

# Electric Field Structures in Thin Films: Formation and Properties

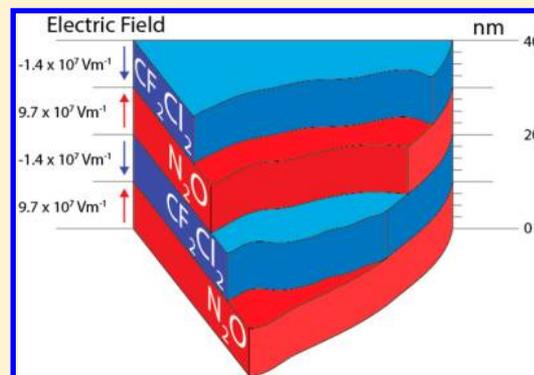
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**ABSTRACT:** A newly discovered class of molecular materials, so-called “spontelectrics”, display spontaneous electric fields. Here we show that the novel properties of spontelectrics can be used to create composite spontelectrics, illustrating how electric fields in solid films may be structured on the nanoscale by combining layers of different spontelectric materials. This is demonstrated using the spontelectric materials nitrous oxide, toluene, isoprene, isopentane, and  $\text{CF}_2\text{Cl}_2$ . These yield a variety of tailored electric field structures, with individual layers harboring fields between  $10^7$  and  $10^8$  V/m. Fields may be of the same sign or of opposite sign, the latter enabling the creation of nanoscale potential wells. The formation of fields is followed using an established electron beam technique, employing the ASTRID synchrotron storage ring. The influence of temperature on heterolayer structures, displaying new Curie effects, and the nature of the interfacial region between different spontelectrics are also discussed.



## INTRODUCTION

The formation of spontaneous electric fields in thin solid films, in excess of  $10^8$  V/m, has recently been described in the *International Reviews in Physical Chemistry*.<sup>1</sup> Further references to the formation of such films, termed “spontelectric”, may be found in refs 2–6. Materials which produce and harbor electric (and magnetic) fields, and the layering of such materials to produce composite multiferroic heterostructures, stimulate great interest in the physicochemical and material science communities.<sup>7–12</sup> The search for new materials and properties has centered on inorganic species<sup>7,8,13</sup> and in particular metal oxides of the perovskite structure. All of these rely on the displacement of heavy elements to polarize the solid and thus to generate electric fields. Solids made from molecular species have received far less attention, despite the interest in molecular solids in the field of organic semiconductors.<sup>14–16</sup> In the present work we examine the properties of heterostructures formed by molecular spontelectric materials. These materials by contrast with, say, perovskites, produce electric fields through the spontaneous ordering of molecular dipoles upon growth as thin films.<sup>1–6</sup> We show that these materials can be layered to produce new composite heterostructures which can be made to harbor tailored configurations of electric fields. We examine both the interface between layers of different materials in these films and the Curie behavior of composite systems on heating.

The present work is a first-principles study, introducing spontelectrics as a new form of material to aid in the creation of complex nanostructures with special electrical properties. Long-range order in spontelectric films arises from the interaction

between individual molecular dipoles and the nonlocal electric field permeating the entire film.<sup>1</sup> Thus, spontelectrics form a new class of solid materials, whose structures are dictated by an interplay between microscopic and macroscopic phenomena, with a degree of macroscopic coherent order imposed on the system through the action of the electric field and with local microscopic thermal fluctuations in competition with this tendency to long-range order. Note that spontelectrics are quite distinct from ferroelectrics, a point which is discussed at length in ref 1 and which is referred to above with respect to perovskites. Notwithstanding, the spontaneous field within spontelectrics is in some ways analogous to the Weiss field of ferromagnetic materials.<sup>17</sup>

The relevant features of the properties and structure of spontelectric films may be summarized as follows:<sup>1</sup> (i) The characteristic of spontaneous polarization, exemplified by a spontaneous potential on the film surface, has been studied for films of individual species for a dozen dipolar molecules of diverse structure. The spontelectric species involved are familiar molecules such as propane, toluene, nitrous oxide, isoprene, etc., and their only common property is that they possess permanent dipole moments. (ii) The presence of the field within the film is due to partial orientation of the dipolar

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molecules of which the film is composed. (iii) The strength of the spontelectric field within a film varies strongly as a function of film deposition temperature. For example  $\text{N}_2\text{O}$  films deposited at 38 K show a field of  $1.2 \times 10^8$  V/m and deposited at 65 K,  $1.6 \times 10^7$  V/m.<sup>1</sup> (iv) The spontaneous potential on the surface of a film may be either positive or negative. The polarity is characteristic of the material chosen. (v) Heating of a film at first creates little change in the spontelectric field, but a critical temperature is reached at which the spontelectric field decays abruptly. The critical temperature is termed the Curie point by analogy with ferromagnetism. (vi) A parametrized mean field model has been shown to fit data for electric fields, as a function of deposition temperature, for a variety of species for single component spontelectric films. This model is based on the following concepts: first, that local dipole orientation is influenced by short-range and dipole–dipole interactions between component species; second, that an initial dipole orientation, formed locally through thermal fluctuations, creates an opposing unidirectional electric field, the spontelectric field, which leads to effectively infinite range interactions; third, that dipole order in the system is moderated by thermal fluctuations.

We show here that the creation of composite spontelectric molecular structures, or heterostructures, yields tailored electric fields on the nanometer scale. Since the interactions which are responsible for structuring a single spontelectric film extend over the entire film of any desired thickness, spontelectric materials are therefore ideally suited in principle for building ordered structures of electric fields from molecular materials. Further, under our experimental conditions, we can show that there is negligible mixing of materials at the interface for the interfaces studied.

