Retarders based on total internal reflections are discussed. Quarterwave retardation can be obtained by a single reflection when one is using material of high refractive index ($n > 2.4$), as it is available for the IR range. Alternatively, the influence of the beam divergence can be efficiently compensated for. Several optical designs and first results are presented.

Index Headings: IR; Circular dichroism; Retarder.

INTRODUCTION

Circular polarization is commonly produced by phase retardation in a linearly polarized beam. The only way known to obtain circular polarization without linear pre-polarization is by using a cholesteric mesophase: in the spectral range of the so-called selective reflection, the reflected and transmitted radiation is circularly polarized with opposite sign.

Transmitting retarders are often based on inherently birefringent materials. Adjusting the thickness, one obtains any desired phase shift for a given wavelength. The variation of the retardation with wavelength can virtually be compensated for within a certain interval by an appropriate combination of different materials. Such achromatic devices are used in the visible part of the spectrum; however, it is more difficult to cover the infrared range because of its width and because, here, the choice of suitable materials is quite limited.

Phase retardation in the IR range is obtained in most cases by using a photoelastic modulator, where birefringence is achieved by mechanical stress. Such a device grants the advantage of high modulation frequencies, while its efficiency for producing circular polarization is restricted due to the sinusoidal variation of the stress and to changes with the wavelength.

Another type of retarder, such as the Fresnel rhomb, employs the phase shift caused by internal total reflection. For such a prism, any transmitting material can be used and it will be achromatic to a high degree. The use of a Fresnel rhomb for measuring VCD has been reported in the literature. Since in the IR range a number of materials exhibit high refractive indices, phase shifts of up to more than 120° can be obtained with a single reflection. In this contribution, we discuss different designs for both single and double reflection retarders to be used in the IR spectral range. Some experimental applications have already been briefly reported.

PHASE RETARDATION BY INTERNAL REFLECTION

Internal reflection causes different phase shifts for the components of the incident radiation being polarized parallel and perpendicular to the plane of reflection. The phase difference $\delta$ between the components of the reflected beam is given by

$$\tan(\delta/2) = (\sin^2\phi - n_r^2)^{1/2}\cos\phi/\sin^2\phi$$

where $\phi$ is the angle of reflection, and $n_r = n_n/n$, the ratio of the refractive indices $n_n$ of the ambient material ($n_n = 1$ will be used throughout this paper) and $n$ of the crystal in which the internal reflection takes place. For some refractive indices characteristic of commonly employed IR transmitting materials, the resulting retardation ($\delta$) in dependence on the angle of reflection is given in Fig. 1. The lower angle of reflection for zero phase shift represents the critical angle $\phi_c = \sin^{-1}n_n$, below which no total reflection occurs. Its dependence on $n$ is shown in Fig. 2, along with those of the maximum phase shift $\delta_m$ and of the angle of reflection $\phi_c$, at which $\delta_m$ occurs.

![Fig. 1. Retardations $\delta$ due to one reflection in different materials vs. angle of reflection $\phi$. $n$(Ge) = 4.05; $n$(ZnSe) = 2.43; $n$(AgCl) = 2.00; $n$(KBr) = 1.53.](image-url)
FIG. 2. Maximum attainable retardation $\delta_m$ for one reflection which occurs at the angle $\phi_\text{m}$ as well as the critical angle $\phi_c$ for total reflection vs. refractive index of the prism material.

In order to produce circular polarization, a retardation of $90\degree$ is necessary; this can be achieved by a single reflection whenever the refractive index exceeds 2.4. Fortunately enough, several IR transparent materials are available which meet this condition. Among these "high-$n$" materials are ZnSe, GaAs, Si, and Ge. Other very common IR materials like KBr, NaCl, etc., belong to the class of "low-$n$" compounds, which can be used as quarterwave retarders with two reflections.

The graphs shown in Fig. 3 correlate the refractive index $n$ with $\phi$, the angle of reflection, for certain phase shifts. For a given refractive index, from this diagram the value of $\phi$ that is necessary for the desired retardation can be found. Conversely, if a certain geometry is to be used (e.g., in order to substitute a plane mirror by the reflecting retarder), the diagram indicates the appropriate refractive index.

