normally neglected, can cause the more than 10 times increase in the O(^{1}S) yield derived in our experiment (27). Only a relatively small coupling to other dominating DR channels may cause a significant increase in the DR channel leading to O(^{1}S) (27). Furthermore, it seems appropriate to investigate the effect of rotational excitation which, through the energy term $J(J + 1)\hbar^2/2\mu R^2$ (where μ is the reduced mass and R is the internuclear distance) perturbs the potential energy curves in a way that may cause an enhanced Franck-Condon overlap of the initial state $O_2^+(X^2\Pi_g, v = 0, J)$ with the repulsive valence $^1\Sigma_u^+$ state.

By our measurement we have demonstrated that the O(^{1}S) yield from the DR of O_2^+ in the vibrational ground state is not negligible and that DR may be responsible for the 5577 Å green light from upper planetary atmospheres, as suggested many years ago. The information is important for the large number of ground- and satellite-based projects that take advantage of airglow emission lines for determining information about winds, temperatures, heating, density profiles, and escape of atoms from planetary atmospheres. It appears that we have moved a step forward toward a better understanding of the upper atmosphere by addressing this long-standing classical problem in aeronomy. However, we also find a need for better quantum-chemical calculations that address the issue of DR with an improved Hamiltonian and the effect of vibrational and rotational excitation.

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Design of Surfaces for Patterned Alignment of Liquid Crystals on Planar and Curved Substrates

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Molecularly designed surfaces formed by chemisorption of alkanethiols on ultrathin films of gold permit control of both the azimuthal and polar orientations of supported nematic liquid crystals (LCs). These surfaces, when patterned, form simple and versatile templates for the fabrication of complex optical structures from LCs. Surfaces patterned with odd or even alkanethiols, or mixtures of long and short alkanethiols, were used to fabricate tunable, micrometer-scale LC diffraction gratings that differed in their polarization sensitivity. Patterned alignment of LCs on curved surfaces is also demonstrated, thereby providing principles for fabrication of optical elements that combine diffractive and refractive optics.

Past interest in the orientations assumed by LCs near surfaces has been largely driven by their use in electrooptical devices such as flat-panel displays (FPDs). A goal of many studies has, therefore, been the development of methods for the fabrication of surfaces that uniformly orient LCs over large areas. Future uses of LCs in electrooptic devices, in contrast, will rely increasingly on LCs with patterned orientations over small areas (1–5). For example, light can be diffracted or redirected by using patterned LC structures that are tuned by application of a uniform electric field (5), and FPDs with wide viewing angles and broad gray scales can be fabricated by using pixels that are divided into subpixels, where each subpixel is defined by a different orientation of the LC (6). Methods capable of patterning LCs on curved surfaces are also required for the development of new types of tunable electrooptic LC devices, including devices that combine the diffraction of light from the patterned LC structure with the refraction of light at the curved surface (7).

Current procedures for the fabrication of patterned LC structures use either spatially nonuniform electric fields from patterned electrodes or patterned "anchoring" surfaces. Fringing of electric fields from patterned electrodes prevents high-resolution patterning of LCs by this method (1, 8). Patterned anchoring surfaces have been prepared by using mechanical rubbing of spin-coated polymer films, photolithographic masking, and a second rubbing step performed in a direction orthogonal to the first (3, 5, 9). This method of patterning LCs on surfaces is complex and suffers from the disadvantages of rubbing-based methods, such as the generation of dust and static charge. Recently developed photo-alignment techniques for orienting LCs provide promising alternatives (1, 6, 10). However, because light-based methods generally require surfaces to be spin-coated by uniformly thin films of photopolymer, and because the orientations of LCs on photo-aligned surfaces are determined by the angle of incidence of the light used for alignment, these methods are not easily applied to the patterning of LCs on nonplanar surfaces.

