Detection of Monolayer Gratings of Adsorbates by Linear Optical Diffractions

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Abstract. We report the detection of linear optical diffraction of a He–Ne laser probe beam from a monolayer grating of molecular adsorbates up to the fifth order with no electronic or electromagnetic enhancement. The advantages of using linear diffraction to probe surface diffusion of adsorbates are discussed.

Optical diffraction from periodically modulated structures has long been used to study the dynamics of the excitations and the transport of energy and mass in materials [1]. Recently, Zhu and coworkers demonstrated that nonlinear optical diffraction from monolayer molecular gratings could be used effectively to probe surface diffusion of adsorbates [2, 3]. The optical method has the desirable capability of covering a large dynamic range of diffusion coefficients (10^{-7} to $10^{-14}\,cm^2/s$) and of readily resolving the anisotropy of diffusion dynamics [3, 4]. However, one drawback of the second-harmonic diffraction technique is the weakness of the absolute signal strength. Usually limited by the multi-pulse damage threshold, a typical second-harmonic diffraction signal from a fully modulated monolayer grating of small molecules covering an area $10\,mm^2$ is 0.05–0.2 photon-counts per pulse [2–5]. Thus in some cases, the nonlinear optical technique suffers from poor signal-to-noise ratios. For example, it will be difficult to use the technique to study the coverage dependence of diffusion coefficients by simply using weakly modulated coverage profiles. This motivated us to reexamine linear optical diffraction from monolayer gratings which was previously considered difficult to detect due to the large diffuse scattering background.

The typical signal strength of a linear diffraction from a monolayer grating of adsorbates is around 10^{-7} of the incident probe beam (Sect. 1). Using a 2mW He–Ne laser with 10^{16} photons per second, even a 10% modulated coverage profile leads to a typical signal strength that is expected to be rather large, in the range of 10^7 photons per second. The main obstacle to the use of a linear diffraction probe is that the diffraction signal is ac-companied by strong diffuse scattering due to the inevitable residual roughness on a nominally flat surface. The diffuse scattering into a pinhole of 3 mm diameter at 100 cm from the surface is typically around 10^{-6}–10^{-8} of the incident beam intensity, depending upon the angular separation of the scattering direction from the specular reflection. In this paper, we report a successful suppression of the diffuse scattering by a factor of 1000–2000 by reducing the solid angle for the optical detection and by using a modulation technique. The residual background is contributed mostly by the speckle pattern. Since this does not change with the adsorption of molecules, by subtracting it out electronically, we reduced the diffuse scattering by at least another two orders of magnitude. Therefore the achieved detection limit is 10^{-11}–10^{-13} of the incident beam intensity. To demonstrate the sensitivity of the linear diffraction technique after such a background suppression, we measured the linear diffraction of a He–Ne laser probe beam up to the fifth order from a monolayer coverage grating of Rhodamine 6G dye molecules adsorbed on a fused quartz plate. The intensity of the fifth order diffraction was 10^{-11} of the incident beam intensity.

1. Theoretical Background: Linear Optical Diffraction from a Monolayer Grating

Radiation from a monatomic or mono-molecular layer of a material has been extensively investigated in the context of surface optical reflectance spectroscopy and surface second-order nonlinear optics [5–12]. The basic physical considerations are the same here. We will use the recent results by Shen [8]. Consider a monolayer periodic density

profile of adsorbates sandwiched between two bulk media with dielectric constants ε_1 and ε_2. In an optical field $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t)$ incident from medium ε_1, the response of the monolayer can be described by an induced dipole sheet $\mathbf{P}_s(\mathbf{r}, t)\delta(z) = \mathbf{P}_{s0}\theta(\mathbf{r})\delta(z)\exp(ik_x x - i\omega t)$ with

$$\theta(\mathbf{r}) = f_0 + \sum_{n=1} f_n \cos(n\pi x/a). \tag{1}$$

Thus

$$\mathbf{P}_s(\mathbf{r}, t) = \mathbf{P}_{s0}\left[f_0 + \sum_{n=1} f_n \cos(n\pi x/a)\right]$$
$$\exp(ik_x x - i\omega t). \tag{2}$$

