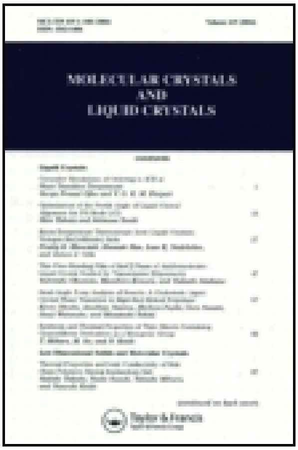

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Liquid-Crystalline Infrared Gas Sensors

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Liquid-Crystalline Infrared Gas Sensors

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A mid-infrared gas sensor on the basis of a liquid-crystalline (LC) cell was developed. The main element in the sensor of the type proposed is a liquid-crystalline cell possessing marked dichroism of optical absorption in the mid-infrared spectral range. By fitting the absorbance and alignment parameters of the LC cell, it is possible to create the effect of the absorption edge shift when varying the magnitude of the electric field applied (2–10 V). This leads to some kind of wavelength modulation of an external optical radiation in the predetermined spectral area. By adding an appropriate light-emitting diode and photodetector to the system described, one can obtain a miniature scanning spectral instrument (sensor) of the new type without any moving parts and without usage of high voltages.

Keywords: absorption edge shift; liquid-crystalline cell; spectrometric sensor

INTRODUCTION

The most important tasks in the environmental-monitoring field are detection and concentration measurements of different ingredients in natural and artificial mixtures of substances, for example, nitrogen oxides, methane, or other minor components in the atmosphere, inside mines or other underground cavities, and communications, as well as novel compounds emanating from certain technological processes.

Types of sensors for these items are very numerous. For example, a lot of optoacoustical devices (sensors) are used for this purpose [1]. There are many handbooks dedicated to such sensors (see, e.g., Refs. 1 and 2).

In the past few years, there has been increasing interest in the detection of methane and other hydrocarbons in the atmosphere and for industrial applications. For instance, there is a market for remote sensing techniques for minor greenhouse gases (CH_4, hydrocarbons).

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Leakage from pipe lines and tanks or the emission of toxic substances from chemical production plants are hazards associated with storing, processing, and transporting hydrocarbon products. Fast detection and location of leak in technical installations are important to minimize the emission of hazardous chemicals into the environment.

The majority of methane or hydrocarbon sensors industrially applied at the moment use the catalytic mechanism of operation [3]. The obvious drawbacks of these sensors are that they can be easily poisoned by halogens and their derivatives, some volatile Si-organic compounds, and so forth. Detection of methane and other hydrocarbons has also been achieved using optical fiber sensors, thin film SnO_2, or thin-film Fe_2O_3-based sensors [4,5]. One of the disadvantages of these conductivity-based sensors, however, is their high cross-sensitivity. This high cross-sensitivity of semiconductor-based sensors has been decreased using thick-film sensors, adsorption selective filters, catalytic filters, or differential conductivity sensors [5].

The sensors that operate by revealing some predetermined spectral characteristics of the monitored ingredients (gases or fluids) are considered to be the most refined and precise [1]. The rigorous role of the sensor (gas analyzer) is to get a concentration value of the gas determined or simply to determine the presence of the gas. This is a rational approach. For a user, an absorption line contour shape of the gas monitored does not matter.

However, a contour shape of the line contains very important information. In such a cases, we are not users but investigators. The information can be very miscellaneous: from gas temperature to the percentages of chemically close ingredients. Thus, spectral sensors that can not only reveal a spectral characteristic (line, band, etc.) but also carry out spectral scanning across the predetermined spectral band are very attractive from the point of view of investigation.

The modulation of external optical radiation is usually organized with the help of some interrupting device. Interrupting devices are as a rule multiwaved in the spectral sense (for example, mechanical) or wideband (for example, electrooptical). However, application of narrowband modulators, tuned to the absorption range of determined gas, increases sensitivity of the method [2].

There are many attempts to create analyzers using a derivative spectroscopic approach that permits study of the shape of a line [6–8].

