Excited-state spectroscopy of organic dyes by use of population gratings

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Excited-state spectroscopy of organic dyes is demonstrated with a laser-induced grating technique. The basis of this method is the creation of a population grating in the material that is being investigated and the use of a probe detuned from the pump, permitting a great increase in effective contrast. The absorption-emission spectrum of transitions from $S_1$, the first singlet state, were determined from the diffracted signal of the tunable probe laser. The resulting theory of the grating function and the results of experiments on Nile Blue and Rhodamine 640 are presented. In conjunction with other techniques such as flash photolysis, population gratings may provide useful information on excited-state structures of dye molecules.

INTRODUCTION

Laser-induced population gratings are powerful tools for spectroscopy and investigation of relaxation dynamics. In a typical experiment two light beams derived from the same laser source interfere within an absorbing sample, inducing a spatially modulated distribution of excited-state molecules (a population grating). This population-grating structure can then diffract either the writing beams (self-diffraction) or a third beam used as a reading probe.

The use of population gratings for excited-state spectroscopy was studied in Refs. 3–5. This technique is more responsive than conventional flash (or laser) photolysis because the diffracted signal is essentially free of background and can thus be amplified to the desired level. In photolysis measurements, on the other hand, a small change in transmission has to be subtracted from a large signal, which often requires the use of highly linear detectors, high-dynamic-range electronic circuits, and in digitized data-acquisition systems, high-precision analog-to-digital converters. Furthermore, the population grating also provides information about the real and the imaginary parts of the complex refractive index, whereas conventional photolysis measures only the imaginary (absorption) part.

We consider in this paper the technique proposed in Ref. 5, in which a population grating is created at a fixed wavelength and a tunable probe is used to make the spectroscopic measurements. Diffraction of the probe occurs at optical frequencies for which the molecular polarizability of the excited state differs from that of the ground state. By measuring the grating efficiency as a function of the probe frequency, one can obtain a spectrum of the excited-state resonances. We show that the excited-state absorption and emission cross sections can be directly measured by a simple normalization of the grating efficiency, and, if the absorption and fluorescence bands are well separated, one can measure the fluorescence emission cross section directly, without calibration standards or laborious evaluation of the collecting-optics correction factors, as is the case with fluorescence spectroscopy. In this investigation we analyze the essential points of the technique and critically discuss its advantages and limitations. We present experiments in two organic dye molecules: Nile Blue and Rhodamine 640. In Nile Blue we demonstrate the potentials of the technique, and in Rhodamine 640 some of its limitations.

THEORY

The arrangement for the production of laser-induced population gratings is simple. Two beams from a single writing laser (wavelength $\lambda_w$), propagating close to the $z$ axis, intercept at a small angle $\theta$ as in Fig. 1. In this figure the input face of the sample (thickness $l$) is the $z = 0$ plane, the writing beams are in the $x-y$ plane, and the modulation occurs along the $x$ axis with a spatial period $\lambda = 2\pi/q = \lambda_w/\theta$, where $q$ is the modulus of the grating wave vector. If the two beams have the same intensity $I_w$, then the total writing intensity in the interference region is

$$I(r) = 2I_w(x)[1 + \cos(qx)].$$

Also shown in Fig. 1 is the incident probe beam (wave vector $k$, optical field $E$) that is being diffracted by the grating into the first diffraction order $k_{\perp}$. Consider now an isotropic medium of dilute molecules in a transparent host matrix or solvent (such as organic dyes in solutions) and assume that, under stationary excitation by the writing beams, the molecules are distributed between the ground and the excited states, with respective population fractions $f_0$ and $f_1 = 1 - f_0$. Consider a quasi-monochromatic probe field (reading beam) at a frequency $\omega$,

$$E(r, t) = \frac{1}{\sqrt{2}}E(r)\exp(i\omega t) + \text{c.c.}$$

The linear response of the medium to this field can be described by a polarization $P(r, t) = \frac{1}{\sqrt{2}}P(r)\exp(i\omega t) + \text{c.c.}$, with

