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ABSTRACT

We present the technique and experimental laboratory setup for measuring and analysis of diffuse reflectance spectra. The Experimental spectra obtained by tunable infrared quantum cascade laser with average power of 15 mW. Using causality relations for real and imaginary parts of reflectivity we can calculate the extinction coefficient. We use dumped harmonic oscillator (DHO) model to calculate synthetic spectra and test Kramers-Kronig relations for spectra calculations. Using experimental setup and numerical methods of spectra analysis we could identify the diethyl phthalate (DEP). The proposed method can be used in routine laboratory analysis to complement the ATR and DRIFTS methods of IR spectroscopy.

Keywords: infrared spectroscopy, identification, quantum cascade laser, Kramers-Kronig relations, diffuse reflectance

1. INTRODUCTION

Substances identification is one of the important tasks that can be solved by spectroscopy methods. For example, with THz spectroscopy we can investigate a matter in an aggressive environment,\textsuperscript{1} or with fluorescence spectroscopy we can investigate membranes in water\textsuperscript{2,3}. In the present work we propose using a quantum cascade laser (QCL) to obtain diffuse reflectance IR spectra to identify the irradiated substance. The presence of unique properties in quantum cascade lasers,\textsuperscript{4} such as wide tuning range, determines their promising use. A wider range of spectra registration allows getting more useful information for spectral analysis. Choosing of the most effective method of experimental data processing is one of the main tasks. Firstly we propose the Lorentz dispersion model for determining the parameters of molecules. Then we receive the molecule parameters as ensemble of damped harmonic oscillators. After that we automatically obtain the reflectance spectrum, the extinction coefficient, refractive index, and the dielectric constant of the substance. We have created an algorithm, that approximates the spectrum in a wide range with high correlation and a high accuracy degree. Also dumped harmonic oscillator (DHO) could be used to distinguish one substance from another and for finding the best parameters combination for same substances.

2. EXPERIMENTAL SETUP

Figure 1 shows the experimental setup for registration of diffuse reflectance spectra.\textsuperscript{5} Infrared radiation from the QCL is incident normally on a nonreflecting substrate, where the test substance is located. The solid particles size is about 0.1–1.0 mm; droplets size is about 2–5 mm. The laser emits in a pulsed mode with a peak power of up to 150 mW and the average power of about 20 mW. The pulse duration is about 50 ns and a repetition frequency is about 1 MHz. The emitted radiation is in the spectral range from 5.3 to 12.8 µm with a tuning step of 2 cm\textsuperscript{-1}. The laser beam cross-section is about 2 × 4 mm\textsuperscript{2}, the divergence is < 5 mrad, and the power instability is 5 %. The test sample is located on a substrate 50 cm away from the laser. The infrared radiation falls on the

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sample and is reflected diffusely and/or specularly. The photodetector optics collect the reflected radiation at a certain angle within the solid angle of 40 deg on a sensitive area of a photodetector. The photodetector is a HgCdTe thermoelectrically cooled MCT photodetector (type Vigo PVMI-4TE) with a detectivity \( D^* \sim 6 \times 10^9 \) cmHz\(^{1/2}\)/W and time resolution of at least 4 ns. Signal-to-noise ratio (SNR) for laser emitted spectra is about \( 10^4 \) to \( 10^5 \). For tryptophan reflectance spectra [see Fig. 1(b)], SNR is about 45 to 50. The Pearson correlation coefficient for spectra in Fig. 1(b) is 0.97, that indicates good reproducibility of the measured spectra. The instability of the spectral lines’ intensity is due to fluctuations of the laser power (about 5% for LaserTune QCL). In the described setup, we first measured the radiation reflected from a golden plate to measure the spectral power of the incident radiation. Reflectivity of the plate in the working spectral range is no less than 98%. For further analysis, all reflectance spectra were normalized by the intensity of the incident radiation. The influence of laser power fluctuations can be weakened by introducing a reference infrared channel for measuring the incident radiation power.

