamental frequency of the diatomic molecules by the methods already described. All of these frequencies should fall in the infrared region of interest.

As an example, the flame from combustion of the following composition should radiate intensily in the desired infrared region.

elemental red phosphorus (fuel)	49% by weight
manganese dioxide (oxidant)	38%
elemental boron (fuel)	8%
binder	5%

The flame plume is expected to be composed mainly of vibrationally excited oxides of boron, phosphorus and manganese. If the binder were a halogenated dimethyl-siloxane polymer for example, the metal halides would be formed as well. The composition combinations which can be formulated are limited by compatibility considerations and the ingenuity of the formulator.

It is clear that in a flame as complex as the one described,
many different species will be present although the species, in
themselves, may be simple in form (diatomic, triatomic, or molecules
with few atoms). It then becomes our problem to identify those
molecules which are most beneficial to our purpose. We need also to
consider that, for example, at the effective temperature of our flame
the oxide of boron may not be predominantly B_2O_3 but may be BO or
BO_2. This being the case, it is the vibrational features of these
species which become of interest to us. Knowing that the direct study
of the flame from the composition presented may not be initially fruit-
ful, intermediate experiments will be conducted to provide preliminary
data about the selected species.

PLAN OF ATTACK

After we have decided what molecules may be good emitter candidates,
we will use this information in a three way approach. (1) Using Raman
and infrared spectroscopy techniques, the neat candidate molecules in
their solid, liquid, and gas phases will be characterized vibrationally.
This applies only to molecules for which data is not available from the
literature and only for molecular species which can be isolated
outside of the flame environment. (2) Using the techniques of flame
photometry, emitter candidates will be fed into idealized flames of
various composition and temperature and the resulting radiation will be
measured and recorded. (3) And finally, the radiation from flames
which contain the candidate molecules formed as products of the
combustion reaction will also be recorded and measured.

The multiple approach is necessary because of the problem complexity. First, for example, we note that vibrational assignments are not the same for the molecule in the gas phase as in the solid phase. Compare Tables 2-27B and 2-1 from Adams[8] reproduced on page 5. Since we want to consider our molecules in a flame environment, ma ·· of them may be gaseous at this temperature. Thus, we need data f this phase in addition to similar data for other phases. Such da: are not always available. In this case, we obtain it by infrared Raman spectroscopy. Having the data, it should be emphasized that we only have reference data. This does not tell us how the material will behave in the flame.

If we were to try to compare a flame spectrum directly to that of a vibrational spectrum of one of our candidates molecules, we might consider it to be hopeless. This is because the flame spectrum will be made up of many overlapping spectra. To alleviate this problem, we will need to conduct some intermediate experiments. As in flame photometry,[9] we create a flame at the desired effective temperature[10] with as little radiation in the region of study as possible. We then "seed" this flame with known quantities of candidate materials and measure the spectral differences. Although we cannot remove all extraneous sources, we can at least reduce these interferences to hopefully a tolerable degree. In this way, we will obtain spectra of radiation from our molecule in a flame environment. These spectra are likely to show a different set of overtones, combination bands, etc. than did the spectrum of the neat molecule. The differences are thus due to the different behavior of the molecule in the flame environment.

Finally, the radiation from the flame which contains one or more candidate molecules formed as combustion products is compared to the other data. If sufficient information has been collected, we may be able to assign features of the flame spectra to a particular emitter (molecule).

By way of example, let us consider BO_2 which belongs to point group C_{2v}. From group theory and symmetry considerations,[14] we can predict the infrared and Raman vibrational lines which we should see in the spectrum. The following total representation of the C_{2v} molecule for BO_2 results from the computation.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
No. of unshifted atoms	3	1	3	1
Contribution to character per unshifted atom	3	-1	1	1
Total representation	9	-1	3	1