$$P(r) = \epsilon_s(n^2 - 1)E(r) + \epsilon_s(f_0\chi_0 + f_1\chi_1)E(r).$$
The first term on the right-hand side of Eq. (2) is the polarization that is due to the solvent, which is assumed to be linear with refractive index \( n \) (\( \varepsilon_0 \) is the vacuum dielectric permittivity). The second term represents the contribution of the absorbing molecules. If all the molecules are in the ground state (\( f_0 = 1, f_1 = 0 \)) the total susceptibility of the medium is given by \( n^2 - 1 + \chi_0 \). On the other hand, if all molecules were in the excited state, the total susceptibility would be \( n^2 - 1 + \chi_1 \).

At low writing intensities (\( I_w \ll I_s \)), where \( I_s \) is the saturation intensity of the molecules at the writing wavelength, the excited-state population is \( f_1 = I(r)/I_s \); using Eq. (1), we obtain

\[
P(r) = \varepsilon/[n^2 - 1 + \chi_0 + (2I_w/I_s)(\chi_1 - \chi_0)] - (2I_w/I_s)(\chi_1 - \chi_0)\cos(qx)]E(r). \tag{3}
\]

The term in \( \cos qx \) represents the polarization source for the diffraction of the probe. In the absence of the writing laser, the probe is described by \( E(r) = E_0 \exp[-i(k_z z + k_x x)] \), where \( k_z \) and \( k_x \) satisfy the dispersion relation

\[
k_z^2 + k_x^2 = (\omega/c)^2(n^2 + \chi_0). \tag{4}
\]

Note that \( k_z \) is complex, \( k_z = k_z^* + ik_z^\prime \), and (in the absence of the grating) \( E_0 \) is constant; the attenuation of the probe intensity is accounted for by the factor \( \exp(-ik_z z)^2 = \exp(2k_z z^2) \), i.e., \( -2k_z^2 = \alpha(\omega) \) is the linear absorption coefficient at the probe frequency.

In the presence of the grating the probe field is still given by \( E(r, t) = \frac{1}{2}\eta E_0(r)\exp(i\omega t) + c.c., \) but now

\[
E(r) = E_0 \exp[-i(k_z z + k_x x)]
+ E_1 \exp[-ik_z z - i(k_x + q)x]
+ E_{-1} \exp[-ik_z^* z - i(k_x + q)x], \tag{5}
\]

where \( E_{\pm 1} \) are the amplitudes of the first-order diffracted waves and \( k_{\pm 1} \) are obtained from the dispersion relation

\[
k_{\pm 1}^2 + (k_x \pm q)^2 = (\omega/c)^2(n^2 + \chi_0). \tag{6}
\]

The diffracted intensity at \( z = \ell \) is given by

\[
I_{\pm 1}(\ell) = \frac{1}{2}\eta \varepsilon_0 n \chi_{\pm 1}(\ell) \exp(-ik_{\pm 1} \ell), \tag{7}
\]

and the grating efficiency for first-order diffraction is

\[
\eta_{\pm 1} = I_{\pm 1}(\ell)/I_0(0). \tag{8}
\]

To calculate the diffracted field amplitudes at \( z = \ell \), we introduce the wave equation

\[
[\nabla^2 + (\omega/c)^2]E(r) = (\omega^2/\varepsilon_0 c^2)P(r). \tag{9}
\]

Using the slowly varying envelope approximation \( [\partial E_m/\partial z] \ll |h_m E_m| \) (\( m = 0, \pm 1 \)) and assuming low diffraction efficiency \( |E_{\pm 1}| \ll |E_0| \), we obtain the following set of equations:

\[
2i\kappa_1 z E_0/\partial z = (\omega/c)^2(\chi_1 - \chi_0)(2I_w/I_s)E_0,
2i\kappa_{\pm 1} z E_{\pm 1}/\partial z = (\omega/c)^2(\chi_1 - \chi_0)(I_w/I_s)E_0
\times \exp[i(k_{\pm 1} - k_z)z]. \tag{10}
\]