Demonstration of the principle of the formation of electric field structures in heterolayered spontelectrics was briefly furnished in earlier work for a single heterostructure composed of  $\text{N}_2\text{O}$  and isopentane.<sup>1,4</sup> Here we generalize this result, describing spontelectric behavior in a number of such combinations of films, involving both positive and negative going spontelectric materials. Present data demonstrate that spontelectric films may be deposited one upon the other to create electrical structures which can be described *approximately* by the independent properties of the individual materials. Further, the spontelectric properties of the pure material are *exactly* recovered in the overlying layer when the thickness of this layer exceeds tens to hundreds of monolayers (ML). The materials chosen in the present exploratory study are  $\text{N}_2\text{O}$ , toluene, isoprene, isopentane, and  $\text{CF}_2\text{Cl}_2$ , the first three of which are positive going and the last two, negative; that is, the two groups support fields of opposite sign.<sup>1,6</sup> In the two cases of  $\text{N}_2\text{O}$ /isoprene and  $\text{N}_2\text{O}$ / $\text{CF}_2\text{Cl}_2$ , we have looked closely at the interfacial region where there are apparent discontinuities in the potential. Such discontinuities could introduce a significant energy cost, in a manner similar to polar discontinuities for abrupt heterointerfaces between ionic crystal planes in thin oxide films.<sup>18</sup> We also report the effects of heating of a chosen heterospontelectric through the respective Curie and/or sublimation points of the component materials, showing the result that the materials appear to behave independently of one another.

## ■ EXPERIMENTAL SECTION

All experiments were performed on the SGM2 beamline at the ASTRID synchrotron storage ring at Aarhus University ([www.isa.au.dk](http://www.isa.au.dk)). The electric field permeating a film was evaluated by

measuring the surface potential at the film–vacuum interface as a function of film thickness. Details of the experimental method of measurement of the surface potential are described elsewhere.<sup>1</sup> In brief, values of surface potentials are obtained by interrogating the system with an electron beam, using the principle that electrons formed at some point at a certain potential can just reach another point at the same potential, potential barriers apart. In our experiment, a high-resolution electron beam is formed using monochromatized synchrotron radiation to ionize Ar gas at  $\sim 5$  meV above the photoionization threshold (78.56 nm). The resulting electrons, formed nominally at a potential of zero volts, have an energy spread given by that of the photoionizing radiation, set here to be  $\sim 1.5$  meV. Electrons are expelled from the photoionization region in a very weak electric field and formed into a beam, accelerated, focused through a series of lenses, and made to fall upon a clean substrate or upon a film surface. The substrate is floated to a potential such that the onset of current flow ( $\sim 2$  fA) is detected. This potential in turn yields the electric field within the film, given a known film thickness.

The substrate is composed of a polycrystalline Au sample, cooled to a minimum of 38 K, using a closed cycle He cryostat, and heated using a cartridge heater to give an adjustable temperature ( $\pm 0.5$  K). Currents are detected using a Keithley 6340 femtoammeter. If the potential at the Au substrate changes, say, to a more positive value due to the growth of a spontelectric film, electrons are attracted and a current is measured. The potential at the Au surface is floated negative, or positive for negative going spontelectrics, until the threshold for current detection is achieved, as described above. The floating potential, positive or negative, corresponds to the inverse of the surface potential generated by the spontelectric material at the film–vacuum interface. Using this technique, surface potentials can be measured with an accuracy of  $\sim 2$  mV.<sup>19</sup>

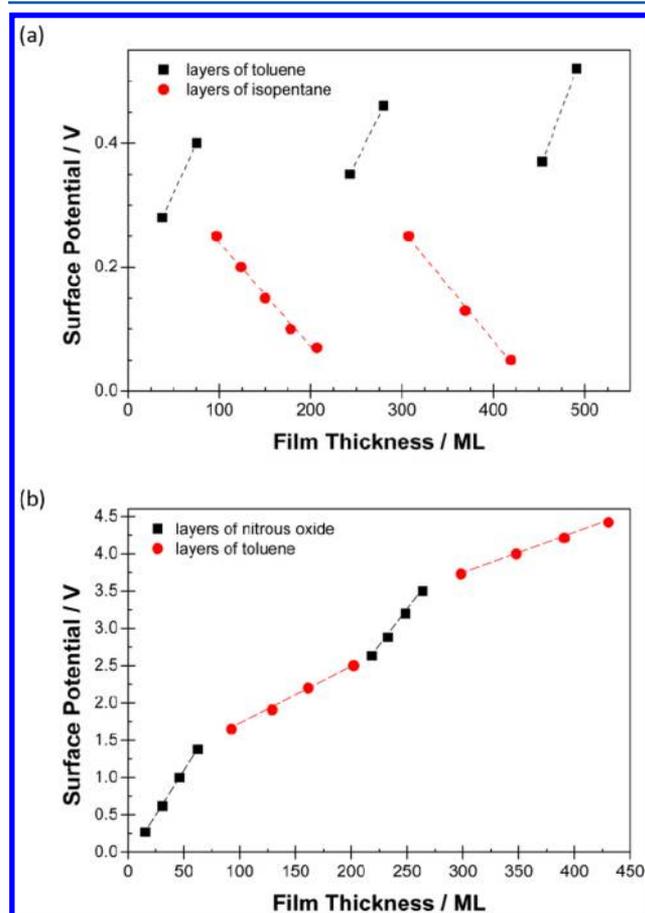
All experiments were performed under UHV with a base pressure of  $\sim 10^{-10}$  mbar. The Au substrate was cleaned by annealing to 700 K. Uniform molecular films were deposited using standard background vapor deposition techniques. The molecular flux was estimated by controlling the dosing rate using results from the standard temperature-programmed desorption (TPD) method. Throughout, film thicknesses are described in monolayers (ML), where a ML of coverage was determined by integrating the area beneath the high temperature peak attributed to single ML desorption, as distinct to the peak at lower temperatures attributed to multilayer desorption. The quoted absolute film thicknesses for a given species are accurate to within 20–30%, but relative thicknesses for any experiment are accurate to within a few percent. All compounds ( $\text{N}_2\text{O}$  ( $\geq 99.998\%$ ), toluene (99.8%), isoprene ( $\geq 99\%$ ), isopentane ( $\geq 99\%$ ),  $\text{CF}_2\text{Cl}_2$  ( $\geq 99.5\%$ )) were used as received (Sigma-Aldrich). Liquids were degassed via a standard freeze–pump–thaw technique. The stability of each species on the Au substrate was assessed by mass spectrometry, and no decomposition was observed.