Here $\theta(\mathbf{r})$ is the density or coverage profile of the molecules, and $\mathbf{P}_{s0}$ is the induced dipole moments per unit area at $\theta(\mathbf{r}) = 1$. $2a$ is the periodicity. $x-z$ is in the plane of incidence with x in the surface plane of the dipole sheet, and z along the surface normal. Except for the zeroth order "diffraction" which is accompanied by the reflection from the bulk medium ε_2, the $n \geq 1$ order diffraction is simply the radiation emitted by a polarization sheet

$$\mathbf{P}_s(\mathbf{r}, t) = \mathbf{P}_{s0}(f_n/2)\exp[i(k_x + n\pi/a)x - i\omega t]. \tag{3}$$

Using the notation of Shen, the corresponding radiation fields $E_{p(or\,s), n}\exp[i(k_x + n\pi/a)x - i\omega t]$ in medium ε_1 are

$$E_{p, n} = \frac{i2\pi k_1}{\varepsilon_1 k_{1z}}[k_{1z}L_{xx}P_{s0, x} + k_x L_{zz}P_{s0, z}](f_n/2). \tag{4}$$

$$E_{s, n} = \frac{i2\pi k_1^2}{\varepsilon_1 k_{1z}}L_{yy}P_{s0, y}(f_n/2). \tag{5}$$

L_{xx}, L_{yy}, and L_{zz} are the macroscopic local field factors due to the differences in the dielectric constants of the monolayer ε' and the two bulk media ε_1 and ε_2 [8]. They approach unity as ε', ε_1 and ε_2 become equal. From the radiation fields, we can calculate the output signal in photons per second:

$$S_{p, n}(\omega) = \frac{c\varepsilon_1}{2\pi}|E_{p, n}(\omega)|^2\frac{2\pi A}{\hbar\omega}. \tag{6}$$

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To estimate typical signals from a monolayer grating of molecules on a quartz plate, we take $L_{xx} = L_{yy} = L_{zz} = 1$, $\varepsilon' = \varepsilon_1 = \varepsilon_2$, and the molecular polarizability $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$. Thus the signal is given by

$$S_{p(or\,s), n} = S_{p(or\,s), i}\left(\frac{2\pi k_0}{\cos\theta_{inc}}\right)^2 |N_s\alpha|^2\left(\frac{f_n}{2}\right)^2. \tag{8}$$

$S_{p(or\,s), i}$ is the incident photon flux. For $N_s\alpha \sim 5 \times 10^{-9}$ esu, $\cos\theta_{inc} \sim 1$, $f_n \sim 0.5$, $2\pi k_0 \sim 6 \times 10^5$ cm^{-1}, we find

$$\frac{S_{p(or\,s), n}}{S_{p(or\,s), i}} \sim 6 \times 10^{-7}. \tag{9}$$

Here, we also give an estimate of the diffraction signal from a metal surface covered with a periodic distribution of adsorbates given by (1). This is particularly relevant to

our ongoing experimental studies of surface diffusion of small molecules on metals using the linear optical diffraction technique. Usually small molecular adsorbates have small intrinsic polarizabilities compared to a bare metal surface. However, as a result of the adsorbate-metal interaction, they change the polarizability of the metal surface [8–12]. If we model the linear susceptibility of the surface layer $\chi(\mathbf{r})$ in terms of the polarizabilities of an unaffected metal atom, α_m and of an metal atom interacting with an adsorbate, α_{int}, we find

$$\chi(\mathbf{r}) = N_s\alpha_m + N_s(\alpha_{int} - \alpha_m)\sum_{n=1} f_n\cos(n\pi x/a). \tag{10}$$