In any case, the graphs display a minimum from which point the "wings" rise steeply and differently, for lower as well as higher angles of reflection. A certain retardation can be achieved only with a material, the refractive index of which is higher than that in the minimum of the corresponding curve $n(\phi)$. The minimum of the curve $\phi = \pi/2$ at about 2.4 gives the border between what was before called "high-$n$" and "low-$n$" materials. Additionally, a (real) retardation can be achieved only with reflection angles smaller than $\phi_\text{c} = (\pi - \delta)/2$. This is approached for $n = 0$, i.e., $n \to \infty$. On the other hand, whenever a certain retardation is attainable with a given material, one generally has the choice of two different angles of reflection, as is also obvious from Fig. 1. For preference of choice, the sensitivity to changes in the refractive index (achromatic behavior) and in the angle of reflection (divergence of incident radiation) should be taken into account. The gradient $\delta n/\delta n$ along the curves of constant retardation (Fig. 4) decreases monotonously with increasing angle of reflection, reaching zero at $\phi_\text{i}$, so that the smaller value of $\phi$ is less preferable. Another disadvantage of this value is the close vicinity to the critical angle $\phi_c$. 

FIG. 3. Refractive index $n$ necessary to produce a certain phase shift $\delta$ in dependence on the angle of reflection $\phi$. Additionally, the limit of total reflection is indicated by the critical angle $\phi_c$. 

FIG. 4. Partial derivatives of $\delta$ for constant retardation (left: $\delta = \pi/2$; right: $\delta = \pi/4$) vs. angle of reflection $\phi$. $\delta n/\delta \phi$; $\delta n/\delta \phi^2$; $\delta n/\delta \phi^3$. 

FIG. 4. Partial derivatives of $\delta$ for constant retardation (left: $\delta = \pi/2$; right: $\delta = \pi/4$) vs. angle of reflection $\phi$. $\delta n/\delta \phi$; $\delta n/\delta \phi^2$; $\delta n/\delta \phi^3$. 

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FIG. 5. Influence of the beam divergence (α) on the retardation δ produced by one reflection in an material of the given refractive index (Ge). The center ray is reflected under 43.0°; α refers to the divergence angle outside the retarder prism.

The stability with respect to changes in φ is primarily given by the gradient dδ/dφ. This is zero in the minimum of n(φ) and displays positive values at smaller angles and negative values at larger angles (Fig. 4). From this point of view, the minimum would be the best choice, provided that a material of this particular refractive index is available. For materials of higher refractive index, the stability is better when one is using the larger angle out of the two possible ones.

Next, the refraction occurring at the front surface of the retarder prism shall be taken into account. With normal incidence of the center ray provided, the opening angle α₀ of the beam is reduced to α₀/n(α₀ ≪ 1). For any ray of the beam outside the prism forming an angle φ + α with the normal of the reflecting surface, the effective angle of reflection becomes φₑ ≡ φ − α/n for small values of α.

Therefore, one has to compare nₑ(dδ/dφ), which is also shown in Fig. 4. Apart from the minimum of n(φ), this function also vanishes for φₑ. However, this stable position cannot be fully exploited in practice, since no material of more or less infinitely large refractive index is available.

A quantitative measure of the performance of a retarder is its efficiency in converting linearly polarized radiation into circularly polarized radiation, which can be defined by

\[ \eta = 1 - \sin \psi \sin \delta \]  

where \( \psi \) denotes the angle between the plane of polarization of the incident radiation and the plane of reflection in the retarder prism (azimuth of the electric vector). \( \eta \) varies from zero, for purely linear polarization of the emerging beam, to unity, for complete circular polarization. The latter is achieved only for \( \delta = \pi/2 \), along with \( \psi = \pm \pi/4 \). If we assume \( \psi \) to be set properly, Eq. 2 simplifies to

\[ \eta = \sin \delta. \]  

and \( 1 - \eta \) gives the remaining linearly polarized frac-
tion. In the case of a diverging beam, we have to average over the contributions from the different angles $\alpha$ concerning both the varying retardation and the distribution of radiant power. For a homogeneous beam with a circular cross section and an opening angle $\alpha_o$, the latter will approximately follow $(1 - (\alpha/\alpha_o)^2)^n$.