## ■ RESULTS

The five species just mentioned,  $\text{N}_2\text{O}$ , toluene, isoprene, isopentane and  $\text{CF}_2\text{Cl}_2$ , have been deposited in various combinations and results have been selected in order to exemplify the salient properties of heterostructured spontelectrics. Qualitative properties may be summarized as follows: (i) films of spontelectrics may be laid down one upon the other without evidence for interpenetration of material. Each film,

sufficiently far from the interface, has properties associated with an independent film of the species concerned. (ii) Following from above, and remarkable as it may seem, spontelectrics which individually harbor electric fields in opposing directions can be stacked directly while maintaining their individual properties. (iii) The response to heating of a heterolayered spontelectric film is of the separate materials, showing independent temperature behavior, retaining the Curie properties of separate, pure materials. (iv) The region at the interface can be characterized in general by an interface dipole and thereafter close to the interface by an interfacial decaying field, a “compensation region”.

The systems chosen to illustrate points (i)–(iv) are the toluene/isopentane and the  $\text{N}_2\text{O}$ /toluene heterolayered spontelectric systems, in Figure 1a,b, the  $\text{N}_2\text{O}$ /isoprene and  $\text{N}_2\text{O}/$



**Figure 1.** (a) Surface potentials for the spontelectric materials toluene and isopentane, deposited at 50 K, to create a complex heterostructure. Since the materials polarize in opposite senses, a positive–negative zigzag pattern of potential and of electric field evolves as the heterostructure is grown. (b) Surface potentials for  $\text{N}_2\text{O}$  and toluene, deposited between 48 K and 50 K (see text), to produce a second type of heterostructure in which each material generates a positive potential at the film interface.

$\text{CF}_2\text{Cl}_2$  systems, in Figure 2a,b, the  $\text{N}_2\text{O}/\text{CF}_2\text{Cl}_2$  system in Figure 3 for Curie properties, and again the  $\text{N}_2\text{O}/\text{isoprene}$  and  $\text{N}_2\text{O}/\text{CF}_2\text{Cl}_2$  systems in Figure 2c,d, the latter to show fits to a simple model of the interface.

**Examples of Composite Heterostructures: Far from the Interface.** Heterostructures were created by the simple prescription of depositing one material upon another, as in the

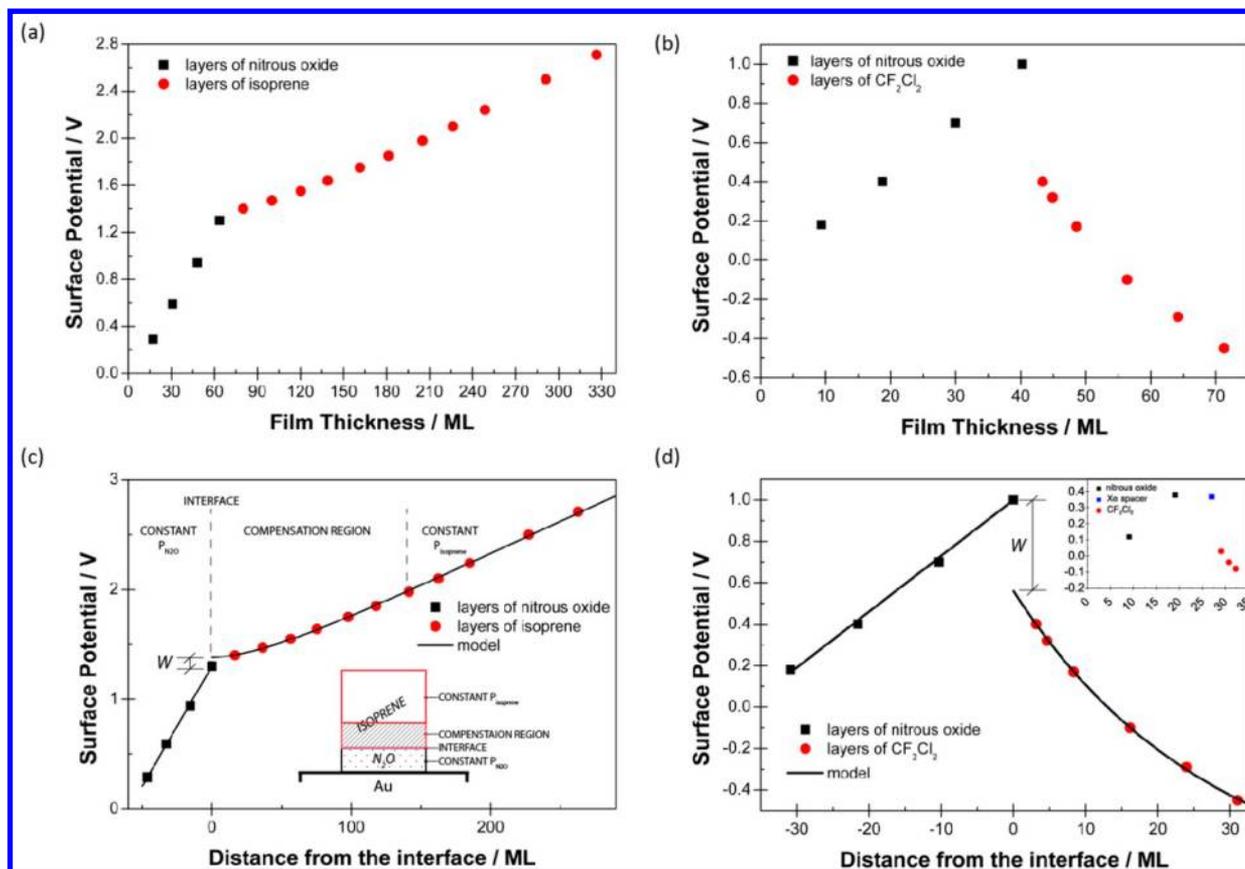
example of  $\text{N}_2\text{O}$  and isopentane mentioned in the introduction.<sup>1</sup> The surface potential at the film–vacuum interface was measured at fixed thicknesses during the growth of such composites and may be extended to the deposition of as complex a structure as desired. Figure 1a,b shows the results of two such experiments. In Figure 1a, a toluene/isopentane structure is shown, where toluene forms a positive film–vacuum surface potential and isopentane a negative film–vacuum surface potential. Data are for a deposition temperature of 50 K. Note that the absolute value of the spontelectric field of pure solid toluene deposited at 50 K is greater than that of isopentane at 50 K, the figures being  $5.04 \text{ mV ML}^{-1}$  and  $-1.80 \text{ mV ML}^{-1}$ , respectively, for the individual species.<sup>1,4</sup> In order to form this structure, 75 ML of toluene were deposited in two steps on the polycrystalline Au substrate producing 400 mV on the surface of the layer. In this connection, toluene has a surface dipole potential on Au of  $\sim 180 \text{ mV}$ .<sup>1</sup> On top of this film, 140 ML of isopentane were deposited in five steps reducing the surface potential to 70 mV. Toluene was again dosed, leading to an increase in the film–vacuum potential. Alternate layers of toluene and isopentane were deposited until a composite structure was built up containing three layers of toluene, with layers of isopentane sandwiched in between. This combination produced an oscillating potential in the multilayered composite structure, with the potential reaching maxima on the top of toluene layers and minima on the top of isopentane layers. The measured slopes of the data were  $4.96 \text{ mV ML}^{-1}$  for toluene and  $-1.70 \text{ mV ML}^{-1}$  for isopentane and thus were the same within experimental error as for the individual species.<sup>1</sup>