Here we assume that α_m and α_{int} do not change with adsorbate coverage $\theta(\mathbf{r})$. The $n \geq 1$ order diffraction is then calculated from (4) and (5) with $\mathbf{P}_{s0}$ replaced by $N_s(\alpha_{int} - \alpha_m)$ and the appropriate local field factors. Assuming that the surface layer has the same dielectric constant as the metal substrate and hence the transmitted electric field induces the dipole sheet, we may ignore the $\mathbf{P}_{s0, z}$ term. We take $\varepsilon_1 = 1$ (vacuum). Since $\varepsilon_2 = \varepsilon_m \gg 1$, $L_{xx} \sim 2/[\varepsilon_m^{1/2}\cos\theta_{inc}]$, $L_{yy} \sim 2\cos\theta_{inc}/(\varepsilon_m^{1/2})$, we find

$$\frac{S'_{p, n}}{S'_{p, i}} \approx \left(\frac{2\pi k_0}{\cos\theta_{inc}}\right)^2\frac{4}{|\varepsilon_m|}|N_s(\alpha_m - \alpha_{int})|^2\left(\frac{f_n}{2}\right)^2. \tag{11}$$

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For an estimate, we deduce α_m from the bulk dielectric constant ε_m. We take Ni(111) with $\varepsilon_m = -10.06 + i\,14.77$ at $\lambda = 0.633\,\mu$m [13]. Since $\varepsilon_m = 1 + 4\pi N_b\alpha_m$, $N_b = 9.14 \times 10^{22}$ cm^{-3}, we have $|\alpha_m| = 1.6 \times 10^{-23}$ esu. Assuming $\alpha_m \gg \alpha_{int}$, from $N_s = 1.8 \times 10^{15}$ cm^{-2}, we find $N_s(\alpha_m - \alpha_{int}) \approx 3 \times 10^{-8}$ esu. For $\cos\theta_{inc} \approx 1$, $f_n \approx 0.5$, we arrive at

$$\frac{S'_{p(or\,s), n}}{S'_{p(or\,s), i}} \approx 4 \times 10^{-6}. \tag{13}$$

Usually, a finite α_{int} may lead to a smaller diffraction signal. Another independent estimate may be obtained from the experimentally measured surface reflectance change of a metal due to adsorption [9–12]. The differential reflectance upon adsorption comes mainly from the addition of the zeroth order radiation from the dipole sheet to the reflection from a bare metal substrate. The total electric field of p-polarization in reflection (i. e., in medium $\varepsilon_1 = 1$) is given by

$$E_{p, 0} = E_{p, i}\{r_p^0 + i2\pi k_1 L_{xx}(1 + r_p^0)N_s[\alpha_m(1 - f_0) + \alpha_{int}f_0]\}. \tag{14}$$

The differential reflectance is obtained as

$$\frac{\Delta R}{R_0} = (4\pi k_0 N_s)\,\text{Im}\left\{\frac{L_{xx}(1 + r_p^0)[\alpha_m(1 - f_0) + \alpha_{int}f_0]}{r_p^0}\right\} \tag{15}$$

If we ignore α_{int} and assume that the real part and the imaginary part in the parentheses are comparable, we can express the $n \geq 1$ order diffraction in terms of $\Delta R/R_0$:

$$\frac{S'_{p, n}}{S'_{p, i}} \geq \frac{1}{2}\left(\frac{\Delta R}{R_0}\right)^2\left[\frac{f_n}{2(1 - f_0)}\right]^2. \tag{16}$$

For hydrogen on W(110), for example, $\Delta R/R_0 \approx 3 \times 10^{-3}$ [12]. Using $f_0 = 0.5$, and $f_n = 0.5$, we find

$$\frac{S'_{p,n}}{S'_{p,i}} \approx 4 \times 10^{-6}. \qquad (17)$$

2. Experimental Results

The experiment was carried out in two steps. We first measured the diffuse scattering of a 2 mW He–Ne laser beam from three nominally flat samples without adsorbates: a $\lambda/10$, 10–5 research grade polished fused silica from CVI Corporation, a polished Cu single crystal disc and a polished Ni single crystal disc. The latter two are representative of the metal substrates routinely used in optical studies of surfaces. We then used three detection procedures to reduce the diffuse background with the consideration of not losing potential linear optical diffraction signals. In the second step, we prepared a monolayer grating of Rhodamine 6G molecules on the fused silica plate using a laser-induced desorption technique, and measured the diffraction of the He–Ne laser from the grating.