![Photo of the experimental setup](image-url)

**Figure 1:** (a) Photo of the experimental setup for measuring diffusely reflected IR radiation spectra of substances in solid and liquid phases. Position 1, QCL (Laser Tune, Block Engineering, United States); position 2, MCT photodetector cooled by a cascade of Peltier cells; position 3, collecting optics of the detector; position 4, test sample on a nonreflecting substrate. (b) Typical forms of the measured spectra for 5 mg tryptophan. Position 5, picture of the test sample on the substrate.

### 3. EXPERIMENTAL RESULTS

To show that the experimental results are highly independent of external conditions and it is advisable to conduct further studies of reflected radiation, experiments were carried out both on the setup shown above in Figure 1 and from spectrometers at Chemnitz Technical University and Fraunhofer ENAS laboratory. The Figure 2 shows Thermo Fisher Nicolet 6700 with Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy setup (see Fig. 2b).

At two different experimental facilities, reflection spectra for KClO\(_3\) and KClO\(_4\) were recorded in the frequency range from 950 to 1900 cm\(^{-1}\). The reflectance spectra from Nicolet 6700 recorded with the resolution of 4 cm\(^{-1}\) and averaged over 64 frames. The Happ-Genzel function used for Apodization and Mertz method for phase correction. The results can be seen in Figures 3 and 4. Pearson’s correlation coefficients are 0.76 for KClO\(_3\) and 0.74 for KClO\(_4\). The spectra are quite similar to each other; the spectral lines are at the same frequencies in a fairly wide range.
Since the results are very similar, we can conclude that any physically inferior setup for obtaining reflected radiation spectra can be used and compared with other experimental setups. Also we can conclude that the results obtained at the experimental setup are suitable for database and substance identification system on the setup with QCL.

4. APPLICATION OF THE CASUALITY PRINCIPLE FOR THE TRANSFORMATION OF THE OPTICAL CHARACTERISTIC OF A TEST SUBSTANCE

In the case of a normal incidence of an electromagnetic wave at the interface between two media, according to Fresnel equations, algebraic relations take place for the reflection, refraction, and absorption coefficients. The reflectance of the medium can be represented as a complex function:

\[ \hat{r} = \frac{(n - 1) + ik}{(n + 1) + ik} = \eta e^{i\phi} \]  

(1)
where n is the refraction of the test substance, k is extinction, \( \nu \) is the amplitude of the reflected wave, and \( \phi \) is the phase of the reflected wave.

Eq. (1) written for the case of normal incidence of radiation on the interface between two media is oversimplified compared to the accurate theory of diffuse reflectance spectra. The use of this equation, however, may still be justified by assuming that there exists a model solid, whose optical characteristics match those of a real substance in the spectral region of interest. The experimental setup has been designed to avoid registering specularly reflected radiation. The rest of the registered input (diffuse reflection) comes from chaotically oriented surfaces of a substance (e.g., powder), and the input from different polarizations is effectively averaged. In this case, the registered data are independent of incident light polarization, and polarization-independent is used to create an effective substance model.

Measured value is normalized reflectance defined as the square of the amplitude of the reflected wave \( R(\nu) = \eta^2(\nu) \). By taking the logarithm of Eq. (1), we get \( \ln[r(\nu)] = \ln[\eta(\nu)] + i\phi(\nu) \). Since reflectance in Eq. (1) must be causal, the amplitude \( \eta(\nu) \) and phase \( \phi(\nu) \) satisfy the Kramers-Kronig relations:

\[
\ln[\eta(\nu)] = V.p\left(\frac{2}{\pi} \int_0^\infty \frac{\nu' \phi(\nu')}{\nu'^2 - \nu^2} d\nu'\right) \tag{2}
\]

\[
\phi(\nu) = V.p\left(-\frac{2\nu}{\pi} \int_0^\infty \frac{\ln[\eta(\nu)]}{\nu'^2 - \nu^2} d\nu'\right) \tag{3}
\]