In Figure 1b, a second type of composite structure is illustrated composed of  $\text{N}_2\text{O}$  and toluene, both of which generate positive spontelectric potentials. Experiments were performed at deposition temperatures of between 48 K and 50 K. Figure 1b shows that  $\text{N}_2\text{O}$  harbors a stronger field than toluene.<sup>1</sup> It is evident that the growth of the spontelectric potential on  $\text{N}_2\text{O}$  is the same when deposited upon toluene as upon the gold substrate, since the data for  $\text{N}_2\text{O}$  in Figure 1b form parallel lines. For example, the field harbored by layers of  $\text{N}_2\text{O}$  grown at 48 K on a Au substrate yielded a measured potential of  $19.4 \text{ mV/ML}$ , reported in ref 1 and, from data in Figure 1b, the value is  $19.3 \text{ mV/ML}$  for  $\text{N}_2\text{O}$  deposited on a layer of toluene. One may note that the data for toluene in Figure 1b do not form precisely parallel lines and therefore do not represent the same electric field. This discrepancy arises because of a rise in temperature from 48 K to 50 K during the course of the deposition experiments coupled with the experimental difficulty of controlling flow rates of toluene.

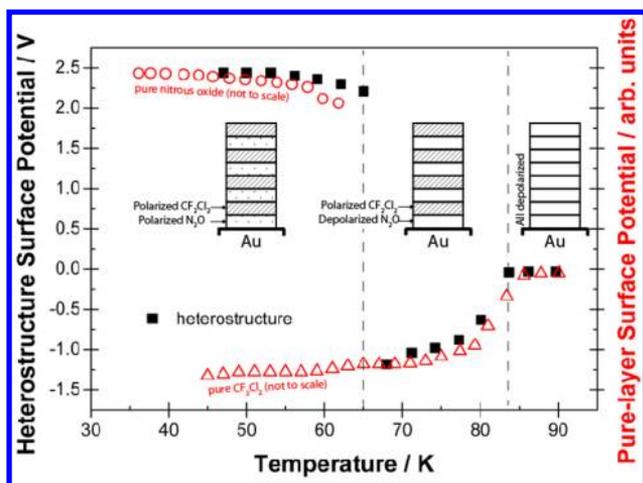
Data show that in the bulk, the two materials behave independently of one another, corroborating remarks in section 3.1 of ref 1 that the magnitude of the spontelectric field is independent of the underlying material, at any rate for sufficiently thick films. However, analysis of the field very close to the interface, to which we now turn, shows that the heterojunction can influence the observed film–vacuum potentials.

