A Notion of Adjoint Spectrum in the Application to Air-pollution Monitoring

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Synopsis

This report deals with a notion of adjoint spectrum
which is applicable to air-pollution monitoring by using
pulsed lasers. Both Raman and absorption spectra of
multiple gas complex are linear combinations of the
spectra, each of which is specific to a gas species and
its magnitude is proportional to the density.
An extended formulation of the method of least
squares is made in terms of a new notion, adjoint spec-
tra, which visualizes the structure of the numerical
filter. Applications of the derived numerical filters
to the two methods are shown and features are described
about the synthesized filters.

1. Introduction

An optical method requires no chemical process to measure complex
gas densities, and a quick response and remote measurement are possible.
Introduction of a pulsed laser as the light source results in various
merits on the atmospheric pollution detection. Raman scattering from
the atmosphere exited by pulsed laser light is composed of disctete
lines specific to the constituents of the atmosphere and the line in-
tensities correspond to the gas densities[1]. The absolute intensities

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are, however, very weak even though a high powered pulsed laser is em-
ployed, which implies overlaps of the line profile observed by a very
sensitive spectrometric facility. For research use, a double-monochro-
meter is employed to obtain necessary resolution. This is, however,
impractical for the field application.

Differencial absorption method utilizes the differences of the
absorption cross section at two wavelengths, one of which is "on" the
resonance absorption line and, another, "off". Significance of this
method lies in the point that the sensitivity is some orders larger
than the Raman scattering method[2].

In the ultraviolet region of 224~226 [nm] wavelength, NO, SO_2 and
NH_3 shares the absorption band and their spectra have clear distinc-
tion[3,4]. The overlap of the absorption lines also requires a scheme
to separate each gas concentration. In the molecular correlation spec-
troscopy, a couple of correlating masks which have multiple slits and
locate alternately on the slit position of a monochrometer[5], or a
polychrometers[6] are used. The attainable accuracy is not sufficient
for the pourpose of air-pollution monitoring because of the low signal
to noise ratio in the photo-electric conversion process and the geo-
metrical accuracy of the mask, though effort has been made to optimize
the mask design.

Similar correlation procedure can be executed by a micro-computer
installed in the measuring unit, which will produce more accurate re-
sults than that by an analog method along with the employment of the
pulsed dye laser as light sourses.

This report deals with a mathematical filters which is generated
by a notion of adjoint spectra, though a part of this research has
been in a previous paper written in Japanese[7].

The notion "adjoint" already has been familiar to those who are
engaged in solving neutron governing equation which determines power
distribution in a nuclear power reactor[8]. The mathematical foundation
is on the least squares method.

Two applications are made for the Raman and the resonance absorp-
tion methods. In the Raman method, a synthesyzed numerical filter
pickes up the densities of N_2 and O_2 in the atmosphere which is the
calibration signal to the pollutant densities from a photon-counting
spectrum of the Raman scattering. Also from an absorption spectrum
of a gas simplex of NO and SO_2, this filter can extract each densities
within enough accuracy. The numerical filter can also reduce an ef-
fect of long term drift of instrument parameters.

2. A numerical filter

2.1 Adjoint spectra

Let an inner product $<x(\lambda), y(\lambda)>$ be defined for two spectra $x(\lambda)$ and $y(\lambda)$ on a closed set Λ of real numbers λ, wavelength. In the following, two set of integers i, k are denoted as I and K respectively.

Also $F_I = \{s_i(\lambda), i\varepsilon I, \lambda\varepsilon\Lambda\}$ and $F^* = \{s_i^*(\lambda), i\varepsilon I, \lambda\varepsilon\Lambda\}$ are two sets of spectra $s_i(\lambda)$ and $s_i^*(\lambda)$, $i\varepsilon I$. The spectra $s_i^*(\lambda)\varepsilon F_I^*$ are called as the adjoint of $s_i\varepsilon F_I$ if a bi-orthonormality

$$<s_i(\lambda), s_j^*(\lambda)> = \delta_{ij} \quad \text{(Kronecker's)} \tag{1}$$

holds.