In principle Eqs. (10) can be solved numerically to yield the grating efficiency [Eq. (8)] with \( \chi_1 \) used as a fitting parameter for each probe frequency. \( \chi_0(\omega) \) can be obtained from a Kramers–Kronig transformation of \( \chi_0(\omega) \), which in turn is obtained from the linear absorption spectrum, since \( \alpha(\omega) = -\omega \chi_0(\omega)/n\varepsilon \). However, an approximate analytical solution to Eqs. (10) can be obtained, which greatly simplifies the analysis of experimental results and reveals several features of the population-grating technique. If the medium is optically thin for both the writing and the probe lasers, we can neglect the \( z \) dependence of \( I_w \) and \( E_0 \); and, if the incidence of the probe is at a small angle, we can also neglect phase-mismatch effects (\( |k_{\pm 1} - k_z|/\ell \ll 1 \); Eqs. (10) can then easily be integrated to yield

\[
I_{\pm 1} = (\omega/2nc)^2[\chi_1 - \chi_0]^2(I_w/I_s)^2 I_0 \ell^2. \tag{11}
\]

Thus the first-order diffraction efficiency as a function of the probe frequency is given approximately by

\[
\eta_{\pm 1}(\omega) = (\omega \ell I_w/2nc I_s)^2[\chi_1(\omega) - \chi_0(\omega)]^2. \tag{12}
\]

It is useful to define a population-grating spectral function with the dimension of area:

\[
G(\omega) = (2I_s/NI_w\varepsilon)[\eta_{\pm 1}(\omega)]^{1/2} = (\omega/N \varepsilon \varepsilon_0 c^2)[\chi_1(\omega) - \chi_0(\omega)], \tag{13}
\]

where \( N \) is the number density of absorbing molecules. Note that in this approximation \( G(\omega) \) is independent of the writing and the probing intensities. It is also convenient to introduce the complex cross section for a state \( |j \rangle \),

\[
\sigma_j(\omega) = (\omega/ncN)\chi_j(\omega) = (\omega/ncN)\chi_j(\omega) + i\sigma_j^*(\omega), \tag{14}
\]

where \( \sigma_j(\omega) \) is the absorption cross section for molecules in state \( |j \rangle \). In terms of the complex cross sections, we have that

\[
G(\omega) = |\sigma_j^*(\omega) - \sigma_j^*(\omega)|. \tag{15}
\]

One can see that if a frequency \( \omega_0 \) exists for which \( \chi_j(\omega_0) \approx 0 \) and \( \sigma_j^*(\omega) \approx 0 \) (for example, at an isolated ground-state transition resonance with no overlap with an excited-state
in absolute values (without any other correction). The shape of $G(\omega)$ is not exactly the shape of that of the absorption–emission bands; rather, it is deformed by the contribution from the real part of the susceptibility. This limitation is not absolute, however, and variants can be implemented to separate the contributions from the phase and the amplitude gratings in the diffracted signal. On the negative side, the technique has a clear limitation in that for a definite interpretation of the recorded spectra the ground and the excited-state bands should be well separated.

**EXPERIMENTS**

For the investigation of population-grating spectra, we mounted the experimental arrangement shown schemati-
Fig. 4. Experimental setup for population-grating spectroscopy. Two-headed arrows indicate translatable components.

cally in Fig. 4. A \( \text{N}_2 \) laser (1-MW peak power, 5-Hz repetition rate, and 8-ns pulse duration, wavelength \( \lambda = 337.1 \text{ nm} \)), is used to pump two dye lasers. One of these, the more intense, is used to write the grating and is maintained at a fixed wavelength. The other dye laser was used as a tunable probe to read the grating as a function of wavelength and thus to measure the population-grating spectral function, \( G(\lambda) \).

The output of the writing laser is divided into two beams (with approximately equal intensities) in a modified Michelson interferometer and recombined in the sample to induce the grating. One of the interferometer arms incorporates a movable prism to adjust the optical path difference for maximum contrast of the interference fringes, and one of the mirrors is mounted on a translation base for controlling the grating period \( \Lambda \).