#### Examples of Heterojunctions: Close to the Interface.

Figure 2a,b shows data for surface potentials close to the interface, as a function of number of ML, for two types of heterojunctions. In Figure 2a, both materials,  $\text{N}_2\text{O}$  and isoprene, separately harbor positive electric fields. In this figure, 64 ML of  $\text{N}_2\text{O}$  are shown deposited in four stages at 48 K, yielding 1.3 V at the film–vacuum interface. Isoprene was then deposited at the same temperature on top of this layer of



**Figure 2.** (a) Surface potentials for the interface between two spontelectric materials, N<sub>2</sub>O and isoprene, where both materials carry a positive potential. Films were grown at 48 K. (b) The interface between the spontelectric materials N<sub>2</sub>O and CF<sub>2</sub>Cl<sub>2</sub> showing an inversion of the electric field at the material interface as in Figure 1a. Films were grown at 47 K. (c and d) The solid line shows fits, using the model described by eqs 1 and 2, to observed surface potentials for data for both N<sub>2</sub>O–isoprene and N<sub>2</sub>O–CF<sub>2</sub>Cl<sub>2</sub> interfaces in parts a and b. (c) N<sub>2</sub>O–isoprene where  $W$ , the step change in potential, is indicated. The inset schematically illustrates how the model and observations are related. “P” refers to the polarization of the named species. (d) N<sub>2</sub>O–CF<sub>2</sub>Cl<sub>2</sub>. The inset shows data for a N<sub>2</sub>O–CF<sub>2</sub>Cl<sub>2</sub> interface with a Xe buffer layer sandwiched between the spontelectric materials. Values of parameters  $\delta$ ,  $D$ , and  $W$ , eqs 1 and 2, are given in Table 1.



**Figure 3.** Surface potentials for a heterostructure containing alternately N<sub>2</sub>O and CF<sub>2</sub>Cl<sub>2</sub> each deposited at 47 K, with four layers of each material as shown in the insets, with subsequent heating to 90 K. Data for the heterostructure are shown as filled symbols. The red open circles and red triangles show the surface potentials for pure films of N<sub>2</sub>O and CF<sub>2</sub>Cl<sub>2</sub>, respectively, scaled from data in ref 6, with their respective responses to heating.

N<sub>2</sub>O. Close to the N<sub>2</sub>O–isoprene interface, however, the electric field within isoprene varies as a function of the distance from the surface of the nitrous oxide layer. The field is lower in this region and the field rises as the isoprene increasingly tends to exhibit its bulk spontelectric behavior. This is fully achieved after ~150 ML of isoprene have been deposited.

In Figure 2b, materials are chosen which separately harbor electric fields of opposite sign. A total of 40 ML of N<sub>2</sub>O were deposited at 47 K in four stages, yielding 1.0 V at the film–vacuum interface. This was followed by deposition of CF<sub>2</sub>Cl<sub>2</sub> at the same temperature in six unequal stages, paying special attention to the interface. CF<sub>2</sub>Cl<sub>2</sub> harbors a negative electric field<sup>6</sup> with respect to N<sub>2</sub>O and so the surface potential at the CF<sub>2</sub>Cl<sub>2</sub> film–vacuum interface dropped as the thickness of the CF<sub>2</sub>Cl<sub>2</sub> layer was increased. This drop is not initially linear with layer thickness but settles down into a linear regime, that is, a constant electric field, when the layer becomes sufficiently thick. This occurs at ~140 ML (not shown in Figure 2b) with a slope of  $-3.85 \text{ mV ML}^{-1}$ , in agreement with data reported in ref 6.

At the N<sub>2</sub>O/CF<sub>2</sub>Cl<sub>2</sub> interface, represented by the deposition of two molecular layers of CF<sub>2</sub>Cl<sub>2</sub> on the underlying N<sub>2</sub>O, a “step change” in potential is apparent in Figure 2b. Close inspection of the data presented in Figure 2a reveals that a step change, though smaller, is also present. The step changes have

Table 1. Parameters Used in Equations 1 and 2 to Fit Data in Figure 2a,b<sup>a</sup>

interface	$\delta/\text{ML}$	$D/\text{mV ML}^{-1}$	$W/\text{mV}$	$E_1$ and $E_2/\text{mV ML}^{-1}$
N <sub>2</sub> O/isoprene	43.6 ± 1.3	5.24 ± 0.23	79.4 ± 4.4	$E_1 = 21.6$ $E_2 = 5.88$
N <sub>2</sub> O/CF <sub>2</sub> Cl <sub>2</sub>	25.1 ± 0.6	49.20 ± 0.64	-448.6 ± 3.0	$E_1 = 26.6$ $E_2 = -3.85$

<sup>a</sup>Errors were estimated using nonlinear  $\chi^2$  fitting. The fits are shown in Figure 2c,d.

values in Figure 2a, for N<sub>2</sub>O–isoprene, of 79.4 mV and in Figure 2b for N<sub>2</sub>O–CF<sub>2</sub>Cl<sub>2</sub> of -439 mV. This phenomenon is discussed further below.

**Heating a Composite Material.** A pure layer of a spontelectric material depolarizes when heated above a specific temperature, the Curie point. Here we describe what takes place if a two-component composite structure is formed at some low temperature and is heated to a temperature which takes the structure above the Curie point or evaporation point for the materials involved.

Figure 3 shows the results of such an experiment performed on a composite structure containing four alternating layers first of N<sub>2</sub>O and then of CF<sub>2</sub>Cl<sub>2</sub>, representing a total deposition of 168 ML of N<sub>2</sub>O and 76 ML of CF<sub>2</sub>Cl<sub>2</sub>. The structure was deposited at 47 K and subsequently heated in 3 K steps up to 90 K. The surface potential was measured when the temperature equilibrated at each step. Up to 65 K, the surface potential dropped by a few hundred millivolts, but between 65 and 68 K the potential dropped abruptly, from +2.21 V to -1.18 V. On further heating, the surface potential rose again, settling out at -0.03 V at 83 K and beyond.