The total representation reduces to

$$\Gamma = 3A_1 + 1A_2 + 3B_1 + 2B_2$$

which corresponds to the 9 allowable energy modes for the BO_2 molecule. We identify the translational modes ($1A_1 + 1B_1 + 1B_2$) and rotational modes ($1A_2 + 1B_1 + 1B_2$) from the C_{2v} character table and subtract these from the total. This leaves one A_1 species, one A_2 species and one B_1 species; one for each of the three vibrational modes of the molecule (symmetric, bending, and asymmetric). The character table for C_{2v}

species tells us that the A_1 vibrational mode is infrared and Raman
active. This Raman line will be polarized. The A_2 mode is Raman
active but not infrared. The B_1 mode is Raman and infrared active.
Thus, in the infrared absorption spectrum, we will see two lines.
In the Raman spectrum, we will see three lines one of which is polarized
and two of which are not. This information along with the predicted
location of these lines should allow us to make identification of the
origin of the energy from the BO_2 molecule which appears in our emission
spectrum. We should also take note that the line from the vibration
with A_2 symmetry may be seen in the infrared emission spectrum
although it is not active in infrared absorption. Its position in the
infrared will be as determined from the Raman spectrum.

In an analogous manner, by viewing different regions of the flame,
we may be able to follow the decomposition of MnO_2 in the flame by
this technique. That is, we can observe the lines attributable to
MnO_2 disappear and those of MnO appear. The study of other flame
species can be approached in a similar manner.

EXPERIMENTAL

In the preceeding discussion, infrared measurement techniques
were suggested. For study of the neat molecule, one can use the
instruments and techniques described by Willard, Merritt and Dean.[11]
These are well known and will not be discussed here. To do the flame
work, we need to use a rapid scanning instrument such as described by
Pimentel.[12] In this way, fluctuations due to flame variation, combustion

changes, smoke, etc. can be minimized. In our work, we would use these
in a somewhat conventional manner. In addition, it may be possible
to apply the Raman technique to our problem so that we can acquire
data which otherwise would not be accessible.

Laser Raman Spectroscopy

I am proposing to apply laser Raman techniques to the study
of neat molecules at high temperature (for example 1500°K). This
involves (1) a high power laser at a frequency at which the sample
does not absorb, (2) a sample holder capable of taking the temperature
and pressure, and (3) other necessary instrumental modifications.
This is to be considered as a technique which complements the infrared
analysis and is not without some problems. One mainly can expect low
Stokes line intensity from gaseous species due to the low concentration.
The elevated temperature reduces the window regions at which there will
be minimum absorption as required for successful application of this
method. I propose also to apply the Raman method to a "seeded"
idealized flame as well. In this case, we can certainly expect
absorption problems. That is, we must select a laser with a frequency
(such as ultraviolet) which not only will not be absorbed by the unseeded
flame but also will not be absorbed by the sample molecule. Here we
no longer use a "sample holder" but will have to position the flame in
relation to the laser and the instrumental optics such that the
scattered light can be detected. For the flame work, we would need
to scan the spectral region rapidly in the Raman set-up[13] as we did in
the infrared technique.

There are several features of this experiment which should be noted. First, if we can use a near-ultraviolet or visible laser, this will mean that we can acquire data about infrared properties of a substance by taking Raman spectra in the visible or UV region. Experimentally, this is an advantage. Secondly, since the selection rules of Raman require a change of polarizability as compared to infrared which requires a dipole change, we will observe some transitions which would be forbidden for absorption IR spectroscopy. Also, since we are at a high temperature, some of the upper vibrational states of the molecule will be appreciably populated in accordance with a Boltzmann distribution. Because of this, the anti-Stokes lines, which in normal room temperature Raman are very weak, may be stronger by several orders of magnitude. If this turns out to be the case, we may be able to make use of these lines to identify vibrations whose Stokes lines happen to fall at a frequency which is absorbed and thus would not have been identifiable.

SUMMARY

In this article has suggested a research problem which deals with identification and characterization of the vibrational features of flame combustion products which radiate intensily in the 700 to 1400 /cm region. It was pointed out that data are needed about the vibrational modes of candidate emitters at flame temperatures and in a flame environment. To acquire these data, Raman and infrared spectroscopic techniques are suggested as the experimental means.

It is proposed that candidate emitters be characterized vibrationally: (1) in their neat form, (2) in an idealized flame, and (3) in a flame Cont'd

(Cont'd)

in which they form naturally as a combustion product. Conventional rapid scan infrared methods are suggested for the study under each of the three conditions. On the other hand, hi-temperature rapid scan laser Raman spectroscopy is proposed as a complementary method. This unique approach to the problem promises to permit us to get vibrational data about inorganic flame species which are inaccessible by other means.

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82