Unfortunately, the spectrometric sensors of types known today have some essential drawbacks that restrict their wide applicability and make them poorly suited to field, mobile, and high-altitude jobs. Those drawbacks are the construction complexity, cumbersome embodiments, control difficulty, and (the main) obligatory presence of the

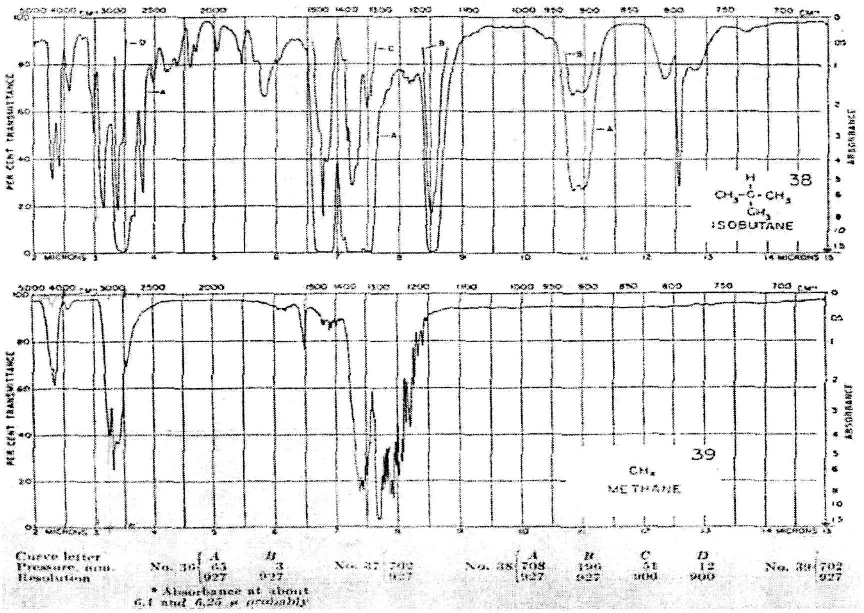


FIGURE 1 Transmittance of methane and isobutane at 710 mm Hg, 27°C [9]. There are several spectral regions with high absorption coefficients: the region with wavelength 3–4 μm and the region with wavelength 7–8 μm.

moving parts (mirrors, prisms, or gratings). Meanwhile, there could be applications where any vibrations caused by moving parts were strictly inadmissible.

Figure 1 shows the spectra of methane [9] and isobutane. There are several spectral regions with high absorption coefficients—the region with wavelength 3–4 μm and the region with wavelength 7–8 μm; however, gases such as water vapor and carbon dioxide have much higher absorption in the second spectral region and only the first one, the so-called “atmospheric window” (3–4 μm), can be used for measurements of methane or other hydrocarbons. The wavelength of this window corresponds to the C–H absorption in various organic structures.

There is an increased interest in the spectrometric sensors in the mid-infrared region because of their applicability in some industrial processes with hydrocarbons and control of their concentration in the environment. There are several types of spectrometric sensors (optrodes, interferometer, etc.). The most attractive from the point of view of sensitivity and cost is a miniaturized gas sensor using a micromachined Fabry–Perot interferometer for carbon dioxide, ethylene, and water vapor with the measurement range 0.01 to 10 ppm. This spectrometer can be used only for a certain gas, so it is not multichannel [8]. The interferometer is based on the Fabry–Perot principle; light comes down the single optical fiber and strikes a partially reflecting surface. Some of the light is reflected, and some traverses an optical cavity and then is reflected. When it joins the first reflected light, the two interfere and form bright and dim interference fringes. Any change in the depth of the cavity produces a predictable change in the wavelengths at which the interference fringes occur.

In conclusion, measurements of the atmospheric greenhouse gases are required to be made with miniature, simple-to-control, cheap devices with at least an adequate level of sensitivity, accuracy, and resolution. Also, the environment itself imposes restrictions (such as absence of moving parts in the measurement devices) or other criteria on the form of the instrument encompassing an optical sensor. Optical techniques are often well suited to meet dual requirements of measurement performance and environmental suitability while at the same time offering the solutions that are acceptable to market forces.