On this basis, we have calculated the efficiency of two single reflection quarterwave retarders: (1) a Germanium prism for an angle of reflection $\phi = 43^\circ$, and (2) a ZnSe prism for an angle of reflection $\phi = 32.5^\circ$.

The former serves as an example for a high refractive index, the latter for a refractive index close to the minimum value for quarterwave retardation. In both cases, an opening angle $\alpha_o = 6^\circ$ was assumed, which is quite typical for commercially available spectrometers. The retardations in dependence on $\alpha$ are given in Figs. 5 and 6, while the efficiencies are summarized in Fig. 7.

As far as the center ray is concerned, the Ge retarder is highly achromatic. In the range from 4000 to 600 cm$^{-1}$, the efficiency $\eta_c$ for a collimated beam deviates from unity by less than 3.10$^{-4}$. This interval could be further reduced by slight adjustment of the angle of reflection to $\phi = 42.93^\circ$. However, for a diverging beam ($\alpha_o = 6^\circ$) the reflected radiation comprises retardations in a range as

![Fig. 7. Efficiency $\eta$ of the Ge and ZnSe prisms vs. wavenumber for a beam of 6° opening angle outside the retarder prism.](image)

![Fig. 8. ZnSe Mooney rhomb for compensating the influence of the beam divergence ($n = 2.43, \phi = 65^\circ$).](image)
FIG. 9. Influence of the beam divergence (α) on the retardation δ_{total} achieved by two reflections in Mooney rhombs made from the materials indicated. (FG: flint glass.)

As a consequence, the total efficiency is about 0.9997 and is almost constant throughout the entire IR range.

For a collimated beam, the ZnSe retarder would be less advantageous due to the comparably large changes of the retardation with wavelength (Fig. 6). On the other hand, as outlined before, the deviations from the center retardation are more or less equal for positive and negative values of α, so that the range of retardations in the reflected beam is smaller than in the case of Ge. As a consequence, the efficiency for a diverging beam is higher for a ZnSe retarder, but below 800 cm\(^{-1}\) (see Fig. 7).

In the case that even such high efficiencies are not sufficient to meet the experimental requirements, or when larger angles of divergence are to be used, one can use two reflections, producing a retardation of 45° each in such a way that the influence of the divergence would be compensated for. This could be achieved by a device whereby a ray being reflected the first time under an angle smaller than the reflection angle of the center ray reaches the second reflecting surface under a larger angle, and vice versa (Fig. 8). Such a Mooney rhomb is well known for its large angle of acceptance.\(^6\) The compensation is better, the less the dependence of the retardation on the reflecting angle deviates from linearity, i.e., the smaller the absolute value of the second derivative \(\partial^2 \delta / \partial \phi^2\) is. These values—again multiplied by the refractive index \(n = n_\lambda / n\) in order to account for refraction—are given in Fig. 4. Obviously, best results are to be expected for \(\phi\) close to \(\phi_1\) or, in other words, for high-\(n\) materials.

The dependence of the retardation on the divergence has been calculated for three Mooney rhombs made from different materials, and the results shown in Fig. 9 prove the anticipated trend. Provided that the center ray produces a retardation of exactly 45° per reflection, the average efficiency is extremely high. Even for a divergence

\[
\theta = \phi - \sin^{-1}\left(\frac{1}{n}\right)
\]

FIG. 10. Optical design of a quarterwave retarder with two KBr prisms (R). M1, M1', flat mirrors; M2, M2', spherical mirrors; P, polarizer; S, sample.

FIG. 11. Optical design of a quarterwave retarder based on one reflection under 32.5° in a ZnSe prism (R). M1, M2, plane mirrors; M3, spherical mirror; P, polarizer; S, sample; F, instruments focus.
had been rescued before an old IR spectrometer was scrapped. For the sake of simplicity, we chose the layout given in Fig. 10, granting ample space for the sample and the polarizer. The optical scheme of our retarder, based on a single reflection in high-\(n\) material, is given in Fig. 11. The ZnSe prism for a reflection angle of 32.5° had been cut from a block \(2 \times 2 \times 4 \text{ cm}^3\) and shows a roof angle of 115°. Quarterwave retardation without additional focusing is possible with Ge (\(\phi = 43°\)), as outlined in Fig. 12.

