Kramers-Kronig relations in spectral analysis of diffuse reflected radiation

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Abstract. In this paper studied application of Kamers-Kronig relations in spectral analysis of diffuse reflected IR radiation. Two methods of the Kramers-Kronig relations calculation were considered: Maclaurin's Formula (MF method) and Method of Peterson-Knight (PK method). Influence of using MF and PK methods on synthetic and real experimental spectra were studied. Accuracy and calculating time of these methods were compared. According to the results of numerical experiments, conclusions about the perspectives and application possibilities of the considered methods were discussed.

1. Introduction
Identification of various substances in the air and on the surface is one of the most important tasks for different fields of science and technology. For such purpose, methods of optical spectroscopy are used. For trace gas analysis, FTIR spectroscopy is widely used [1 - 3]. Raman spectroscopy is an effective technique provided non-destructive high sensitive and high selective analysis of surface contaminants [4]. However, Raman spectroscopy also has disadvantages. The major difficulty is a low intensity of signal level, which makes it use powerful sources of excitation radiation. Here we face another problem - if excitation intensities are too high, the sample may be thermally decomposed.

Progress in production of wide tunable quantum cascade lasers (QCL) stimulate development of new methods of substance analysis [5 - 8]. One of them is method of identifying solid and liquid substances by diffuse reflected IR-radiation. This non-contact, non-destructive method does not require sample preparation and can be used for studies in field conditions [5, 6]. Moreover, signal level of diffuse reflected radiation is several orders of magnitude higher than levels of Raman scattering signal. Laser with an average power about 10 mW (with a transverse size of laser beam of several millimeters) is sufficient to obtain the spectra of diffuse reflected radiation. In this case there is no risk of physical damage or detonation of the studying sample.

The main challenge of working with diffuse reflected radiation is in increasing the selectivity of the obtained spectra. For this propose Kramers-Kronig (K-K) relations can be used [9, 10]. The K-K relations deal with real and imaginary part of complex reflection coefficient and provide a transition from diffuse reflectance spectrum to the transmission spectrum. Some examples of using K-K relations effects on selectivity of diffuse reflectance spectra are given in [9]. By updating methods of K-K relations calculation, it is possible to enhance reliability and sensitivity of identification techniques based on diffuse reflected radiation spectral analysis.
2. Kramers-Kronig relations
In general, reflection coefficient \( r(\nu) \) is a complex function of the real refractive index \( n \) and the extinction coefficient \( k \) [11]. Complex amplitude reflection coefficient can be written as
\[
r(\nu) = \frac{(n-1) + ik}{(n+1) + ik} = \eta e^{i\phi},
\]
(1)
where \( \eta \) is the amplitude of the reflection coefficient and \( \phi \) is its phase.

Since \( n \) and \( k \) are both functions of frequency \( \nu \), \( \eta \) and \( \phi \) are also functions of \( \nu \). The logarithm of (1) gives
\[
\ln[r(\nu)] = \ln[\eta(\nu)] + i\phi(\nu).
\]
\( \eta(\nu) \) and \( \phi(\nu) \) obey relations [11]
\[
\ln[\eta(\nu)] = \frac{2\nu}{\pi} \int_0^\nu \frac{\nu' \phi(\nu')}{\nu'^2 - \nu^2} d\nu',
\]
(2)
\[
\phi(\nu) = -\frac{2\nu}{\pi} \int_0^\nu \ln[\eta(\nu')] d\nu'.
\]
(3)
Equations (2) and (3) are the K-K relations. From these relations follows that phase angle can be calculated from amplitude of the reflection coefficient. Volume of \( \eta(\nu) \) can be obtained directly from experimental data. Since the experimental reflectance spectrum is associated with the amplitude of the reflection coefficient
\[
R(\nu) = \left| \frac{E_{ref}}{E_{inc}} \right|^2 = \eta^2(\nu),
\]
it can be written as \( \eta(\nu) = \sqrt{R(\nu)} \). Real refractive index and the extinction coefficient can be calculated using equations (1) - (3) from measurements of the reflectivity as a function of frequency as
\[
n(\nu) = \frac{1 - R(\nu)}{1 + R(\nu) + 2\sqrt{R(\nu)} \cos \phi(\nu)},
\]
\[
k(\nu) = \frac{2\sqrt{R(\nu)} \sin \phi(\nu)}{1 + R(\nu) - 2\sqrt{R(\nu)} \cos \phi(\nu)}.
\]
We have experimentally confirmed that relations above are applicable for diffuse reflected radiation analysis [9]. So we can calculate the extinction coefficient and absorption spectrum by using measured low-selective diffuse reflectance spectrum. These optical parameters are widely used in spectral analysis.