Our approach to the patterning of LCs on flat and curved surfaces is based on the use of patterned self-assembled monolayers (SAMs) of molecules to direct both the polar (away from the surface) and azimuthal (in the plane of the surface) orientations of LCs supported on surfaces. The methods are simple and flexible, and any of the recently established procedures for patterning SAMs

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on surfaces (for example, microcontact printing or photopatterning) (*11–14*) can be used. The principles reported here can be easily extended to sizes ranging from hundreds of nanometers (*13*) to millimeters and permit both planar (parallel to the surface) and homeotropic (perpendicular to the surface) orientation of LCs; methods based on the rubbing of polymer films mainly provide manipulation of the in-plane alignment of LCs and cannot homeotropically align LCs. The SAMs we used have surface energies ($\sim$19 mJ/m^2) about half those of films of polyimides used for alignment of LCs; low-energy surfaces are less prone to contamination by molecular adsorbates and dust particles than are high-energy ones. Because SAMs can also be patterned on nonplanar surfaces (*14*), patterned LC structures formed with SAMs can be replicated on curved surfaces.

We illustrate the capability of our approach to the patterning of LCs on surfaces by fabrication of three linear diffraction gratings (Fig. 1). These gratings differ in the manner of distortion of the LCs and thus their optical properties. Patterned SAMs were prepared by microcontact printing with an elastomeric stamp (*12*). The stamp was inked with an ethanolic solution of $CH_3(CH_2)_{15}SH$ and put in contact with ultrathin ($\approx$100 Å thick), semi-transparent films of polycrystalline gold. SAMs were then formed on the unreacted areas of gold by immersion of the gold films in ethanolic solutions containing 1 mM of a second alkanethiol for 2 hours. Two surfaces supporting SAMs were subsequently paired and spaced apart with Mylar film. The space between the surfaces was filled with the nematic LC 4-cyano-4′-pentylbiphenyl (5CB) by capillarity. A polarizing microscope with white light was used to image the patterned LCs. Descriptions of experimental procedures have been reported elsewhere (*15, 16*).

Fabrication of the periodic LC structure shown in Fig. 1A (grating A) requires uniform planar anchoring of the LC on the top surface of the cell and patterned planar anchoring of the LC with orthogonal azimuthal orientations in adjacent stripes on the bottom surface. Planar anchoring of nematic LCs can be achieved by using single-component SAMs formed from $CH_3(CH_2)_{n-1}SH$ (n = 4 to 17) on gold (*17*); the anchoring is azimuthally uniform on SAMs supported on films of gold deposited with a 50° angle of incidence (*16, 18*). The anchoring of 5CB is perpendicular to the direction of deposition of the gold on SAMs formed from odd alkanethiols (for example, n = 11; Fig. 2A) and parallel to the direction of deposition of gold on SAMs formed from even alkanethiols (for example, n = 12; Fig. 2B) (*19, 20*). Differences in the orientation of the methyl groups at the surface of SAMs formed from odd and even alkanethiols on gold direct the in-plane orientation of the nematic LC (*19, 21, 22*).

We used patterned SAMs formed from $CH_3(CH_2)_{14}SH$ and $CH_3(CH_2)_{15}SH$ on obliquely deposited gold to fabricate grating A. The polarization of linearly polarized light is not changed by transmission (along the z direction in Fig. 1A) through the regions of LC with uniform planar anchor-

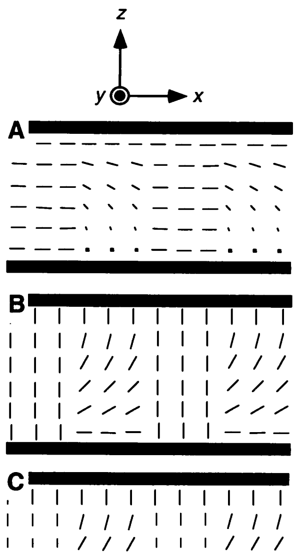

Fig. 1. (**A** to **C**) Schematic illustrations of optical cells with patterned surfaces for the anchoring of LCs. The deformation of the LC within each cell results from patterned anchoring of the LC on the surfaces of the cells. Thick horizontal lines indicate the top and bottom surfaces of the cell.