THEORY

New opportunities can be found out by using liquid crystals (LCs). As is well known, one can observe several electrooptical effects in LCs, which are accompanied by changing the color [10]. However, changing the color is a spectroselective transformation of incident optical radiation. If one can control this transformation, in particular, by gradually varying the magnitude of the electric field applied (see Fig. 2), it will be spectral scanning (or spectroselective modulation).

The main element in a sensor of the type proposed is an LC cell that possesses market dichroism of optical absorption in some spectral range. It should be noted that the dichroism magnitude of the LC substance is of minor importance because one can change the dichroic characteristics of the cell by varying its thickness.

By fitting the absorbance and alignment parameters of the LC cell, it is possible to create the effect of the absorption edge shift when varying the magnitude of electric field applied. This leads to some kind of wavelength modulation of an external optical radiation in the predetermined spectral range. By adding an appropriate light detector to the system described, one can obtain a miniature scanning spectral instrument (sensor) of the new type without any moving parts, without using dangerous high voltages, and without other drawbacks. The principle of the method can be seen from Fig. 3. One can see in

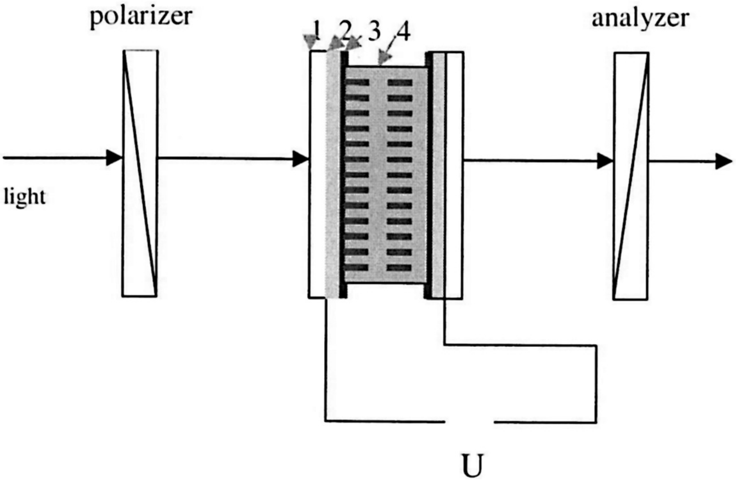


FIGURE 2 Electrically controlled LC cell and its basic components: 1, quartz; 2, transparent electrodes; 3, orientant for orienting LC molecules in one direction; and 4, LC layer.

this figure an absorption band (curve a) of some imaginary LC cell. It is important that minimum transmission reaches down to almost 0% at a certain wavelength.

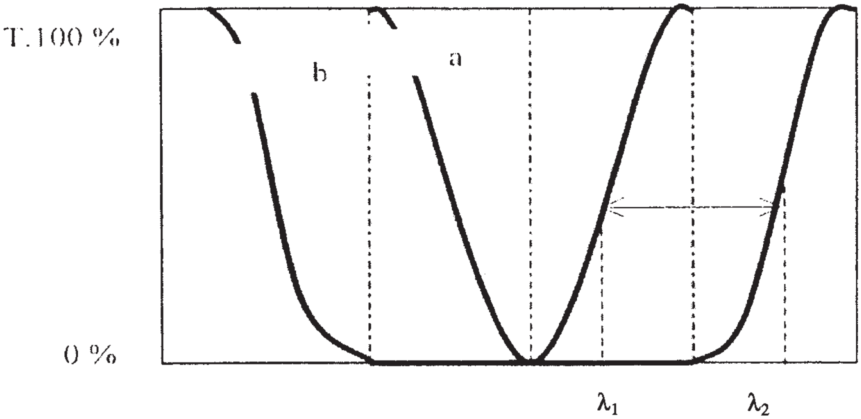


FIGURE 3 Effect of the absorption edge shift: applying an appropriate electric field (usually from 2 to 8 V) to an absorption band (curve a) of some imaginary LC cell with the minimum transmission reaching down to 0% at a certain wavelength results in an increase of the band integral intensity (curve b).

We considered the case where the LC matrix molecules are aligned initially in planar way, that is, parallel to the capillary wells. When the LC matrix consists of molecules with positive dielectric anisotropy (rod-like ones or those having a permanent dipole moment along of their long axes), an applied electric field of sufficient magnitude normally to the LC layer will turn from the planar orientation to perpendicular one when molecular long axes align normally to the capillary wells [11].

