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A Spontaneously Electrical State of Matter

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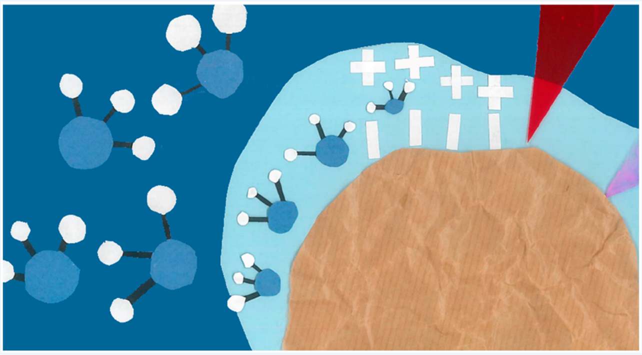

CONSPECTUS: Molecular deposition on solid surfaces forms crystalline or amorphous/glassy thin solid films. Intermolecular interactions govern the packing and dynamics of these films. The connection between molecular structure and intermolecular interactions is based on understanding electrostatic forces, dispersion forces and hydrogen bonding. Recently, an entire class of dipolar molecular species have demonstrated counter-intuitive self-organization such that the dipole moments of individual molecules are oriented in thin films. This leads to the spontaneous generation of polarized molecular films manifesting a polarization charge equivalent to tens to hundreds of volts in strength at the film-vacuum interface, relative to the film-substrate interface. These voltages, and the corresponding electric fields present in such films, result from a collective and spontaneous orientation of molecular dipoles throughout the film during film growth and represent a metastable state of polarized material. The existence of these materials should encourage reconsideration of the importance of solid-state intermolecular electrostatic interactions.

This account will detail observations of the spontaneous electric fields in molecular solids, provide insights into the dynamics and structure of molecular materials that the emergence of these electric fields can facilitate, and present a dipole-alignment based mean-field model that reproduces the temperature dependence of the electric field strength. Species as diverse as carbon monoxide, nitrous oxide, freons, simple alcohols, and *cis*-methyl formate have been demonstrated to spontaneously generate electric fields. We have reported electric fields more than 10^8 V m^{-1}, have shown how field strength varies with the film deposition temperature, and have reported temperature-dependent Stark shifts observable in both infrared and ultraviolet absorption spectra. The latter has led to the reporting of large Wannier−Mott excitons in wide band gap molecular materials, such as solid carbon monoxide and ammonia.

Changes in the field strength with time, at specific temperatures, can be related to the structural dynamics of glassy molecular solids. Measurement of surface potentials is a very sensitive technique by which to observe the rotation and translation of molecular species buried in thin films. This is particularly true for polarized, supercooled molecular glasses, where surface potentials have been used to report on secondary relaxation processes that have hitherto been hidden from measurement.

Characterizing spontaneously electric molecular films, and understanding their behavior, requires the inclusion of nonlocal and nonlinear effects. The mean-field model that we present describes the data by connecting the energy of interaction of an average dipole with the mean effective field in the film, where this field is itself a function of the degree of polarization. This feedback loop produces a smooth function with a nonintuitive, discontinuous differential. The condensation of thin molecular films is an important means by which molecular solids are generated in the interstellar medium and represents a key pathway for the generation of organic optically and electrically active materials. It may also be possible to manipulate chemistry with the intense, localized electric fields acting as or acting on catalysts. The repercussions of the spontaneous generation of bound surface charges and the presence of electric fields in molecular solids will be discussed in these contexts.

■ KEY REFERENCES

- Cassidy, A.; Jørgensen, M. R. V.; Glavic, A.; Lauter, V.; Plekan, O.; Field, D. A Mechanism for Aging in a Deeply Supercooled Molecular Glass. *Chem. Commun.* **2021**, 57, 6368−6371.[1] We used temporal instabilities in the degree of molecular orientation in supercooled glassy films, to measure the extent of molecular rotation and separately measured molecular translation using neutron scattering. This gives new insight into the aging process in a glass.