These spectra have several properties as follow.

(a) The adjoint spectra $s_i^*\varepsilon F_I^*$ can be generated as linear combinations of $s_i\varepsilon F_I$.

(b) Given F_I and $F_{I'}$. Then the adjoint of $F_{I\cup I'}$ gives a F_I^* of F_I such that

$$F_I^* \subset F_{I\cup I'}^* \tag{2}$$

holds, that is, the adjoint F^* of F is not unique.

(c) A linear combination

$$\tau(\lambda) = \sum_{i\varepsilon I} c_i \cdot s_i(\lambda) \tag{3}$$

of $s_i(\lambda)$ gives

$$c_i = <s_i^*(\lambda), \tau(\lambda)>. \tag{4}$$

This expression directly gives a numerical filter which gives a density c_i from the obtained spectrum.

2.2 A numerical filter for pulsed-laser system and the response for noise.

A general definition of the inner product is

$$<x(\lambda), y(\lambda)> = \int_\Lambda x(\lambda) y(\lambda) d\mu(\lambda), \tag{5}$$

where the measure $d\mu(\lambda)$ should be substituted by

$$d\mu(\lambda) = \sum_{k \in K} v_k \delta(\lambda-\lambda_k) d\lambda \tag{6}$$

for a discretely tunable laser system, where δ stands for Dirack's distribution.

If a computer is installed in the instrumentation, the adjoint spectra $s_i^*(\lambda_k)$, $k \in K$ can be retained in it, then a gas density of species i is calculated by Eq. (4) out of the spectrum $\tilde{\tau}(\lambda)$. The measured spectrum $\tilde{\tau}(\lambda)$ inherently includes random noise n, then the result of the numerical filter becomes

$$\tilde{c}_i = \sum_{k \in K} s_{ik}^* \tilde{\tau}(\lambda_k) v_k \tag{7}$$

and the variance of $\tilde{c}_i$ is given by

$$\text{Var}(\tilde{c}_i) = \text{Var}(n) \sum_{k \in K} (s_{ik}^*)^2 v_k^2. \tag{8}$$

This is reduced from the assumption that the noise is independent of the wavelength. The notation s_{ik}^* is short for $s_i^*(\lambda_k)$.

If the $\tilde{\tau}$ value is averaged over m_k laser shots retaining the wavelength at λ_k, the variance reduces to

$$\text{Var}(\tilde{c}_i) = \text{Var}(n) \sum_{k \in K} (s_{ik}^* v_k)^2 \cdot \frac{1}{m_k}. \tag{9}$$

The deduction mentioned above is a version of the well-known least-squares method. But the notion of the adjoint clarifies the function of the method that prevents an error caused in the guess for one parameter propagates to others.

2.3 Immunity of the adjoint spectra for interferences

More than one adjoint spectrum exist for a F_I. Let the adjoint has been extracted from the F_{I+J}^*. The bi-orthonormality relation, Eq. (1), holds not only for a $s_i(\lambda)$, $i \in I$ but also for a $s_j(\lambda)$, $j \in J$ with thus synthesized adjoint spectra $s_i^*(\lambda)$, $i \in I$. Immunity of F_I^* from an interference is then extended from F_I to F_{I+J}. The numbers of the elements of F_{I+J}, however, cannot exceed K that intrincically limit the number of independent spectra. Further more the number $I+J$ should be enough smaller than K, because the round-off error also disturbes the bi-orthonormality, Eq. (1).

3. Optimization of the pulse-number allotment for discrete wavelength

Given a set of adjoint spectra, the variance of the resulting densities c_i can be minimized by an proper allotment of the pulse shots to each wavelengths, λ_k, under a restriction

$$M = \sum_{k \in K} m_k, \tag{10}$$

where M is also a given number. Hereafter, the parameter v_k is set to be unity because it can be included in s_{ik}^*.