Molecular orientation of the LC matrix molecules much correspond to their minimum interaction with the light, that is, the integral intensity of the band must be minimal for this orientation of an LC director. When one changes the orientation of the dichroic LC matrix by applying an appropriate electric field (usually from 2 to 8 V), an increase of the band integral intensity must be observed. In the transmission spectrum, this effect must be expressed as some increase in the band width (curve b) because there is no possibility to diminish the transmission—it is already at zero at its minimum. Visually, this effect is manifested as an absorption edge shift. We can use this as a mean for some kind of wavelength (or wave number) modulation for an external spectral characteristics carried with the light to be transmitted by the cell [12].

According to the Bouguert–Lambert–Beer's law, one can write

$$I(\nu) = I_0 e^{-\alpha(\nu)d} \tag{1}$$

where $I(\nu)$ is intensity after the LC cell, I_0 is intensity before traversing the LC cell, $\alpha\ (\nu)$ is the absorption coefficient, and d is width of LC layer.

Thus,

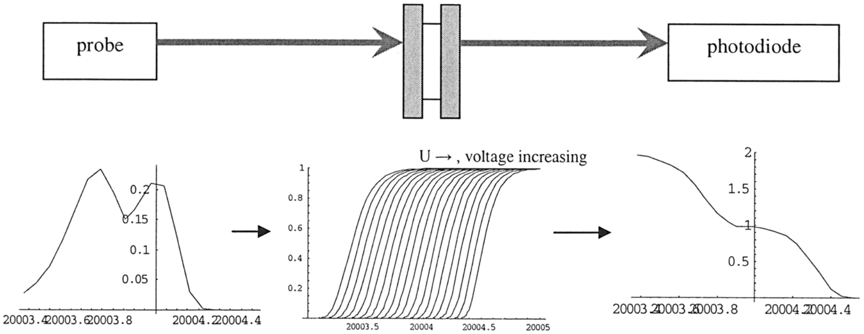
$$T(\nu) = \frac{I(\nu)}{I_0} = \mathrm{Exp}[-\alpha(\nu)d], \tag{2}$$

where $T(\nu)$ is transmittance of the LC layer.

As it is shown in Refs. 12 and 13, the absorption edge of LC can be modeled with Gaussian line shape:

$$\alpha(\nu) = \alpha_0(\nu)\cos(\theta) = -\frac{1}{\sqrt{\pi}\gamma} e^{-\frac{(\nu-\nu_0)^2}{\gamma^2}} \cos(\theta)$$

where □ is a constant describing the oscillation of molecules; □ is a wave number near the investigated region; and □ is an angle between the director of LC molecule and a direction perpendicular to the transmitted light. The angle □ is connected with the applied voltage,



Spectrum of analyzing gas

Absorption edge shift of LC cell, modulation procedure

Obtained response

FIGURE 4 Scheme of modulation process of a gas spectrum with the help of an LC cell. Increasing the applied voltage shifts the absorption edge of liquid crystal. A response from a photodiode placed after the LC cell is similar to the original external spectrum but can be reduced to the original spectrum with the help of some computational operations (differentiation, iteration).

U [14]; thus, by changing the applied voltage one can change the absorption coefficient according to wave number (wavelength) and obtain a wavelength modulation.

Figure 4 shows the scheme of modulation procedure with an LC cell. Increasing the applied voltage shifts the absorption edge of the LC according to Eq. (2).

A response from a photodiode placed after the LC cell is similar to the original external spectrum, but can be reduced to the original spectrum with the help of some computational operations (differentiation, iteration). Good results revealing the external spectral band shapes with the help of iterations were achieved by computer programming and simulation in Mathematica 4.2 and MatLab 6.5 [15]. The technique for reducing true external spectrum from the signal detected after the modulation process is described in detail in Refs. 14 and 15.

The spectral resolution of the method proposed is calculated according to the Raleigh principle [14]. If two close spectral lines have the same intensity and form, the Raleigh principle means that the minimum between these lines is 80% of the maximum. By applying this principle to our spectrometric sensor, we obtain the resolution of about $0.01\,\mathrm{cm}^{-1}$ considering the random noise of about 10%. The obtained value is a good result as compared with the other spectral devices (interference and diffraction types).