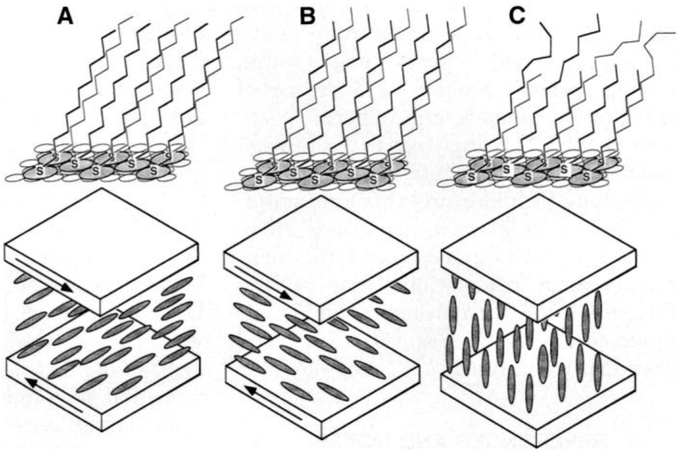

Fig. 2. (**A**) Cartoon of a SAM formed from alkanethiols with odd numbers of carbon atoms on gold. A nematic LC anchored between two such surfaces is aligned parallel to the surfaces and perpendicular to the direction of deposition of gold (indicated by the arrows). (**B**) Cartoon of a SAM formed from alkanethiols with even numbers of carbon atoms. A nematic LC anchored between two such surfaces aligns parallel to the surfaces of the cell and parallel to the direction of deposition of gold (indicated by the arrows). (**C**) Cartoon of a mixed SAM formed by coadsorption of long and short alkanethiols. Nematic LCs are anchored perpendicular to surfaces that support these mixed SAMs. Details of the bonding of sulfur to gold and the superlattice formed by alkyl chains within the SAMs (*29*) are not shown in these cartoons.

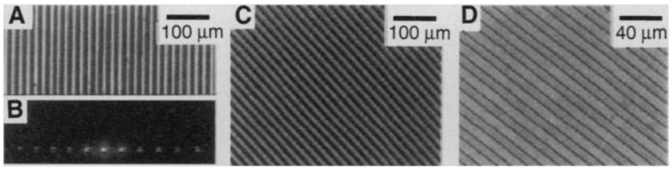

Fig. 3. (**A**) Optical image (crossed polars) of a LC grating of type A. The bottom surface of the cell is patterned with stripes of SAMs formed from $CH_3(CH_2)_{15}SH$ or $CH_3(CH_2)_{14}SH$; the top surface supports a SAM formed from $CH_3(CH_2)_{15}SH$. The dark stripes in the optical image correspond to regions where 5CB is anchored on SAMs formed from $CH_3(CH_2)_{15}SH$, whereas bright stripes correspond to regions where 5CB is anchored on a SAM formed from $CH_3(CH_2)_{14}SH$ (bottom surface) and a SAM formed from $CH_3(CH_2)_{15}SH$ (top surface). (**B**) Diffraction pattern formed by the LC grating shown in (A). (**C**) Optical image (crossed polars) of a LC grating of type B. The bottom surface of the cell is patterned with stripes of SAMs formed from $CH_3(CH_2)_{15}SH$ and mixed SAMs formed from an ethanolic solution containing 85% $CH_3(CH_2)_9SH$ and 15% $CH_3(CH_2)_{15}SH$ (total thiol concentration of $\sim$1 mM); the top surface supports a mixed SAM with the same composition as the bottom surface of the cell. (**D**) Optical image (crossed polars) of a LC grating of type C. The bottom surface of the cell is patterned with stripes of SAMs formed from $CH_3(CH_2)_{15}SH$ or $CH_3(CH_2)_{14}SH$; the top surface supports a mixed SAM with the same composition as used in (C). In the optical micrographs [(A), (C), and (D)] the axes of the polarizer and the analyzer are horizontal and vertical, respectively.

ing but is rotated by 90° upon transmission through regions of LC that are twisted by 90° (*23*). When viewed through crossed polars, therefore, twisted regions of grating A appear bright (light is transmitted by the analyzer) and uniform regions appear dark (light is extinguished by the analyzer) (Fig. 3A). The periodic change in refractive index across the grating causes diffraction of laser light (Fig. 3B).