3.1 The optimal solution for a single gas species

The optimal solution to minimize $\mathrm{Var}(c_i)$ expressed by Eq.(9) under the restriction, Eq.(10), is

$$m_{ik} = M \cdot |s_{ik}^*| / \sum_{k \in K} |s_{ik}^*|. \tag{11}$$

This solution is given through the Lagrange's method of indeterminate coefficients regarding the integer m_k as continuous variables, though it is an approximation.

3.2 The optimal solution for multiple gas species

For the given data set $\bar{t}_k$, $k \in K$, multiple densities c_i, $i \in I$ are obtained if necessary adjoint spectra s_{ik}^*, $i \in I$, $k \in K$ are prepared, but common solution m_k, $k \in K$ that minimize $\mathrm{Var}(\tilde{c}_i)$ for every $i \in I$ at the same time exists. The multi-objective programming technique[9] which realizes a notion of the Pareto optimality can cope with this problem. A non-inferior or the Pareto optimal solution is such that

$$\delta \{\mathrm{Var}(c_i)\} \geqq 0, \quad i \in I, \tag{12}$$

holds for any m_k, $k \in K$ that satisfies Eq.(10).

Another problem statement is made by the min-max problem with the criterion

$$\min_{m_k, k \in K} \cdot \max_{i \in I} \{ w_i \cdot \mathrm{Var}(c_i) \}$$

where w_i, $i \in I$ are weights. The solution of a min-max problem corresponds to a solution of the non-inferior solution, which is not unique.

4. Application to an gas analyzer by Raman scattering

This system gives molecular densities of pollutants from a Raman scattering spectra of the polluted atmosphere excited by a pulsed Nd: YAG laser light. The scattered light is fed into a monochrometer attached with a photo-multiplier and a photon-counter.

The Raman spectra is composed of discrete lines each of which corresponds to a specific gas species. The collected photon-counts spectrum is, however, broadened and the lines overlap each other, because of the inherently poor spectral resolution of sensitive apparatuses.

The spectrum is expressed as

$$n_s(\lambda) = KI_0 \sum_{i \in I} N_i F_i(\lambda), \tag{13}$$

where

λ : the spectrometer wavelength setting,

n_s: photon counts,

K : a coefficient specific to the instrument,

N_i: the molecular number density of the i-th gas species,

F_i: the response of the instrument for a simplex of the i-th gas species,

I_0 : incident laser energy per pulse.

Figure 1 shows a Raman spectrum of atmosphere excited by the Nd: YAG laser light. The Nd line is predominant and O_2 and N_2 lines are clearly separated. The NO_2 line is to locate at 572.6 nm where the O_2 trail overlaps. Thus distributed response must be reduced to the line intensities by the numerical filters.

At first , the Nd, N_2 and O_2 spectra separated at 460 and 580 nm were chosen. Other 23 base spectra were generated by Lagrange's, interpolation taking the center wavelengths with equal spacing as the

parameter.   The result is shown in **Fig.2** where O_2 line is clearly re-
constructed.   The N_2 line is, however, associated with spurious res-
ponses around it.   This is attributed to a grating anomaly of the
spectrometer and the quantum noise of the photon counting method.

Fig.1 Raman scattering of atmosphere
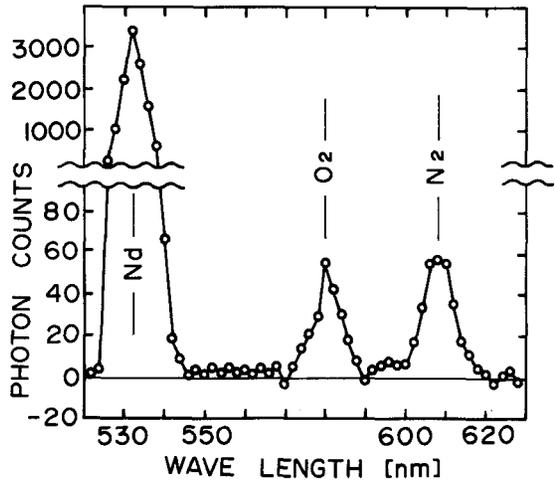 exited by the second harmonic of
  Nd:YAG laser light.