The probe pulse passes through a variable delay line that is used to compensate for the path difference between the writing and the probing pulses. The relative temporal position of the reading and writing pulses was monitored with fast photodiodes and an oscilloscope, with a combined rise time of less than 1 ns. We adjusted the optical delay line so that the reading pulse always arrived 1 ns after the writing pulse. Ensuring a constant delay between writing and reading pulses is important for eliminating artifacts that are due to the \( \lambda - \tau \) effect, i.e., the fact that the lasing delay of the tunable laser varies with the selected wavelength.

The first-order diffracted probe beam was carefully isolated from the scattered writing light and spurious reflections. Slow photodiodes were used to detect the energy of the first-order diffracted pulse (signal proportional to \( I_0 \)), principal signal of the experiment, and reference signals from the writing (\( \propto I_w \)) and reading (\( \propto I_0 \)) pulses. The signals from the three photodiodes were captured with a three-channel homemade sample-and-hold circuit. The sampling gate was set 200 ns after the \( \text{N}_2 \) laser pulse, when the discharge noise of this pulsed gas laser was negligible. The analog signals were digitized by a 10-bit analog-to-digital converter placed into a slot of a microcomputer. Approximately 50 laser pulses were collected for each probe wavelength. The microcomputer was programmed to trigger the \( \text{N}_2 \) laser and the sample-and-hold circuits, read the analog-to-digital converter, calculate a quantity proportional to \( G(\omega) \approx (I/I_0)^2 I_0 \) for each shot, and then average this quantity over the 50 shots.

The probe wavelength (measured with a resolution of \( \approx 0.1 \text{ nm} \) with a monochromator and an optical multichannel analyzer) was varied within a range of 250 nm through convenient change of laser dyes (Coumarins 440, 480, and 540A and Rhodamines 590, B, and 640). The amplified-spontaneous-emission background from the probe laser was greatly reduced by a double-pass grating pair filter (not shown in Fig. 4). However, it was necessary for us to minimize the amplified spontaneous emission by using each laser dye in a reduced central range of its tuning curve. Operation of dye lasers in the central region of the emission spectrum also minimizes the \( \lambda - \tau \) effect.

We investigated the organic dyes Nile Blue (Nile Blue 690, Kodak) and Rhodamine 640 (Exciton) dissolved in ethanol (0.15 and 0.1 mM, respectively). The solutions were placed in a 0.56-mm-thick cell. For each dye solution we measured the absorption spectrum \( \alpha(\lambda) \) with a spectrophotometer, and the fluorescence spectrum \( F(\lambda) \) (normalized as \( \int_0^\lambda F(\lambda) d\lambda \), the quantum yield) with a spectrophluorimeter. From these spectra we determined the absorption and the emission cross-section spectra by using \( \sigma_0(\lambda) = \alpha(\lambda)/N \) and \( \sigma_f(\lambda) = \lambda^4 F(\lambda)/8\pi c \tau n^2 \) where \( \tau \) is the lifetime of the first excited singlet state.

RESULTS

Figure 5 shows the measured population-grating spectral function, \( G(\lambda) \), for Nile Blue (solid curve) together with the absorption (dotted curve) and fluorescence (dashed curve) cross-section spectra. The grating was formed with the writing laser operating at 625 nm (16 000 cm\(^{-1}\)), which is close to the peak of the Nile Blue absorption spectrum. For this dye there is little overlap of the ground computer. Approximately 50 laser pulses were collected for each probe wavelength. The microcomputer was programmed to trigger the \( \text{N}_2 \) laser and the sample-and-hold circuits, read the analog-to-digital converter, calculate a quantity proportional to \( G(\omega) \approx (I/I_0)^2 I_0 \) for each shot, and then average this quantity over the 50 shots.

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![Fig. 5. Measured spectral function for the population grating, G(\(\lambda\)), ground-state absorption spectrum, \(\sigma_0(\lambda)\), and fluorescence spectrum, \(\sigma_f(\lambda)\), for Nile Blue.](image-url)
state and the excited-state bands, and we normalized $G(\lambda)$ to the peak value of the absorption cross section of the ground state, $\sigma_{10} = 2.9 \times 10^{-16}$ cm$^2$. From the measured $G(\lambda_f)$ at the peak of the emission spectrum we estimate the fluorescence cross section to be $\sigma_f = 2.8 \times 10^{-16}$ cm$^2$. We affirm that this grating-diffraction technique provided a particularly simple and rapid method for determining $\sigma_f$.