The grating in Fig. 1B (grating B) is based on homeotropic anchoring of the LC on the top surface of the cell and patterned planar and homeotropic anchoring of the LC on the bottom surface. Light incident on grating B with a linear polarization along the *x* direction will experience a periodic change in refractive index and will be diffracted. In contrast, light with polarization along the *y* direction will experience no spatial variations in refractive index and will not be diffracted. We used mixed SAMs formed by coadsorption of long and short alkanethiols on gold to homeotropically anchor 5CB (Fig. 2C) (*15*, *16*, *24*) in a grating of type B. A polarized light micrograph of the LC grating viewed through crossed polars is shown in Fig. 3C. Dark stripes correspond to regions of the grating in which the polarization of linearly polarized light was not changed by transmission through the LC; these stripes remained dark when the sample was rotated between the crossed polars, thus confirming homeotropic anchoring in these regions. Bright stripes correspond to regions of the LC distorted by planar anchoring of the LC on the bottom surface and homeotropic anchoring of the LC on the top surface of the cell. Patterned homeotropic and planar anchoring of LCs has not been demonstrated in past work that was based on photo-alignment or rubbing techniques.

In contrast to grating B, the diffraction of light by the grating in Fig. 1C (grating C) will be polarization insensitive. When grating C was viewed under crossed polars, we observed either uniformly bright stripes (Fig. 3D, polarization of incident light between *x* and *y*) or uniformly dark stripes (polarization of incident light along *x* or *y*). The boundaries between stripes, which correspond to regions in which two different distortions of the LC meet, were visible in the optical micrographs (dark lines in Fig. 3D). The lack of measurable contrast between adjacent stripes for all polarizations of incident light is consistent with the LC structure of grating C. A similar type of LC structure has been reported by Chen and co-workers who use a two-step rubbing process (*9*).

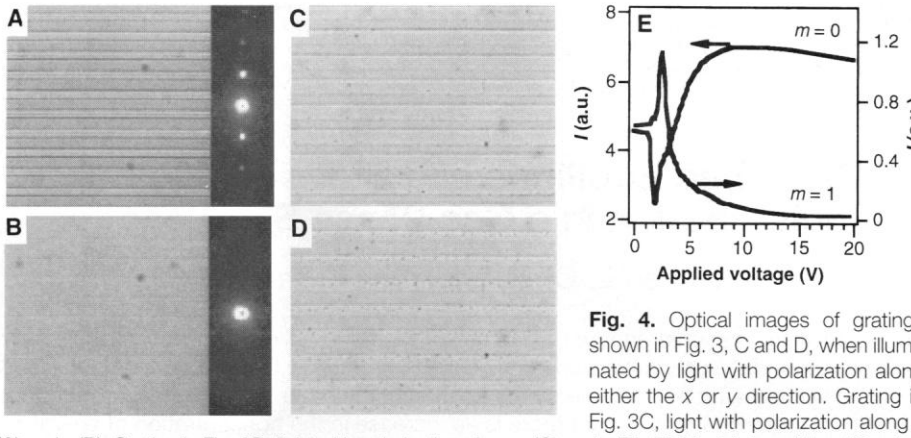

Fig. 4. Optical images of gratings shown in Fig. 3, C and D, when illuminated by light with polarization along either the *x* or *y* direction. Grating in Fig. 3C, light with polarization along *x* (**A**) and *y* (**B**). Grating in Fig. 3D, light with polarization along *x* (**C**) and *y* (**D**). (**E**) Modulation of the diffraction pattern shown in Fig. 3B by application of an electric field perpendicular to the surfaces of the cell. The intensity [*I*, arbitrary units (a.u.)] of the zeroth ($m = 0$) and first-order ($m = 1$) spots is plotted as a function of the applied voltage. The thickness of the cell was 15 μm. The horizontal dimension of the optical images in (A) through (D) is 220 μm.