The observed changes in surface potential with temperature match closely the changes observed when a pure layer of N<sub>2</sub>O and a pure layer of CF<sub>2</sub>Cl<sub>2</sub> are heated individually.<sup>1</sup> The results from such experiments are plotted as a guide over the data in Figure 3. Values of spontelectric potentials for these pure materials have been scaled so that the form of the variation with temperature can be directly compared with data for the heterostructure (full black squares). Note that (i) N<sub>2</sub>O evaporates below or at a temperature very close to its Curie point; hence, the lack of data above 65 K for the pure material and (ii) CF<sub>2</sub>Cl<sub>2</sub> remains adsorbed on the surface up to 117 K, as mentioned below.

Figure 3 illustrates the result that the two components behave apparently independently of one another. Thermal desorption of the complex heterostructure, following the heating experiment in Figure 3, moreover revealed using mass spectrometry that both CF<sub>2</sub>Cl<sub>2</sub> and N<sub>2</sub>O remain on the Au substrate up to the sublimation temperature of pure CF<sub>2</sub>Cl<sub>2</sub> of 117 K. N<sub>2</sub>O was found to desorb together with the CF<sub>2</sub>Cl<sub>2</sub> showing that N<sub>2</sub>O was trapped beneath or within the CF<sub>2</sub>Cl<sub>2</sub> layer and was prevented from being lost at temperatures above 67–68 K, the sublimation temperature of pure N<sub>2</sub>O. The trapped N<sub>2</sub>O was not dipole oriented and thus the surface potentials measured above 68 K refer to the CF<sub>2</sub>Cl<sub>2</sub> film alone.

Figure 3 illustrates the property, likely to be a general characteristic, that the electric field in an underlying spontelectric is maintained when a second spontelectric material is deposited upon it. Results in Figure 3 confirm that polarization is maintained within layers of CF<sub>2</sub>Cl<sub>2</sub> when those layers are sandwiched between layers of N<sub>2</sub>O. The emergence of the negative surface potential when the N<sub>2</sub>O/CF<sub>2</sub>Cl<sub>2</sub> composite film was heated to 68 K shows this feature explicitly. The gradual nulling of the surface potential as the composite

structure was heated further, across the Curie point for CF<sub>2</sub>Cl<sub>2</sub>, also matches the behavior of a pure film of CF<sub>2</sub>Cl<sub>2</sub>,<sup>6</sup> as illustrated by the pure CF<sub>2</sub>Cl<sub>2</sub> data in Figure 3 (red triangles). Given that the surface potential of a spontelectric material, as it approaches its Curie point, is characteristic of the structure of that material, the mapping of the surface potential across the Curie temperature for films of pure CF<sub>2</sub>Cl<sub>2</sub> and CF<sub>2</sub>Cl<sub>2</sub> dosed as part of a composite film, illustrates the conclusion that CF<sub>2</sub>Cl<sub>2</sub> retains its spontelectric properties when part of a complex heterostructure.

#### Analysis of the Heterojunctions Shown in Figure 2a,b.

The present section deals quantitatively with the result that, far from the interface, spontelectrics behave independently of one another, while close to the interface this is generally not the case. It turns out that the behavior of the potential, moving away from the interface, that is, in the overlying film, may be modeled in terms of two independent contributions. These are (i) a contribution caused by interaction with the layer beneath, decaying with distance from the interface. This covers the compensation region mentioned earlier and identified in Figure 2c. (ii) A linear increase or decrease with thickness, depending on the sense of the field within the spontelectric, characteristic of the overlying spontelectric material deposited at the given temperature. Property (ii) is demonstrated directly in Figure 2a,c in which the measured electric field, derived from data in the region labeled “constant  $P_{\text{isoprene}}$ ” in Figure 2c, is that associated with a pure isoprene layer at 48 K, the temperature of deposition for data in this figure. In addition there is the abrupt “contact potential” leading to a very high field (see below) at the boundary, essentially an electrochemical potential corresponding to an interface dipole.

The compensation region, Figure 2c, may be described by the sum of a spatially varying component of the electric field, not spontelectric in nature, superposed on the spontelectric field. We assume that the structure of the underlying film (e.g., N<sub>2</sub>O) remains rigid and that the compensation region forms only in the second material (e.g., isoprene or CF<sub>2</sub>Cl<sub>2</sub>) during deposition. The experimental data in both Figure 2a,b (or 2c,d) can be fitted by eqs 1 and 2, below, for the measured potential and the corresponding electric field. The field is assumed to possess a constant value and a part which decays exponentially from the interface, with a characteristic length scale of  $\delta$  and a magnitude of  $D$  according to

$$E_z(z) = \begin{cases} E_1 & z < 0 \\ E_2 + D \exp(-z/\delta) & z > 0 \end{cases} \quad (1)$$

where  $E_1$  and  $E_2$  are the spontelectric fields for the pure lower and upper species of a heterostructure expressed in  $\text{V ML}^{-1}$  and  $z$  is expressed as the number of MLs from the interface where  $z$  is negative in the N<sub>2</sub>O layer and positive in the isoprene. This yields a potential:

$$V(z) = - \int E dz = \begin{cases} -E_1 z + V_1 & z < 0 \\ -E_2 z + \delta D(\exp(-z/\delta) - 1) + (V_1 + W) & z > 0 \end{cases} \quad (2)$$

where  $V_1$  is the surface potential at the interface and  $W$  describes the abrupt change in potential which occurs over the first two to three ML from the interface. The resulting fits to the data are shown in Figure 2c,d for  $N_2O$ -isoprene and  $N_2O$ - $CF_2Cl_2$  interfaces, respectively. The values of fitting parameters are given in Table 1.