Fig.2 A result obtained by the numeri-
  cal inverse filtering with the base
  spectra generated from three responses
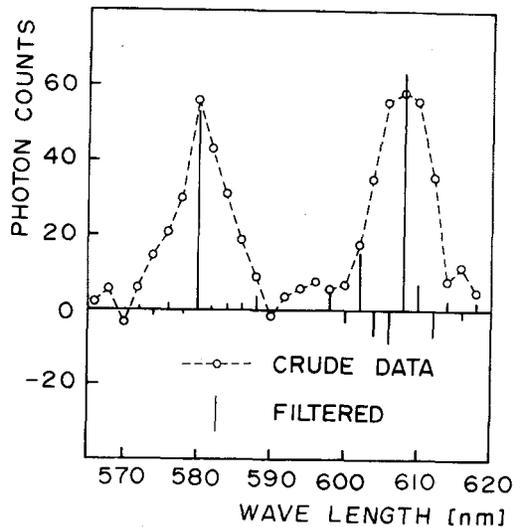 shown in Fig.1 using the Lagrange's
  interpolation.

Figure 3 is the three adjoint spectra for Nd, O_2 and N_2 chosen
out of the adjoint that were used to give the result of Fig.2.   Each
of the adjoint spectra has violent profile swinging to both signs, and
double word-length calculation was necessary to obtain these results
that retain the bi-orthonormality defined by Eq.(1).

Fig.3 Adjoint spectra for the excitation light of Nd:YAG laser and for Raman scattering from O_2 and N_2 molecules, which gives result of Fig.2.
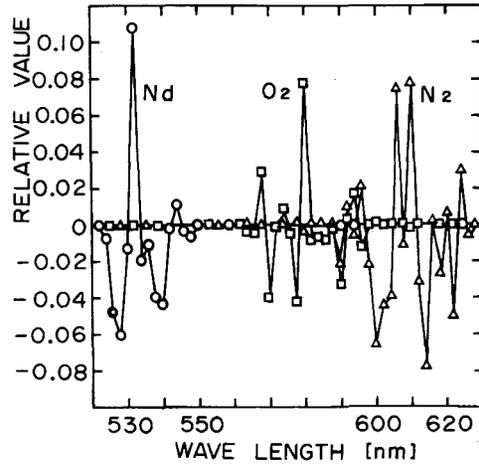
5. Application to a gas analyzer by resonance absorption

Three gasses SO_2, NO and NH_3 shares their absorption band on 217-227 nm. The small attenuation over a short path can be measured by a system of a pulsed dye laser and of a low noise electronic apparatus that have been specifically developed by the authors.

Let a light pulse with wavelength λ and energy P_I be attenuated by the chromatic gasses of thickness L to P_T. From the Lambert-Beer's law, the optical thickness, or the attenuation, $\tau(\lambda)$ is expressed as

$$\tau(\lambda) \equiv \ln\left(\frac{P_I}{P_T}\right) = \sum_{i \in I} \alpha c_i L s_i(\lambda), \tag{14}$$

where c_i and s_i are the density and the absorption cross section of the i-th gas species, respectively. Here the molecular number sensity is replaced by αc_i.

For small attenuation, Eq.(14) becomes

$$\tau(\lambda) \approx \frac{P_I - P_T}{P_I}. \tag{15}$$

The electronic circuit deals with two quantities $P_I - P_T$ and P_I instead of P_T and P_I, which allows accurate signal processing without requiring intolerably large dynamic range.

The absorption spectra of the three gases which had been given by Thompson et $al.$[3] and Warneck and Marmo[4] are shown in **Fig.4** along

with the adjoint spectra for the wavelength region of 217-227 nm.
Figure 5 is the solutions for optimal pulse number allotment problem
for three different criteria obtained by using the adjoint spectra of
Fig.4.

Ambiguity of the resulting c_i values due to a random noise that
is inherently included in the measured $\bar{\tau}$ is given by

$$\mathrm{Var}(c_i L) = \sum_{k \in K} \{s_i(\lambda_k)\}^2 \mathrm{Var}(n), \quad i \in I. \tag{16}$$

The non-inferior solution was discovered by a search method which con-
sist of a random search and improving steps.