As reproduced in Table 1, we found that the strength of the diffusely scattered light into a pinhole of a diameter $d_0 = 3$ mm at a distance $L = 100$ cm is typically 10^{-6} of the incident beam from the metal samples and 3×10^{-8} from the fused silica (the large difference is presumably due to the difference in reflectivity). The measurements were performed at angles of more than 15° from the specular reflection. The diffuse scattering becomes much stronger when the outgoing angles are within 5° from the specular reflection. Otherwise, the scattering was found to be relatively isotropic, having a slow angular variation presumably due to the random distribution of the scale of the surface roughness. Furthermore, the isotropic distribution of the scattering changed little when the incident beam was more or less focused, as one would expect. Thus, we took advantage of these facts to reduce the diffuse scattering in our experiment.

The experimental arrangement is shown in Fig. 1. First, we reduced the detection solid angle in order to decrease the throughput of the diffuse scattering. To achieve this without reducing potential diffraction
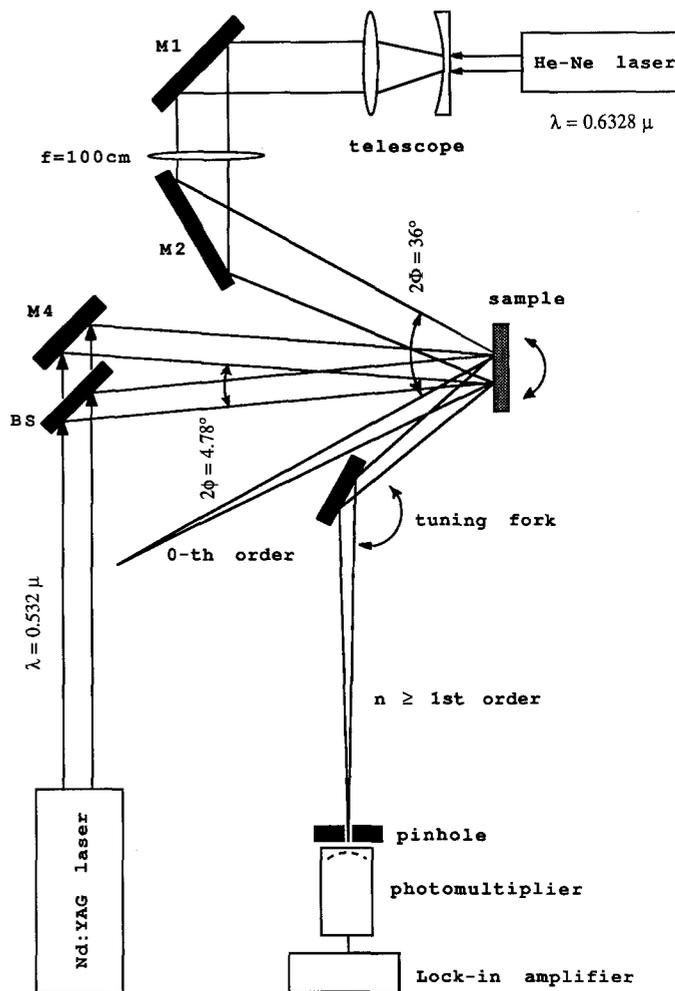
Fig. 1. Experimental setup for the measurement of linear optical diffraction from a monolayer coverage grating of Rhodamine 6G dye molecules on a fused silica plate. A pair of laser pulses, at $\lambda = 0.532$ µm and incident at angles $\phi = +2.39°$ and $-2.39°$ are used to desorb the molecules to create the grating profile. A He–Ne laser probe beam incident at $\Phi = 18°$ is diffracted off the grating. BS is a 50/50 beam splitter. M1, M2, M3, and M4 are the reflectors

signals, we used a converging He–Ne laser beam with the focal point behind the sample where a small pinhole was placed, and we detected the light after the pinhole. Since linear diffraction signals would be focused, but not the diffuse scattering, the latter was cut down significantly.