It is noteworthy that the same expressions, eqs 1 and 2 above, can be used to fit both types of heterojunctions, one which is composed of positive-going spontelectrics (Figure 2c) and the other composed of positive and negative-going spontelectrics (Figure 2d). This arises since the qualitative shape of the interfacial field is the same. In  $N_2O$ -isoprene, Figure 2c, the interfacial field is in opposition to the underlying spontelectric field. By contrast, in the case of the  $N_2O$ - $CF_2Cl_2$ , Figure 2d, the interfacial field acts in the same direction and this field and the spontelectric field reinforce one another. Note that in Figure 2d, data do not extend into the linear region associated with an isolated spontelectric  $CF_2Cl_2$ . However, figures given in Table 1 yield an excellent fit to the data, given  $E_2$  equal to the value of  $-3.85$  mV/ML or  $-1.39 \times 10^7$  V/m associated with the isolated material.<sup>6</sup>

The abrupt change in potential measured very close to the interface is an example of the formation of an interfacial dipole. It is not possible to identify the processes which give rise to the dipole on the basis of our data. In this connection there exists rather little literature on insulator-insulator contacts.<sup>20</sup> A similar "potential jump",<sup>15</sup> described here by the parameter  $W$ , was observed at the junction between polarized organic semiconductors: for example the junction of 2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole ( $\alpha$ -NPD) and tris(8-hydroxyquinoline)aluminum ( $Alq_3$ ) yields  $|W| \sim 200$  mV, noting that such organic semiconductors have otherwise markedly different properties to spontelectrics. At all events, in the case of organic semiconductors, the contact potential originates from a difference in the energy levels of the highest occupied molecular orbital (HOMO) of the species on either side of the heterojunction. This has been referred to as a band offset,<sup>16,21</sup> which causes a local displacement of charge across the heterojunction boundary and a corresponding shift in the vacuum level, for species local to the interface. The effects of such realignment may propagate away from the interface and the properties of the material decay exponentially toward bulk values over length scales of tens of nanometers.

We have shown in Figure 2b,d that spontelectrics which individually harbor electric fields in opposing directions can be stacked directly, without major apparent perturbation to their respective spontelectric properties. In order to investigate this further, in a separate experiment a Xe spacer layer was deposited between the  $CF_2Cl_2$  and  $N_2O$ , to create a buffer zone separating the  $N_2O$  layer from the  $CF_2Cl_2$  layer (19 ML  $N_2O$ , 8 ML Xe, and 5 ML  $CF_2Cl_2$ ). These data may be found in the inset to Figure 2d. Results show that the presence of a Xe layer has no qualitative influence on the behavior of the subsequent layer of spontelectric and, in particular, the value of  $W$  is similar to that given in Table 1 for a direct  $N_2O$ - $CF_2Cl_2$  junction. Data in the inset illustrate that the sudden drop in potential,  $W$ ,

at the interface is not caused by a physical mixing of the  $CF_2Cl_2$  and  $N_2O$  layers. Moreover Xe does not show spontelectric behavior and in addition we know from other experiments that the presence of a Xe film deposited on  $N_2O$  has no measurable effect on the surface potential of the system.<sup>1</sup> There would therefore appear to be no detectable interfacial dipole between Xe and  $N_2O$ , noting that Xe ( $\alpha = 4 \text{ \AA}^3$ ) is fortuitously of similar polarizability and thus of similar tendency to  $N_2O$  ( $\alpha = 3 \text{ \AA}^3$ ) to charge displacement in a local field. Ultraviolet photoemission spectroscopy measurements would be of value to verify experimentally the characteristics mentioned above.<sup>20</sup> The parameter  $W$ , in eq 2 and Table 1, as we have suggested, essentially represents charge displacement at the boundary, giving rise to an interfacial dipole.

An alternative means of describing charge displacement is to fit the change in potential in the region of the interface as a continuous polynomial function. We then find, using the data for  $N_2O/CF_2Cl_2$  (Figure 2d), that the negative electric field in  $CF_2Cl_2$  over 0 to 1 ML is  $1.04 \times 10^9$  V/m, from 1–2 ML is  $6.25 \times 10^8$  V/m, from 2–3 ML is  $4.57 \times 10^8$  V/m and from 3–4 ML is  $2.18 \times 10^8$  V/m, given a layer separation in  $CF_2Cl_2$  of  $0.28 \text{ nm}^{23}$  unchanged from that in the bulk of the material. These large fields distort the electron distribution in the component species, yielding nonlinear effects, ignored in our current treatment of the spontelectric effect.<sup>1</sup> We note that this tendency for charge displacement, when represented as a current, makes the connection with the so-called "modern theory of polarization", in which the polarization is given by the adiabatic accumulated geometric phase ("Berry phase") through passage of the current around some conceptual path in the material.<sup>22–25</sup>

**Concluding Remarks.** Spontelectrics are a recent discovery in the physical chemistry of solids and their properties are far from fully explored. The present paper is part of this exploration and remains therefore an investigation devoted purely to heterostructured spontelectrics, without any attempt at integration with other materials. For the present we have only scratched the surface of this means of creating nanoscale objects with tailored fields. There appears to be no limit, save that imposed by our imagination or laboratory time, to the complexity of structures which may be achieved. At our disposal are the parameters of the temperature of deposition of each layer of spontelectric, the direction of the electric field, determined by the nature of the material chosen, inclusion of diluted layers of material (to be submitted), inclusion of barrier layers of nonspontelectric materials or of spontelectric materials laid down above their Curie points. In addition, spontelectrics can be laid down upon surfaces, patterned, for example, by reactive ion etching to create any desired geometry. Applications might be as part of the fabrication process of nanotraps for solid state quantum computing devices, the creation of an electric field increasing (say) in a controlled manner on the nanoscale by laying down a single spontelectric material such as  $N_2O$  at ever decreasing temperatures or the creation of novel Kerr or Pockels cells, say, through the use of zigzag spontelectric composites.