Fig.4 Resonance absorption spectra
of SO_2, NO and NH_3 over 217~227.4
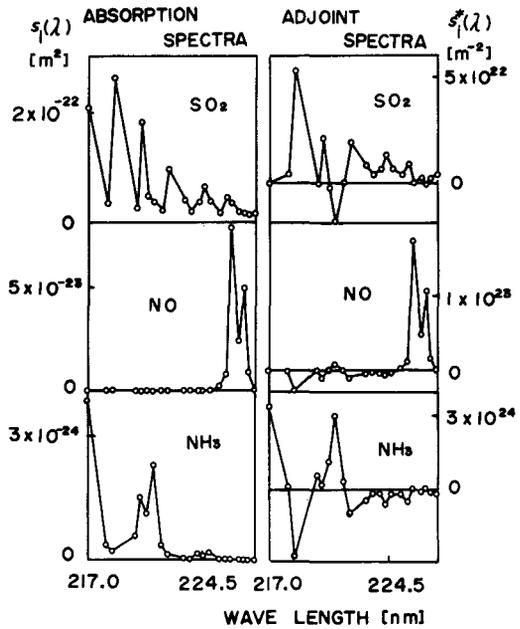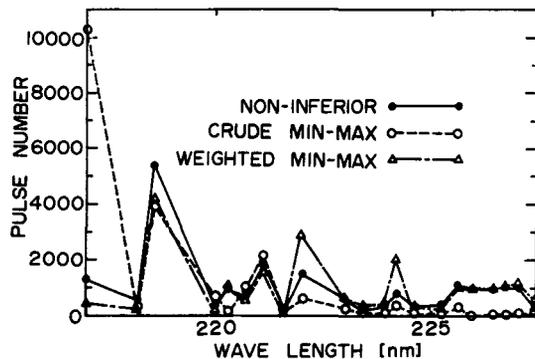[nm][4,5], and the adjoint spectra.

Fig.5 Three optimal pulse number
allotment for the non-inferior,
the crude min-max and the
weighted min-max solutions.

The crude min-max solution is for a criterion

$$\min_{m_k, k \in K} \cdot \max_{i \, I} \mathrm{Var}(c_i L)$$

which is not associated with weights. The method to obtain this is the same as for the noninferior solution. In Fig. 5, the effort is exhausted to reduce the ambiguity of NH_3 only, namely, the pulse numbers are allotted to the left end, where the cross section of NH_3 is large.

This solution is unreasonable and therefore weights

$$w_i = [\min_{m_k, k \in K} \mathrm{Var}(c_i L)]^{-1}, \quad i \in I \qquad\qquad (17)$$

were introduced and the criterion was modified to

$$\min_{m_k, k \in K} \cdot \max_i [w_i \mathrm{Var}(c_i L)].$$

Each term of this criterion is normalized by the extreme value which had been the optimization only for i-th gas species. The solution for this criterion shown in Fig.5 resembles to the non-inferior solution very well, which is compatible with a description in the multiobjective optimization theory that a min-max solution with a set of w_i corresponds to an inferior solution. The weighted min-max solution is more profitable to a practical use, because one can introduce his intuition.

Table 1 Standard deviations of the results of the
filtering, $\sigma(c_i L)$, for a noise of $\sigma(n)=1$.

[ppm·m/Nep]

Pulse number allotment	SO	NO	NH$_3$
Uniform	11.8 (1.72)	9.77 (2.21)	45.0, (1.71)
Optimal for a specific gas	6.88 (1.0)	4.43 (1.0)	26.3 (1.0)
Non-inferior	8.20 (1.19)	9.69 (2.19)	36.2 (1.38)
Crude min-max	11.4 (1.66)	31.3 (7.07)	31.3 (1.19)
Min-max	8.21 (1.19)	9.65 (2.18)	57.3 (2.18)

Standard deviations for different allotments are listed in **Table 1**, where Var(n) is taken to be unity [Nep^2]. For the pourpose of comparison, a result for a uniform pulse number allotment and that for the optimization for a single species are listed as well. The values in parenthesis are those normalized by w_i.