The grating spectrum displays, in addition to the peaks corresponding to absorption (628 nm or 15 920 cm$^{-1}$) and fluorescence (660 nm or 15 150 cm$^{-1}$), many other features that demonstrate the richness in information of this background-free spectroscopic technique. Some of these features are discussed below.

A distinct peak appears near 508 nm (19 690 cm$^{-1}$) in Fig. 5. A probable assignment is an $S_1 \rightarrow S_n$ transition, where $S_n$ is the same state in the transition $S_0 \rightarrow S_n$ that appears in the absorption spectrum at 275 nm (36 500 cm$^{-1}$). This assignment needs further consideration. If we estimate the energy of the equilibrium excited state $S_1$ at the average between the peaks of fluorescence and ground-state absorption, $\nu_1 = (15 150 + 15 920)/2 = 15 535$ cm$^{-1}$, then we should note that the excited-state absorption peak at 19 690 cm$^{-1}$ (508 nm) is lower in energy than the value estimated from the difference of the absorption peak of the $S_0 \rightarrow S_n$ transition and the energy of the $S_1$ state. 36 500 - 15 535 = 20 965 cm$^{-1}$ (447 nm). We believe that this red shift is due to the curvature and displacement of the potential surfaces of this dye, as is explained below.

Figure 6 shows a tentative diagram of the potential surfaces as a function of a structural generalized coordinate for the Nile Blue molecule and the absorption spectrum of this dye as a function of energy. According to the Franck-Condon principle, electronic transitions are represented by vertical lines in this diagram. The maximum in the absorption spectrum corresponds to a transition between the Franck-Condon connected points O and $A'$, while the equilibrium position in the $S_1$ surface is at point A, placed at 15 535 cm$^{-1}$, halfway between the energies of the transitions $O \rightarrow A'$ (15 920 cm$^{-1}$) and $A \rightarrow O'$ (15 150 cm$^{-1}$). Excited-state absorption to the surface $S_n$ occurs at the Franck-Condon connected points $A \rightarrow B'$ with energy $\nu_{B'A} = 19 690$ cm$^{-1}$, as measured from the population-grating spectrum. Note that, because of the relative displacement of the potential surfaces, the energy difference $\nu_{B'O} - \nu_{B'A} = 20 965$ cm$^{-1}$ is larger than $\nu_{B'A}$. This simple argument gives a reasonable explanation of the observed red shift in terms of conventional Franck-Condon shifts.

As another indication of the efficacy of this technique, note that for the $S_1 \rightarrow S_n$ transition being considered we can read directly from the scale in Fig. 5 the value of the cross section, $\sigma_{11} = 0.6 \times 10^{-16}$ cm$^2$.

Returning to Fig. 5, the peak in the absorption spectrum at 324 nm (30 864 cm$^{-1}$) indicates the presence of an excited state $|k\rangle$ that should give a resonance in the grating spectrum somewhere to the red of 652 nm (30 864 - 15 535 = 15 329 cm$^{-1}$) in the region between the absorption and the fluorescence bands. In this region the grating function (with the contribution from the real part of $\sigma^2$ neglected) is given by $G(\lambda) \approx |\sigma_{k1}(\lambda) - [\sigma_f(\lambda) + \sigma_{10}(\lambda)]|$, where $\sigma_{k1}$ is the absorption cross section associated with the transition $S_1 \rightarrow S_k$. Thus the presence of state $|k\rangle$ tends to reduce the value of the grating function and may explain the valley that we observe for $G(\lambda)$ in that region.

The reader may have also noticed in Fig. 5 that a shoulder appears in the grating spectrum near 575 nm, near the grating peak at 628 nm. We believe that this shoulder is real, and it may be due to another excited-state surface or an unusual topology of one of the known states.

Finally, a feature in the absorption spectrum (Fig. 5) is observed near 420 nm that should also give a peak in the grating spectrum, but this would fall toward the infrared, beyond the tuning range of our probe laser.