Relations between the extinction, refraction, and amplitude of the reflected wave can be written as follows:

\[
n(\nu) = \frac{1 - R(\nu)}{1 + R(\nu) + 2\sqrt{R(\nu)} \cos \phi(\nu)} \tag{4}
\]

\[
k(\nu) = \frac{2\sqrt{R(\nu)} \sin \phi(\nu)}{1 + R(\nu) - 2\sqrt{R(\nu)} \cos \phi(\nu)} \tag{5}
\]
It is possible to acquire the extinction spectrum by measuring the reflectance spectrum. Conversion from extinction to absorption spectra can be implemented, as mentioned in Ref. 7. To calculate phase spectra using Kramers-Kronig relations, we need to calculate the integrals in the sense of the Cauchy principal value. In Ref. 8, the main methods for the numerical implementation of the Kramers-Kronig principle have been considered. Mostly, the methods come down to bypassing the singular point. In Ref. 9, the use of double Fourier transforms for causality relations has been proposed. This method has been chosen for implementation in the described real-time identification system due to its high computational efficiency.

5. SPECTRUM MODELING USING HARMONIC OSCILLATORS

To verify the applicability and efficiency of the described algorithm of spectra conversion, a set of model problems has been solved, and the reflectance and transmittance spectra have been calculated based on a certain model of a substance. In this section, we regard the Kramers-Kronig transformation as a semiempirical procedure, part of whose justification rests on the agreement between phases or optical constants obtained from the model with values measured more directly. Complex electric permittivity is represented by its real \( \epsilon' \) and imaginary \( \epsilon'' \) parts.

Based on the Lorentz dispersion model, we treat a molecule as an ensemble of damped harmonic oscillators (DHO model):

\[
\epsilon' = n_0^2 + \sum_j \frac{B_j (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \lambda_j^2 \omega^2} \tag{6}
\]

\[
\epsilon'' = \sum_j \frac{B_j \lambda_j \omega}{(\omega_0^2 - \omega^2)^2 + \lambda_j^2 \omega^2} \tag{7}
\]

where \( \omega_j, B_j, \lambda_j \) and are the oscillator resonant frequency, the strength, and attenuation coefficient, respectively, for the \( j \)-th oscillator of the ensemble; \( n_0 \) – is a constant. The spectral indices of refraction \( n \) and extinction \( k \) can be obtained from the real and imaginary parts of the dielectric constant\(^\text{10} \) as follows:

\[
k = \frac{1}{\sqrt{2} \left[ (\epsilon'^2 + \epsilon''^2)^{\frac{3}{2}} - \epsilon' \right]^{1/2}} \tag{8}
\]

\[
n = \frac{1}{\sqrt{2} \left[ (\epsilon'^2 + \epsilon''^2)^{\frac{3}{2}} + \epsilon' \right]^{1/2}} \tag{9}
\]

The formula calculated the reflection coefficient (1). To ensure a closer similarity between the model spectra and real substances that will be tested in real applications, we created 5 model spectra for KClO3, KClO4, Glycerol, diethyl benzene-1,2-dicarboxylate [diethyl phthalate (DEP)] and tryptophan. The simulation results are given for 2 substances: glycerol and DEP. Using the experimentally measured diffuse reflectance spectra \( R(\nu) \) of the sample of the test substances, the glycerol and DEP model coefficient \( \omega_j, B_j \) and \( \lambda_j \) have been determined by the least square method in the range of 950–1350 cm\(^{-1} \). Table 1 and Table 2 presents the calculated values of the coefficients. The value of additive constant entering Eq. (6) is \( n_0 = 2.71 \) for DEP and \( n_0 = 1.83 \) for glycerol.

<table>
<thead>
<tr>
<th>( \omega_j, \text{cm}^{-1} )</th>
<th>( B_j \times 10^4, \text{cm}^{-2} )</th>
<th>( \lambda_j, \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1025.68</td>
<td>73.12</td>
<td>10.92</td>
</tr>
<tr>
<td>1183.09</td>
<td>21.34</td>
<td>27.87</td>
</tr>
<tr>
<td>1194.04</td>
<td>181.11</td>
<td>354.07</td>
</tr>
<tr>
<td>1281.58</td>
<td>22.74</td>
<td>32.79</td>
</tr>
<tr>
<td>1427.86</td>
<td>67.58</td>
<td>74.02</td>
</tr>
</tbody>
</table>