The crude min-max solution and the weighted min-max solution gives almost equivalent results for NO and NH_3. This is because the spectrum of SO_2 overlaps with both spectra of NH_3 and NO, whereas, spectra of NO and NH_3 are independent and scramble for the pulse numbers.

5.2 NO and SO_2 complex measurement

Despite the spectrum in Fig.4, the NO spectrum of $\gamma(0,0)$ band near 260 nm is composed of discrete lines each of which stands for the rotational sublevel though they are broadened to 1.2 cm^{-1} FWJM. As for the spectrum of SO_2 in this band, no discrete lines are resolved even if a laser diode spectrometer is employed[11]. The lines are dense and collapsed due to the pressure broadening. These contrasting spectral profiles suggests that a rather narrow width of wavelength band is enough to separate the SO_2 and the NO densities by using the numerical filter stated above.

Figure 6 shows absorption spectra of NO and SO_2 in the designated band. Each gases are contained in a cell of 3 cm long. The gases are for span calibration use and are diluted in N_2 gas. Also the complex spectra which was obtained by arranging these two cells in tandem configuration, is shown in the figure. Employment of the numerical filter which is composed of the NO and SO_2 spectra as the base gives the densities within an accuracy of 0.58% for NO and 3.2% for SO_2.
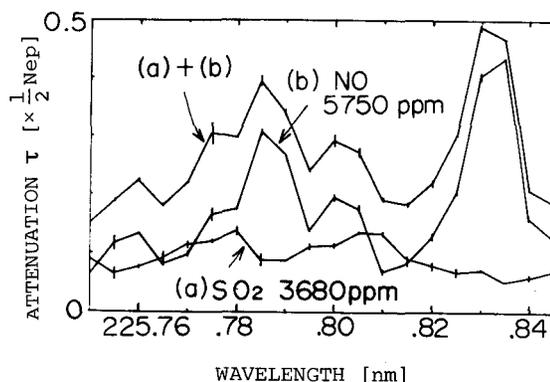

Fig. 6 Absorption spectra of NO and SO_2 under 1 atm. The cell length is 3 cm. The (a)+(b) spectrum is that of the complex of SO_2 and NO.

Three different adjoint spectra for NO with different base spectra are shown in **Fig.7.** In that wavelength region, the SO_2 spectra for NO and SO_2 as the base is smaller than that associated with two echelons, which represents the trade-off between the specificity and the sensitivity or the signal to noise ratio.

Fig.7 Example of the adjoint spectra. The SO_2 spectrum can be replace with the 2-echelon.
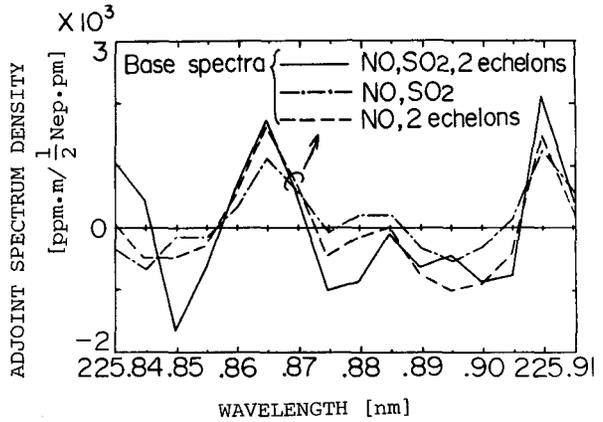
6. Concluding remarks

The notion of the adjoint spectra and the features are stated. Successful applications were made to the Raman method and to the resonance absorption method both for atmospheric air pollution. The densities of constituent gases are extracted from their diffused and overlapping spectra.

This function is realized when a microcomputer is installed in an instrument, which will be a common situation for a sophisticated measuring apparatus in near future.

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