Table 1. Measured strengths of the diffusely scattered light from three nominally flat surfaces before and after using the suppression schemes, and typical linear diffraction signals from monolayer molecular gratings (normalized to the incident He–Ne laser beam intensity)

	Fused silica (glass)	Polished copper (Cu)	Polished nickel (Ni)
Without any suppression: $\Delta\Omega_0 = 3 \times 10^{-6}$ sr	3×10^{-8}	1×10^{-6}	2×10^{-6}
With the reduced detection solid angle only: $\Delta\Omega = 1.2 \times 10^{-7}$ sr	5×10^{-10}	2×10^{-8}	3×10^{-8}
With both the reduced solid angle and the modulation suppression:	2×10^{-11}	1×10^{-9}	1×10^{-9}
With an additional electronic subtraction:	$\leq 2 \times 10^{-13}$	$\leq 1 \times 10^{-11}$	$\leq 1 \times 10^{-11}$
Typical linear diffraction signal strengths	6×10^{-7}	4×10^{-6}	4×10^{-6}

We first expanded the He–Ne laser beam to a cross-section of 10 mm² with a telescope, then focused it down using a 100 cm converging lens. The beam diameter was around 150 μm at the focal point where we put a pinhole of a diameter $d_{pin} = 240$ μm in front of a photomultiplier detector. The sample was placed after the lens at about $L_0 = 60$ cm before the pinhole. The He–Ne beam was incident on the sample at $\Phi = 18°$ from the surface normal. In this arrangement, the detection solid angle was reduced from $\Delta\Omega_0 = \pi(d_0/2L)^2 \approx 7 \times 10^{-6}$ sr to $\Delta\Omega = \pi(d_{pin}/2L_0)^2 \approx 1.2 \times 10^{-7}$ sr. We indeed found that the diffusive scattering was reduced by roughly a factor of 60. We note that the small solid angle of 1.2×10^{-7} sr is close to the diffraction limit. Thus it is not possible to reduce this much further.

To achieve a further reduction, we used a modulation technique. Since the angular distribution of the scattering is relatively smooth, whereas diffraction signals have narrowly peaked angular distributions, the contribution of the scattering could be further reduced by moving diffraction signals in and out of the small pinhole and detecting the difference. If the diffuse scattering is completely isotropic, the differential signals should only come from diffraction. Experimentally, we inserted a tuning fork between the sample and the pinhole, at about $L_1 = 40$ cm away from the pinhole. The tuning fork is a mirror that is rotated about a vertical axis coinciding with the mirror plane with a controllable amplitude and a variable frequency at around 1000 Hz. At small amplitudes of the rotation, the mirror brings the scattering along polar angles which are different by only $(d_{pin}/L_1) \approx 6 \times 10^{-4}$ rad alternately into the small pinhole. The differential signal is detected by a lock-in amplifier. With this arrangement, we found that the scattering background was further reduced by a factor of 20–30.

With these two procedures, we achieved an overall reduction by a factor of 1000–2000, and the contribution of the diffuse scattering was reduced to less than 1×10^{-9} for the metals and 2×10^{-11} for the fused silica. The residual background in the differential detection comes mainly from the speckle pattern. Since such a background does not change upon molecular adsorption, it is easily subtracted out. This brought the detection limit down by at least another two orders of magnitude, namely, to 1×10^{-11} for metals and 2×10^{-13} for the fused silica. In Table 1, we tabulate the measured diffuse scattering strengths for the three samples (normalized to the strength of the incident He–Ne beam) before and after the reduction procedures, together with typical strengths of linear diffraction from monolayer gratings obtained in the last section.