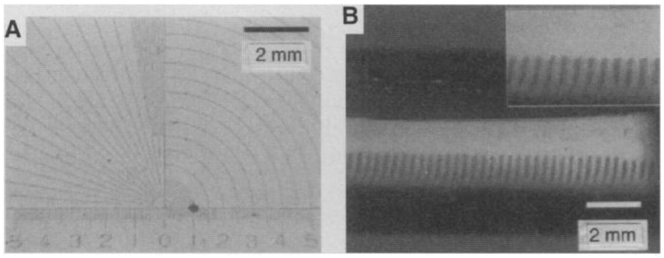

Fig. 5. (**A**) Complex LC structure formed with patterned SAMs. The dark regions correspond to LC anchored between SAMs formed from $CH_3(CH_2)_{14}SH$, and bright regions correspond to areas in which the LC is anchored between SAMs formed from $CH_3(CH_2)_{14}SH$ and $CH_3(CH_2)_{15}SH$. (**B**) LC patterned on the curved surface of a glass test tube (with a radius of ~5 mm). The test tube was coated with a thin gold film and rolled across an elastomeric stamp with a grating-like relief pattern on its surface. The stamp was inked with $CH_3(CH_2)_{15}SH$. One-half of a second glass tube, with its inner curved surface coated with gold and a SAM formed from $CH_3(CH_2)_{14}SH$, was used as the outer surface of the cell. Because glass is optically isotropic and appears dark between crossed polars, the image shown was obtained with the relative angle between two polars set at ≈85°. This arrangement of the polars permitted transmission of light through the glass. A higher magnification (≈×1.5) image of the patterned LC is shown in the inset. The origin of the optical contrast and corresponding alignment of LC is described in (A).

We further tested the polarization sensitivity of gratings B and C by viewing these gratings with linearly polarized light (not crossed polars). When grating B was viewed with light having a linear polarization along the *x* direction, the grating pattern was visible (Fig. 4A) because the incident light experienced a spatially periodic refractive index. With light polarized along the *y* direction, however, only faint edges of the stripes were seen (Fig. 4B); these edges did not cause measurable diffraction of light. In contrast, because grating C is insensitive to the polarization of incident light, the grating was visible upon illumination by light with polarization along *x* or *y* (Fig. 4, C and D).

Tuning of these patterned LC structures is possible by using electric fields. When gold surfaces supporting SAMs are used as electrodes, an electric field can be applied perpendicular to the surfaces. Application of the electric field reversibly reorients the LCs and thus modulates the intensity of light diffracted from the gratings (Fig. 4E). We have also used in-plane electric fields (*25*) to reorient these patterned LC structures. We observe SAMs to be stable upon application of an electric field across a cell filled with LC (*26*). In general, the alignment of LCs on SAMs formed from long-chain alkanethiols is stable over months; we believe that stability over years can be achieved by using polymerizable SAMs (*27*) or LCs doped with alkanethiols or reducing agents to prevent oxidative degradation of the SAMs.

The methods reported here permit fabrication of complex LC structures in two simple processing steps. Surfaces can be patterned with regions of LCs that differ in shape and have sizes ranging from micrometers to centimeters (Fig. 5A). The LCs can also be patterned on nonplanar surfaces (Fig. 5B) (*28*). The capability to pattern LC orientations on nonplanar surfaces pro-vides procedures for the fabrication of tunable hybrid diffractive-refractive devices. For example, devices based on combinations of diffractive and refractive optical processes permit aplanatic or chromatic correction in lenses, spectral dispersion, imaging from a single optical element, and other manipulations of light (7). The capability to pattern LCs on curved surfaces also provides routes for the fabrication of displays with wide viewing angles.