To test the proposed method for calculating the spectral extinction coefficient from the reflectance spectrum using the Kramers-Kronig relations, we have conducted the following numerical experiments. For the ensemble
Table 2: Fitted DEP model parameters

<table>
<thead>
<tr>
<th>$\omega_j$, $\text{cm}^{-1}$</th>
<th>$B_j \times 10^4$, $\text{cm}^{-2}$</th>
<th>$\lambda_j$, $\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>807.46</td>
<td>308.31</td>
<td>157.361</td>
</tr>
<tr>
<td>1070.21</td>
<td>3.99</td>
<td>16.22</td>
</tr>
<tr>
<td>114.15</td>
<td>12.39</td>
<td>33.41</td>
</tr>
<tr>
<td>1254.73</td>
<td>37.92</td>
<td>31.48</td>
</tr>
</tbody>
</table>

of harmonic oscillators with parameters from Table 1 and Table 2 representing the model of liquid glycerol and liquid DEP, we have calculated the reflectance spectra using in the limited range and applied the procedure described above to obtain the transmittance spectra. Then, we have modeled the transmittance spectra directly from Eq. (8) and Eq. (9) (Fig. 5 curve 2b and Fig. 6 curve 2b) and calculate transmittance spectra (Fig. 5 curve 1b and Fig. 6 curve 1b) using Kramers-Kronig Eqs. from a modeled reflectance spectra. The correlation coefficient for the obtained transmission spectra for the same substance is 0.96 for DEP and 0.98 for glycerol. That confirms the reliability of the suggested method for converting optical characteristics. Figure 5(a) shows the experimental (1a) and modeled (2a) diffuse reflection spectra of DEP. Figure 5(b) shows the calculated (1b) and modeled (2b) transmission spectra of DEP. Figure 6(a) shows the experimental (1a) and modeled (2a) diffuse reflection spectra of glycerol. Figure 6(b) shows the calculated (1b) and modeled (2b) transmission spectra of glycerol.

![Figure 5: (a) Experimental and (b) modeled DEP spectral characteristics.](image)

6. IDENTIFICATION

One of the main applications of spectroscopy is the recognition of chemicals. There are many spectrometers that operate on transmission, reflection, etc. In this paper the extinction and transmission coefficients, real and imaginary parts of the dielectric constant obtained from experimental data only via Kramers-Kronig transform without any other instruments.

Figure 7 shows the correlation matrix for 5 parameters (reflectance ($R$), extinction ($k$), refraction ($n$), the real ($\epsilon'$) and imaginary ($\epsilon''$) part of the dielectric constant) for 5 substances that were obtained using the setup described in paragraph 2. For each spectrum, the reflection spectrum was simulated with Kramers-Kronig transforms. The reflection spectrum into the remaining parameters recalculated. The Figure 7 shows the correlation coefficients for the corresponding substances from the database.
In most cases the substances model spectra coincide with the database experimental spectra. Spectra for the database and recognition obtained on the same experimental setup. Averaging several correlation coefficients allows us to create a correspondence coefficient. Thus it helps significantly increase the recognition accuracy. From the experimental results we can conclude that it is possible to create a substance recognition system.
7. CONCLUSION

The present paper describes the construction, technical characteristics, and operating principle of the experimental setup for measuring the diffuse reflectance spectra of substances on different surfaces without preliminary preparation of samples. This setup is designed as an automated system for real-time substance identification. The numerical algorithm for extraction the reflectance and extinction indices of a test substance from the measured diffuse reflection coefficient is suggested. The algorithm is based on the Fresnel equation for the normal incidence case of the wave and the Kramers-Kronig relations for the complex refractive index. The method for registering reflectance spectra and procedures of spectra processing and substance identification is a novel approach for remote detection and identification. The algorithm efficiency for spectra conversion and identification is shown on the set of model examples. Model data are based on the ensemble of damped harmonic oscillators (Lorentz dispersion model). The consistency of the calculated and measured accuracy of spectra reconstruction is shown.

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