With such an effective background suppression, we were ready to observe linear diffraction from a monolayer grating of molecular adsorbates, according to our estimates in the previous section. We chose Rhodamine 6G dye molecules on fused silica as a model system for demonstration. This system is favorable as the dye molecules strongly absorb photons at 0.532 μm. They are thus readily desorbed by the frequency-doubled output of a Q-switched Nd:YAG laser operating at 1.064 μm. We could easily create a monolayer molecular grating on a fused silica using a pair of interfering laser pulses at 0.532 μm [6, 7]. Since it was important that we avoided electronic resonance enhancement so that the result of the present demonstration would be general, we chose the He–Ne laser ($\lambda_p = 0.633$ μm) as the probe beam [6, 7, 13]. The wavelength is far from the first vibronic resonance peaking at $\lambda(S_0 \rightarrow S_1) = 0.532$ μm. Thus the dye molecules should behave almost like an organic dielectric with a bulk dielectric constant $\varepsilon' \approx 2$. This provides a crucial test of the linear diffraction technique as the grating is optically very thin, and, in contrast to the study by Rothenhäusler and Knoll, the radiation is not enhanced by any surface enhancement mechanisms [13].

The monolayer of Rhodamine 6G dye molecules on the fused silica was prepared with a liquid spinning technique [6, 7]. The average surface density of dye molecules was 2×10^{14}/cm². To make a grating, we used the same procedure as adopted by Suzuki and Heinz [7]. We overlapped a pair of equally intense laser pulses at $\lambda_{exc} = 0.532$ μm on the surface. The ablation of the dye molecules due to the absorption of the periodically varying intensity field left behind a periodically modulated coverage profile on the surface. The angles of incidence for desorption were $\phi = +2.39°$ and $-2.39°$, respectively. The grating periodicity was thus $2a = \lambda_{exc}/|2\sin\phi| = 6.38$ μm. The size of the grating was about 3 mm in diameter. Near the center, in a region of diameter 1.6 mm, the laser intensity was calculated to be

$$I(x) = 1.1 \ [1 + \cos(\pi x/a)] \ \text{J/cm}^2 \ . \tag{18}$$

This yielded an almost fully modulated grating as determined from the strength of the first order linear diffraction.

For the linear diffraction measurement, the He–Ne probe beam was incident on the center part of the grating on the sample at $\Phi = 18°$. The diffraction signals emerged at the expected diffraction angles Φ_n,

$$\sin\Phi_n = \sin\Phi \pm n\lambda_p/2a \ . \tag{19}$$

For the actual measurement, we kept the detection system unchanged and rotated the sample to bring different diffraction orders into the detector. We were able to detect diffraction to as high as the fifth order even without electronic subtraction of the scattering background. Most significantly, the ratio of the first order diffraction to the incident beam is 1.5×10^{-7}, as we had anticipated. And for the fifth order diffraction, the relative signal is 2×10^{-11}. The results are plotted in Fig. 2. We were not able to measure the zeroth order diffraction separately as it was accompanied by the reflection from the quartz substrate. Thus it is not shown in the figure. To our knowledge, this is the first observation of linear optical diffraction from a monolayer molecular grating without electronic resonance or any other surface enhancement. The signal was averaged over a few seconds, and the error bars are significantly less than 1% for all the measurements, stemming mainly from the averaging time and the intensity fluctuations of the He–Ne laser at around 1 kHz. The photon statistics was clearly not the limitation.
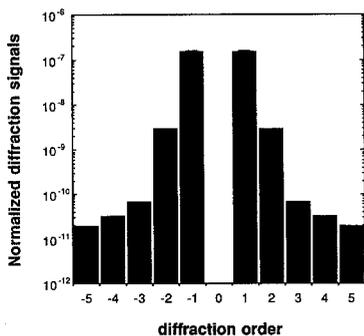
Fig. 2. The measured linear diffraction signal strengths vs diffraction order. All the signals are normalized to the strength of the incident beam