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17. The observation of planar anchoring of LCs on surfaces with energies as low as alkanethiols on gold (19 mN/m) is unusual. For example, monolayers formed from octadecyltrichlorosilane on silica have surface energies as low as alkanethiols on gold (19 mN/m) yet cause homeotropic anchoring of LCs. The anisotropic part of the dispersion force acting between 5CB and gold influences anchoring of 5CB on SAMs formed from $CH_3(CH_2)_{n-1}SH$ [W. J. Miller, N. L. Abbott, J. D. Paul, M. Prentiss, *Appl. Phys. Lett.* **69**, 1852 (1996)].
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21. The orientation of methyl groups exposed at the surface of SAMs formed from $CH_3(CH_2)_{n-1}SH$ on gold differ for odd and even alkanethiols because the aliphatic chains within these SAMs are tilted away from the surface normal by 30° [R. G. Nuzzo, L. H. Dubois, D. L. Allara, *J. Am. Chem. Soc.* **112**, 558 (1990)]. In contrast, chains within SAMs formed from alkanethiols on silver and perfluorinated alkanethiols on gold are tilted by less than 10° to 15°, and there is no odd-even variation in the orientation of the methyl groups (CH_3 or CF_3) at the surface of these SAMs [P. E. Laibinis *et al.*, *ibid.* **113**, 7152 (1991); T. J. Lenk *et al.*, *Langmuir* **10**, 4610 (1994)]. We do not observe an odd-even dependence of the orientation of 5CB on SAMs formed from alkanethiols on silver or perfluorinated alkanethiols on gold: the anchoring of 5CB was perpendicular to the direction of deposition of the gold.
22. A 90° azimuthal reorientation of a LC on a corrugated surface can be caused by a coupling of elastic and flexoelectric effects [G. Barbero and G. Durand, *J. Appl. Phys.* **68**, 5549 (1990)]. The observed odd-even effects of SAMs on the orientations of LCs can be described by the theory of Barbero and Durand by modulation of the dielectric constant of odd and even SAMs about a critical value.
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28. LCs have been anchored within pores of alumina and vycor glass coated with surface-active reagents [G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, S. Zumer, *Phys. Rev. E* **53**, 3647 (1996), and references therein]. Our work differs from this past work in two principal ways. (i) Scale: We have anchored LCs on curved surfaces with radii of curvature that are large compared with the thickness of the layer of LC. The local state of the LC is similar to that of LC anchored on a planar surface and thus properties of the LC are not dominated by elastic energies caused by curvature. Methodologies used for anchoring LCs on planar surfaces (for example, twisted nematic cells) can be translated to our curved surfaces. (ii) Patterns: We used patterned curved surfaces.
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Perturbed Equilibria and Statistical Energy Redistribution in a Gas-Phase S_N2 Reaction

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The relative translational energy of one set of reactants in the gas-phase equilibrium between chloride ion and chloroacetonitrile $^{35}Cl^- + {}^{37}ClCH_2CN \rightleftharpoons {}^{37}Cl^- + {}^{35}ClCH_2CN$ is varied without affecting the energy distribution of the other set. The steady-state ratio of ionic isotopes changes so that there is an increase in the concentration of energized reactants. The ratio provides a measure of the translational energy dependence of the rate constant for the bimolecular nucleophilic substitution (S_N2) reaction. The observed energy dependence is indistinguishable from that predicted by Rice-Ramsperger-Kassel-Marcus theory, suggesting that the increased translational energy redistributes statistically in the collision complex.

We report here two interesting results obtained in a study of the translational energy dependence of the gas-phase, chloride-exchange reaction of chloroacetonitrile

$$^{35}Cl^- + {}^{37}ClCH_2CN \underset{k_b}{\overset{k_f}{\rightleftharpoons}} {}^{37}Cl^- + {}^{35}ClCH_2CN \qquad (1)$$

where k_f and k_b are the rate constants for the forward and back reactions, respectively. First, we show that selectively increasing the center-of-mass collision energy between one set of reactants in Eq. 1 without changing the energy of the other set causes the concentration of the energized reactants to increase. Although this behavior may seem to contradict LeChatelier's principle, it is not exceptional and is qualitatively consistent with a well-known kinetic model. Second, we examine the energy dependence of the rate constant and compare our results to those of earlier studies of gas-phase S_N2 reaction dynamics, which have focused on halide–methyl halide reactions. Although the methyl halide systems exhibit nonstatistical behavior, the dynamics of the larger S_N2 system in Eq. 1 appear to be statistical, in that the reaction rates are consistent with a

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