3. Numerical algorithms for K-K relations
Experimental diffuse reflectance spectra always measured in bounded frequency region. On the other hand, K-K relations include integration over all frequencies. Moreover, integrands in K-K relations have an singularity \( \nu' = \nu \). Therefore, while developing identification methods based on K-K relations we should choose such numerical calculation method, which
- can get results without significant loss of accuracy using bounded experimental measurements;
- avoid a direct calculation of singularity.

In this paper we compared two following numerical calculation methods:

3.1. Maclaurin’s Formula (MF method).
This method calculates the following summation by taking every other data point for approximation of equation (3) [12]
\[
\phi(\nu) = -\frac{2\nu}{\pi} \times 2h \times \left\{ \sum_{i,j}^N f_{ij} \right\},
\]
(4)
where \( h \) is a spectral resolution, \( N \) is a number of points in the spectrum and \( f_{ij} \) is an integrand
\[
f_{ij} = \frac{\ln[\eta(\nu_j)] - \ln[\eta(\nu_i)]}{\nu_j^2 - \nu_i^2}.
\]
In equation (4) summation index is chosen as follows: index $i$ possess values $1 \ldots N$. When $i$ is odd, $j$ possess only even values, and vice versa. It allows to avoid direct calculation of the point at $i = j$.

In this calculation method integral approximated as:

$$
\int_{0}^{\infty} v^{\max} + \int_{v^{\min}}^{v^{\max}} + \int_{v^{\max}}^{\infty},
$$

where $[v_{\text{min}}, v_{\text{max}}]$ is a frequency region of diffuse reflectance spectra, $v_{\text{ext}} \gg v_{\text{max}}$ is an empirical frequency.

Diffuse reflectance spectrum is extrapolated in regions $[0, v_{\text{min}}]$ and $[v_{\text{max}}, v_{\text{ext}}]$ by means of some empirical extrapolation functions [13].

3.2. Peterson-Knight method (PK method).

This method approximate equation (3) by the two times Fourier transform [14]

$$
i\phi(\nu) = -\frac{1}{2\pi} \int_{-\infty}^{0} d\nu e^{-i\nu t} \int_{-\infty}^{\infty} d\xi \eta(\nu) e^{i\nu \xi} + \frac{1}{2\pi} \int_{0}^{\infty} d\nu e^{i\nu t} \int_{-\infty}^{\infty} d\xi \eta(\nu) e^{i\nu \xi}.
$$

This approximation allows us to use algorithm of Fast Fourier Transform (FFT) during calculations. We use no extrapolation of diffuse reflectance spectra in this method because FFT algorithm itself extrapolates data as periodic function.

4. Results

In order to test a methods described above we applied K-K relations to some synthetic and experimental spectrum.

4.1. Synthetic spectrum.

Let’s demonstrate that MF and PK methods of K-K relations calculation allow us to transcend from reflection coefficient to extinction coefficient with sufficient accuracy in ideal model situation.

In this paper two models of synthetic spectra are considered:

- Model A is an approximation of typical experimental data [15].
- Model B is an approximation of quartz optical properties [16].

For spectrum simulating damped harmonic-oscillator (DHO) is used. Equations for real and imaginary part of dielectric constant are well known [15]

$$
\varepsilon' = 1 + \sum_{j} \frac{B_{j}(\omega_{j}^{2} - \omega^{2})}{(\omega_{j}^{2} - \omega^{2})^{2} + \lambda_{j}^{2}\omega^{2}},
$$

$$
\varepsilon'' = \sum_{j} \frac{B_{j}\lambda_{j}\omega}{(\omega_{j}^{2} - \omega^{2})^{2} + \lambda_{j}^{2}\omega^{2}},
$$

where $\omega_{j}$, $B_{j}$ and $\lambda_{j}$ are, respectively, the resonance frequency, the transition strength and the damping factor for $j$th band.

Thus spectrum of $n$, $k$ and $R$ could be define by the following equations [15, 16]

$$
n = \left\{ \frac{1}{2} \left[ \left( \varepsilon'^{2} + \varepsilon''^{2} \right)^{1/2} + \varepsilon' \right] \right\}^{1/2}, \tag{5}
$$

$$
k = \left\{ \frac{1}{2} \left[ \left( \varepsilon'^{2} + \varepsilon''^{2} \right)^{1/2} - \varepsilon' \right] \right\}^{1/2}, \tag{6}
$$

$$
R = \frac{(n-1)^{2} + k^{2}}{(n+1)^{2} + k^{2}}. \tag{7}
$$

For models A and B synthetic spectra of $k$ and $R$ can be calculated by equations (5)-(7). Parameters for DHO models have been taken from papers [15] and [16]. Synthetic $k$ spectra calculated by equation
(6) denote as $k_s$. Using MF and PK methods we obtain $k_{mf}$ and $k_{pk}$ spectra from synthetic $R$ spectra. Comparisons of $k_s$, $k_{mf}$ and $k_{pk}$ are shown on the figures 1 and 2.