To quantitatively compare the measurement with the theoretical estimates, we need to know the linear polarizability of Rhodamine 6G molecule at $\lambda_p = 0.633\ \mu m$. Since the molecule has a strong vibronic transition $(S_0 \to S_1)$ at $\lambda_{exc} = 0.532\ \mu m$ and even though λ_p is sufficiently far from the resonance that the optical response is predominantly dispersive, the two wavelengths are still relatively close so we can reasonably approximate the optical response as dominated by the $S_0 \to S_1$ transition. Thus the molecular polarizability is given by

$$\alpha(\omega) \approx \alpha_{res} \frac{i\Gamma_{01}}{\omega - \omega_{01} + i\Gamma_{01}}, \tag{20}$$

where ω_{01} is the $S_0 \to S_1$ transition frequency, and Γ_{01} is the linewidth of the transition. α_{res} is the polarizability at the transition frequency. We calculate α_{res} from the absorption cross section σ_{res} of Rhodamine 6G. As $\sigma_{res} = (8\pi^2/\lambda_0)\alpha_{res} = 4 \times 10^{-16}$ esu, we find $\alpha_{res} = 3 \times 10^{-22}$ esu [15]. From the recent femtosecond optical relaxation studies in large dye molecules, we estimate the inverse of the linewidth, $1/\Gamma_{01}$ to be around 2×10^{-14} s [16, 17]. From these numbers we estimate $\alpha(\lambda_p = 0.633\ \mu m) \approx 2.6 \times 10^{-23}$ esu. With the maximum coverage $N_s = 2 \times 10^{14}/cm^2$, $N_s\alpha(\lambda_p = 0.633\ \mu m) \approx 5 \times 10^{-9}$ esu. As can be seen, the measured first order diffraction signal strength agrees remarkably well with the theoretical estimate given by (8) and (9). Note that the higher diffraction orders are 2 to 4 orders of magnitudes weaker than the first order diffraction. This shows that the desorption in the present case is not a thermally activated process; instead, the rate of desorption seems to be linearly dependent on the intensity. This result is at variance with the findings of Suzuki and Heinz. However, we notice that their grating profiles also follow the laser intensity profile more closely than predicted by their thermal desorption model, thus seemingly also indicative of a substantial photodesorption in addition to the thermal desorption [17].

3. Discussion and Concluding Remarks

We have shown that linear optical diffraction can indeed be detected with extremely high signal-to-noise ratio after suppressing the diffuse scattering background both

optically and electronically. The success of such detection does not rely on any surface or electronic resonance enhancement mechanisms. The estimates presented in Sect. 1 of typical diffraction signal strengths from a monolayer coverage grating of adsorbates on a surface of either a metal, or a semiconductor, or an insulator should not vary significantly from sample to sample. Therefore, the linear diffraction technique should be widely applicable in probing monolayer adsorbate gratings. If we use 10^{-11} as the detection limit, we should be able to detect with a signal-to-background ratio of 10 a submonolayer grating which has a modulation as small as 3% of a full monolayer coverage. This is very significant if one is to use this technique to probe surface diffusion of adsorbates by monitoring the evolution of the coverage grating. With a small modulation, the diffusion coefficient may be treated as a constant [2–4]. This is particularly important as we can now study the coverage dependence of diffusion coefficients with an accuracy of 3% of a full monolayer and starting from coverages as low as a few percent of a full monolayer. Moreover, it is known that for many adsorbate-substrate systems, surface linear susceptibilities do not vary in proportion to adsorbate coverage. In these cases, equation (10) and the assumption that the nth order linear optical diffraction is proportional to the square of the nth Fourier coefficient of the coverage profile are good approximations only when the variation of the coverage is small. As an additional advantage, the effect of heating the samples with a 2 mW continuous wave He–Ne laser is completely negligible compared to the use of a nonlinear optical probe. This is crucial for surface diffusion measurements at low temperatures. Compared to the nonlinear optical technique [4, 6, 7], we believe that this linear technique is more sensitive and less intrusive, therefore more versatile and powerful for detecting monolayer grating structures [5]. We are currently applying this technique in a series of surface diffusion studies on single crystals of metals at low temperature.

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