TABLE 1 LC-Cell Design Parameters

Parameter	Value of parameter, μm
Thickness of the LC layer	15
Length of the cell	2000
Width of the cell	2000
Thickness of SiO_2 layer	0.1
Thickness of Znl-oxide layer	0.2
Length of contact area of the transparent electrodes	1400

EXPERIMENT AND DISCUSSION

We have investigated several LC cells with absorption bands in spectral range near 3 μm where some greenhouse gases absorb. One example was an LC cell with thickness near 20 μm that gives the absorption edge scanning shift of about 70 cm^{-1} in this region. The LC cell parameters can be seen in Table 1.

Figure 5 shows two transmission spectra: without an electric field applied (2) and under a field of about 11 V (1). One can see that the absorption edge shifts in the range of 3050 to 3150 cm^{-1}. The reason

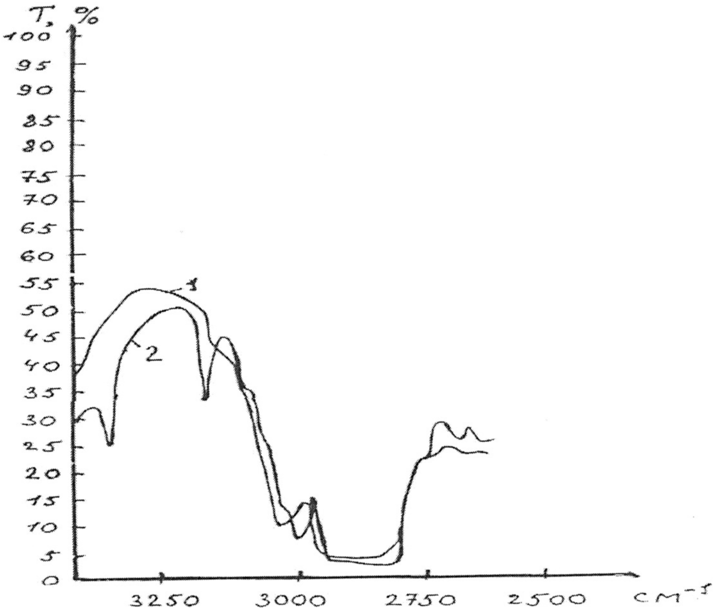


FIGURE 5

for such a small magnitude of the effect is that the director of the long axes of LC molecule alignment inside the matrix did not have proper coordination with the dipole moment of the transition, causing the absorption observed. The absorption near 3 μm is due to CH bond stretching vibrations and these bonds and corresponding transition dipole moments orient in very different ways relative to long axes of the LC molecules. Nevertheless, even this shift can be used, we believe, for the wavelength (wave number) modulation.

From the spectra in Figure 5 one can observe that the absorption edge of this LC is sharp and can be approximated with Gaussian line shape. To increase the width of the shift it is possible to increase the thickness of the LC cell or put several LCs of this type together. However, as can be seen from the spectra the absorption of the LC is not enough—the value of absorption in the maximum is 0.55. In this case the obtained signal will be weaker.

The technique for reducing true external spectrum from the signal detected after the modulation process is developed on the basis of iterative technique for deconvolution [].

CONCLUSION

From the analysis of the LC spectral and polarized characteristics, the following conclusions can be made. The future development of LC sensors can be carried in two different directions:

1. to select the LCs with sharp absorption edges and, with the help of 3–4 cells, overlap the whole investigated region—so-called “observed sensors” for investigation of several gases;
2. to select the LCs with an absorption edge shift specific for the absorption spectral region of some gases—sensors on the concrete substance.

Once again the advantages of the proposed sensor are the absence of any moving parts and low controlling voltages. Additional advantages are the small size of such an instrument: an LC cell is 1 or several cm^2 in area and 1 or 2 mm in thickness. An appropriate attached photodiode, for example, is also of small size. Moreover, LC cell are produced now by well-developed technologies and so are reliable, long-lived, and very cheap.

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