**Figure 1.** Results of numerical experiment for Model A. For MF method $R$ spectrum was extrapolated in regions $[0, 100]$ and $[4100, 10000]$ cm$^{-1}$ by two constant functions. Pearson coefficient for $k_s$ and calculated $k_{mf}$ spectra equals to 0.99. Calculating time is about 260 sec. Pearson coefficient for $k_s$ and calculated $k_{pk}$ spectra equals to 0.83. Calculating time is about 0.01 sec.

**Figure 2.** Results of numerical experiment for Model B. For MF method $R$ spectrum was extrapolated in regions $[0, 300]$ and $[1400, 10000]$ cm$^{-1}$ by two constant functions. Pearson coefficient for $k_s$ and calculated $k_{mf}$ spectra equals to 0.98. Calculating time is about 79 sec. Pearson coefficient for $k_s$ and calculated $k_{pk}$ spectra equals to 0.94. Calculating time is about 0.07 sec.

This numerical experiments confirmed possibility to obtain extinction coefficient from diffuse reflectance spectra using MF and PK methods. Results can be efficiently obtained in wide spectral region (>1000 cm$^{-1}$). For synthetic data both methods get accurately results. However, MF method works much “slower” than PK method.

4.2. **Experimental spectrum.**

Research application MF and PK methods for real experimental spectra are practical important.
We have measured diffuse reflectance spectra of some test-substances in spectral region 5.3-12.8 μm with tunable QCL-laser. The figure 3a represents the scheme of experimental setup for registration of diffuse reflected radiation. The position of the detector (5a) provides the minimization of specular radiated component in the registered spectra. Usage of a non-reflective surface allows to avoid the presence of the surface reflected radiation in the substance spectrum. The QCL (1a) has 4 laser modules (1b) with total tuning-range of 766-1909 cm\(^{-1}\) and spectral resolution 1 cm\(^{-1}\).

Figures 4 and 5 shows results of numerical experiments obtained for diethyl phthalate and glycerol respectively. Experimental spectra denote as \(k_{\text{exp}}\).

**Figure 3.** (a) Configuration scheme of experimental block, (b) laser module.

(a): 1a – QCL; 2a – researched sample; 3a – non-reflective surface; 4a – objective; 5a – MCT detector.
(b): 1b – QCL laser module; 2b – rotating diffraction grating; 3b, 5b – collimating lenses; 4b – QCL-chip.

**Figure 4.** Results of numerical experiment for Diethyl Phthalate. For MF method \(R\) spectrum was extrapolated in regions [0, 766] and [1909 10000] cm\(^{-1}\) by two constant functions. Pearson coefficient for \(k_{\text{exp}}\) and calculated \(k_{\text{ref}}\) spectra equals to 0.67. Calculating time is about 79 sec. Pearson coefficient for \(k_{\text{exp}}\) and calculated \(k_{\text{pk}}\) spectra equals to 0.57. Calculating time is about 0.01 sec.
Figure 5. Results of numerical experiment for Glycerol. For MF method $R$ spectrum was extrapolated in regions [0, 766] and [1909 3000] cm$^{-1}$ by functions $f_{exp}(\omega) = c \times e^{\alpha \omega}$, where $c$, $\alpha$ are empirical constants. Pearson coefficient for $k_{exp}$ and calculated $k_{mf}$ spectra equals to 0.72. Calculating time is about 79 sec. Pearson coefficient for $k_{exp}$ and calculated $k_{pk}$ spectra equals to 0.56. Calculating time is about 0.01 sec.

MF and PK methods for experimental spectra gives lose accuracy, but, in general, obtained results suitable for substance identification.

5. Conclusion
In this paper we have considered two calculating method for K-K relations: Maclaurin’s Formula and Method of Peterson-Knight.

Both methods for synthetic spectra obtain extinction coefficient with high accuracy. Extrapolation of experimental data allows MF method to obtain more accurate results rather than PK method. However, of MF method works much slower because of extrapolation.

Similar situation we can see for experimental diffuse reflectance spectra. Both methods gives lose accuracy but in general obtained results a suitable for successful substance identification.

The long calculation time of the MF method makes applicable for non-laboratory studies worse. Less accurate, but ‘faster’ PK method is more promising for this purpose. Moreover, extrapolation of experimental data and applying algorithms for phase correction can improve the method’s accuracy.

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