The chief practical drawback at present is of course the requirement for cryo-systems. Certain established spontelectrics function above 77 K, such as toluene, but the great majority of known materials function most effectively at 40 K to 50 K. As far as we are aware, there is no fundamental reason why higher temperature or even room temperature spontelectrics may not exist. These might be sought, for example, in

the homologous series of alkyl formates. There remains much exploratory work to be performed.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Field, D.; Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. C.; Dunger, J. Spontaneous Electric Fields in Solid Films: Spontaneous Electric Fields. *Phys. Chem. Chem. Phys.* **2013**, *15*, 345–392.
- (2) Balog, R.; Cicman, P.; Jones, N.; Field, D. Spontaneous Dipole Alignment in Films of N<sub>2</sub>O. *Phys. Rev. Lett.* **2009**, *102*, 2–5.
- (3) Field, D.; Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. A New Class of Spontaneously Polarized Materials. *Europhys. News* **2011**, *42*, 32–35.
- (4) Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. C.; Field, D. A New Form of Spontaneously Polarized Material. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21035–21044.
- (5) Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. C.; Field, D. Spontaneous Electric Fields in Films of Cis-Methyl Formate. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9972–9976.
- (6) Cassidy, A.; Plekan, O.; Balog, R.; Jones, N. C.; Field, D. Spontaneous Electric Fields in Films of CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub> and CFCl<sub>3</sub>. *Phys. Chem. Chem. Phys.* **2012**, *15*, 108–113.
- (7) Birol, T.; Benedek, N. A.; Fennie, C. J. Interface Control of Emergent Ferroic Order in Ruddlesden-Popper Sr<sub>n+1</sub>Ti<sub>n</sub>O<sub>3n+1</sub>. *Phys. Rev. Lett.* **2011**, *107*, 257602.
- (8) Couet, S.; Bisht, M.; Trekels, M.; Menghini, M.; Petermann, C.; Van Bael, M. J.; Locquet, J.-P.; Rüffer, R.; Vantomme, A.; Temst, K. Electric Field-Induced Oxidation of Ferromagnetic/Ferroelectric Interfaces. *Adv. Funct. Mater.* **2014**, *24*, 71–76.
- (9) Scott, J. F. Applications of Modern Ferroelectrics. *Science* **2007**, *315*, 954–959.
- (10) Nguyen, T. D.; Mao, S.; Yeh, Y.-W.; Purohit, P. K.; McAlpine, M. C. Nanoscale Flexoelectricity. *Adv. Mater.* **2013**, *25*, 946–974.
- (11) Srinivasan, G. Magnetolectric Composites. *Annu. Rev. Mater. Res.* **2010**, *40*, 153–178.
- (12) Martins, P.; Lanceros-Méndez, S. Polymer-Based Magnetolectric Materials. *Adv. Funct. Mater.* **2013**, *23*, 3371–3385.
- (13) Ding, J.; Adeyeye, A. O. Binary Ferromagnetic Nanostructures: Fabrication, Static and Dynamic Properties. *Adv. Funct. Mater.* **2013**, *23*, 1684–1691.
- (14) Mas-Torrent, M.; Rovira, C. Role of Molecular Order and Solid-State Structure in Organic Field-Effect Transistors. *Chem. Rev.* **2011**, *111*, 4833–4856.
- (15) Noguchi, Y.; Miyazaki, Y.; Tanaka, Y.; Sato, N.; Nakayama, Y.; Schmidt, T. D.; Brütting, W.; Ishii, H. Charge Accumulation at Organic Semiconductor Interfaces due to a Permanent Dipole

Moment and Its Orientational Order in Bilayer Devices. *J. Appl. Phys.* **2012**, *111*, 114508.

(16) Zhong, S.; Zhong, J. Q.; Mao, H. Y.; Zhang, J. L.; Lin, J. D.; Chen, W. The Role of Gap States in the Energy Level Alignment at the Organic-Organic Heterojunction Interfaces. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14127–14141.

(17) Kliem, H.; Kuehn, M.; Martin, B. The Weiss Field Revisited. *Ferroelectrics* **2010**, *400*, 41–51.

(18) Ramesh, R.; Spaldin, N. A. Multiferroics: Progress and Prospects in Thin Films. *Nat. Mater.* **2007**, *6*, 21–29.

(19) Balog, R.; Cicman, P.; Field, D.; Feketeová, L.; Hoydalsvik, K.; Jones, N. C.; Field, T. A.; Ziesel, J.-P. Transmission and Trapping of Cold Electrons in Water Ice. *J. Phys. Chem. A* **2011**, *115*, 6820–6824.

(20) Greiner, M. T.; Helander, M. G.; Tang, W.-M.; Wang, Z.-B.; Qiu, J.; Lu, Z.-H. Universal Energy-Level Alignment of Molecules on Metal Oxides. *Nat. Mater.* **2012**, *11*, 76–81.

(21) Lee, S. T.; Wang, Y. M.; Hou, X. Y.; Tang, C. W. Interfacial Electronic Structures in an Organic Light-Emitting Diode. *Appl. Phys. Lett.* **1999**, *74*, 670–672.

(22) Resta, R. Electrical Polarization and Orbital Magnetization: The Modern Theories. *J. Phys.: Condens. Matter* **2010**, *22*, 123201.

(23) Vanderbilt, D.; King-Smith, R. Electric Polarization as a Bulk Quantity and Its Relation to Surface Charge. *Phys. Rev. B* **1993**, *48*, 4442–4455.

(24) Rabe, K. M.; Ahn, C. H.; Triscone, J. M., Eds. *Physics of Ferroelectrics: A Modern Perspective*; Topics in Applied Physics, Vol. 105; Springer: New York, 2010.

(25) Resta, R.; Vanderbilt, D. Theory of Polarization: A Modern Approach. In *Physics of Ferroelectrics*; Topics in Applied Physics, Vol. 105; Springer: Berlin, Germany, 2007; pp 31–68.