We now discuss our results for Rhodamine 640, which are less satisfactory. Figure 7 shows the population-grating, absorption, and fluorescence spectra for this dye. The writing laser for the population grating was operated at 565 nm, at the main peak of the ground-state spectrum. For this molecule the absorption and the emission peaks are, respectively, at 17 700 cm$^{-1}$ (565 nm) and 16 530 cm$^{-1}$ (605 nm), giving an equilibrium position

![Fig. 6. Potential energy surfaces (left frame) and ground-state absorption spectrum (right) for Nile Blue. Vertical scale is in wave-number units (inverse centimeters).](image1)

![Fig. 7. Measured spectral function for the population grating $G(\lambda)$, ground-state absorption spectrum $\sigma_0(\lambda)$, and fluorescence spectrum $\sigma_f(\lambda)$ for Rhodamine 640.](image2)
of the $S_1$ surface at approximately 17,115 cm$^{-1}$. The absorption spectrum shows several structures in the region from 266 nm (37,250 cm$^{-1}$) to 310 nm (32,258 cm$^{-1}$) that, in the grating spectrum, should appear in the region of 497–660 nm, which unfortunately overlaps the $S_0 \rightarrow S_1$ absorption and fluorescence bands. In this case the interpretation of the grating spectrum is more complicated than in Nile Blue. For Rhodamine 640 we were not able to unambiguously normalize the grating spectrum to any value of the absorption cross section. The shape of the grating spectral function (Fig. 7) in the fluorescence region of this dye almost coincides with that of the fluorescence spectrum. Because of this coincidence we arbitrarily normalized our measured grating spectrum to the peak value of the fluorescence cross section. Note, however, that for Rhodamine dyes there is a significant overlap between the emission and the excited-state absorption spectra.\(^{12,13}\)

This combination of complications makes a simple interpretation of the Rhodamine 640 spectra in terms of Franck-Condon shifts impossible. In the region of the $S_0 \rightarrow S_1$ absorption band the grating cross-section spectrum shows a minimum. This can be due to a coincidence of values of the susceptibilities of the ground and the excited states canceling each other in that region, thus giving a zero contribution to the grating spectrum.

Although the interpretation of the Rhodamine 640 population-grating spectrum is complicated, its recording is quite simple. We point out that with photolysis it is difficult to record the excited-state spectrum when there is substantial overlapping of ground and excited-state absorption bands.

**CONCLUSIONS**

We experimentally verified some of the essential characteristics of the population-grating technique for excited-state spectroscopy of organic dyes (and have demonstrated some of the pitfalls that can occur when excited-state absorption and fluorescence overlap). This technique is sensitive, background free, and, in favorable cases, has the ability to provide the excited-state cross section directly with a simple normalization procedure. We can not claim that, in itself, the population-grating technique is capable of revealing the excited-state structure of dye molecules. However, we do posit that it is a useful complement to more conventional techniques of excited-state spectroscopy in dyes and perhaps may help in obtaining information concerning the excited-state structure. We presented the theory for population-grating spectroscopy in a quite general case, but the technique is simplified significantly if the sample is optically thin. This ensures that a uniform grating is formed along the cell and avoids spectral distortions that are due to phase mismatch or reabsorption of the diffracted signal. As with all other techniques that use two different pulsed lasers, one of them tunable, care also has to be taken to compensate for the wavelength-dependent delay of the tunable laser (A-τ effect).

The technique can be improved by use of a white-continuum probe pulse with a detector array for simultaneous recording of the whole grating spectral function. Using cw lasers, one can also separate the phase- and the amplitude-grating contributions and thus separate the dispersive and the absorptive parts of the excited-state susceptibility. With these improvements population-grating spectroscopy can be used to investigate several characteristics of excited states, such as the shape of potential surfaces of molecules or ions, and the distribution of trapping states in semiconductor-doped glasses and amorphous semiconductors. Because of the intrinsically high contrast of this technique, we believe that it could also be useful for detecting weak excited-state transitions.

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**REFERENCES AND NOTES**