A train of optical elements consisting of a polarizer, the vector of which defines the azimuth 0°; a birefringent crystal of the thickness \(d\), with its axes at \(\pm 45°\); and an analyzer either at 0° or at 90° azimuth modulates the intensity of the transmitted radiation according to (1 + \(\cos(2\pi d d\Delta n)/2\), when the wavenumber \(\tilde{v}\) is scanned; \(\Delta n\) denotes the birefringence, i.e., the difference between the ordinary refractive index and the extraordinary one. Upon insertion of an additional retarder (phase shift \(\delta\)) between the polarizers, the fringe pattern is shifted within the spectrum and is described now by (1 + \(\cos(2\pi d d\Delta n + \delta))/2\). This provides us with a reliable test for the performance of our retarders. Such patterns are shown in Fig. 13 for sapphire (\(d = 21.14 \text{ mm}\)). Quartz, rutile, and CdS were used for further tests; in all cases phase shifts close to 90° were indicated for both the devices shown in Fig. 10 and Fig. 11, respectively.

Extremely strong "circular dichroism" occurs in the range of selective reflection of cholesteric liquid crystals; due to the helical molecular arrangement, one circularly polarized component of incident radiation is reflected, while the countercurrent component is transmitted. This molecular arrangement can also be induced in a nematic (i.e., untwisted) liquid crystal by an optically active solution. The spectra shown in the upper part of Fig. 14 were taken with the use of such a solution, with its helical axis orientated parallel to the IR beam. For the three different spectra, the vector of the polarizer formed angles \(\psi = 0, +\pi/4, -\pi/4\) with the plane of reflection, re-

**EXPERIMENTAL**

Since every optical element may produce a phase shift or cause depolarization, the polarizer, retarder, and sample should immediately follow one another. For the same reason, there should be as few elements as possible between the sample and the detector. Consequently, for experiments with polarized radiation, preference should be given to an FT spectrometer where the radiation is modulated prior to reaching the sample. The polarizing influence of the monochromator, which in dispersive IR instruments is commonly located posteriorly to the sample, can cause serious artifacts. In any case, an efficient depolarizer (scrambler) would be highly desirable.

Our first retarder was built from KBr prisms which

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**Fig. 12.** Optical design of a quarterwave retarder without additional focusing. M1, M2 plane mirrors; R, retarder (Ge) used for reflection under 43.0°; F, instruments focus.

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as large as \(\alpha_m = 30°\) it deviates from unity only by \(2 \times 10^{-3}\) in the case of flint glass (the originally used material\(^{19}\)), by \(2 \times 10^{-4}\) in the case of ZnSe, and by \(1.3 \times 10^{-4}\) in the case of Ge. At least for the last two materials, the dispersion-dependent change in retardation is predominant again. In any case, however, for limited spectral intervals, an extremely high degree of circular polarization can be obtained, even for diverging beams, provided that the degree of linear polarization of the incident radiation is adequate.

**Fig. 13.** Shift of fringe patterns originallyy due to a sapphire retarder upon adding one of the described quarterwave retarders (see text).
spectively; consequently the sample was irradiated with linearly, left or right circularly, polarized radiation. The spectrum (a) for linear polarization is the average of the two other spectra, and the ratio of these shown in the lower part of Fig. 14 indicates by the compensation of the absorption bands that the selective reflection is indeed based on the molecular arrangement rather than directly on molecular chirality. Less pronounced circular dichroism is found in absorption bands outside the range of selective reflection; these are also easily measurable with the described accessories.

CONCLUSIONS

Retarders based on total internal reflections can be constructed for complete conversion of linearly polarized radiation into circularly polarized radiation. They are highly achromatic over large spectral ranges, what is important for the wide IR range—in particular when an interferometer is used. The retarders can be designed to be insensitive to the beam divergence. Since in the IR range transparent materials are available for which the refractive index exceeds 2.4, quarterwave retardation can be achieved by single reflection. In the case of germanium, this is possible without additional focusing. A common ATR accessory for single reflection (hemicylinder or hemisphere type) can serve as a readily available retarder, the phase shift of which can easily be adjusted by a change in the angle of reflection.

In this paper we confined ourselves to the problem of stationary generation of circular polarization. For measuring effects as faint as the VCD, polarization modulation is necessary in order to compensate precisely for fluctuations of the baseline. This problem will be dealt with in a forthcoming paper.

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