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- Chen, Y.-J.; Muñoz Caro, G. M.; Aparicio, S.; Jiménez-Escobar, A.; Lasne, J.; Rosu-Finsen, A.; McCoustra, M. R. S.; Cassidy, A. M.; Field, D. Wannier−Mott Excitons in Nanoscale Molecular Ices. *Phys. Rev. Lett.* **2017**, 119, 157703.[2] We measured the effect of the electric field strength on Wannier−Mott excitons in thin films of spontaneously polarized carbon monoxide; a molecular solid with a wide band gap.
- Rosu-Finsen, A.; Lasne, J.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Enabling Star Formation via Spontaneous Molecular Dipole Orientation in Icy Solids. *Astrophys. J.* **2016**, 832, 1.[3] We analyzed the reduction of ionization in star forming regions of the interstellar medium, induced by spontaneously polarized films of carbon monoxide coating dust grains, reporting a factor 5 decrease in the time scale to achieve expulsion of magnetic fields and enable gravitational collapse.
- Lasne, J.; Rosu-Finsen, A.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Spontaneous Electric Fields in Solid Carbon Monoxide. *Phys. Chem. Chem. Phys.* **2015**, 17, 30177−30187.[4] Electric fields approaching 4×10^7 Vm^{-1} were measured in thin films of carbon monoxide, obtained indirectly from Stark shifts induced in infrared spectroscopic experiments.

1. INTRODUCTION

Our key observation was the serendipitous discovery that thin films of dipolar molecules, formed by condensation at low-temperatures, may be spontaneously polarized.[5] Such films display large surface potentials, which increase linearly with film thickness. As an illustrative result, data collected on films of nitrous oxide grown at different temperatures are shown in Figure 1. The surface potentials give rise to electric fields within the film, which we term "spontelectric fields". These fields influence the infrared and ultraviolet spectroscopy of solid films, providing new tools to study the structure of these ubiquitous films and their solid-state dynamics.

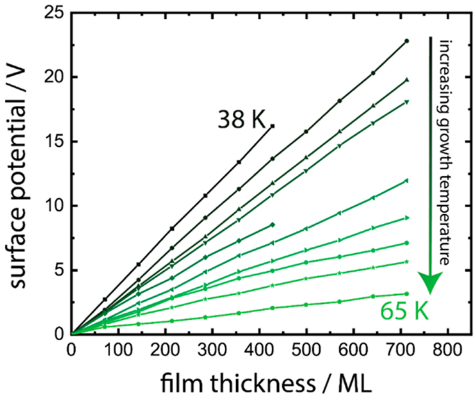

Figure 1. Surface potentials measured on films of N_2O as a function of film thickness, in monolayers (ML), for deposition temperatures of 38, 40, 42, 44, 48, 52, 57, 60, 63, and 65 K. The slope of each set of data gives the electric field in V m^{-1}, for spacings of 2.855 ± 0.02 Å below 48 K and 2.905 ± 0.02 Å above 48 K. Thus, at 38 K, (black squares) the spontelectric field is 1.33×10^8 V m^{-1}. Data were obtained using low energy, high resolution electron beams. Adapted with permission from ref 6. Copyright (2011) Royal Society of Chemistry.

1.1. The Nature of the Spontelectric Effect

The spontelectric effect is a bulk phenomenon, independent of the nature of the surface on which dipolar molecules are deposited and is observed in films with a minimum thickness of 5−10 monolayers (ML). This is well past the limit where one can reasonably expect work function changes to have any effect. To measure the surface potential, films were prepared by condensing the molecular species of interest from background gas onto a cold finger held at a known temperature, under ultrahigh vacuum conditions. The degree of spontaneous polarization was determined by measuring the polarization charge at the surface of the film, as a function of deposition temperature and film thickness, using an electron irradiation technique. A high resolution (1−2 meV) low energy electron beam, of typically ∼200 fA, generated through synchrotron photoionization of argon (ASTRID Aarhus), was directed toward the substrate. The spontaneous potential appearing on the surface of any film was measured by applying a bias potential to the system and effectively adjusting this bias to null the current. This gives a direct measurement of the potential at the film-vacuum interface.[7] Note that the interrogating electron current was insufficient to depolarize the system significantly. Sometime after our "discovery" paper,[5] we came across the neglected data of Kutzner,[8] obtained using a Kelvin probe, in which the spontelectric effect is reported and correctly ascribed to dipole orientation. An occasional glimpse of the spontelectric effect may be found here and there in the intervening period of 50 years.

Bulk polarization arises since molecular dipoles show a small propensity to net orientation, Figure 2. There is no free charge in the film and the spontelectric field is therefore constant in the z-direction, normal to the plane of the film, and is zero in the x−y plane. Figure 1 shows that spontelectric fields are strongly dependent on surface deposition temperature.

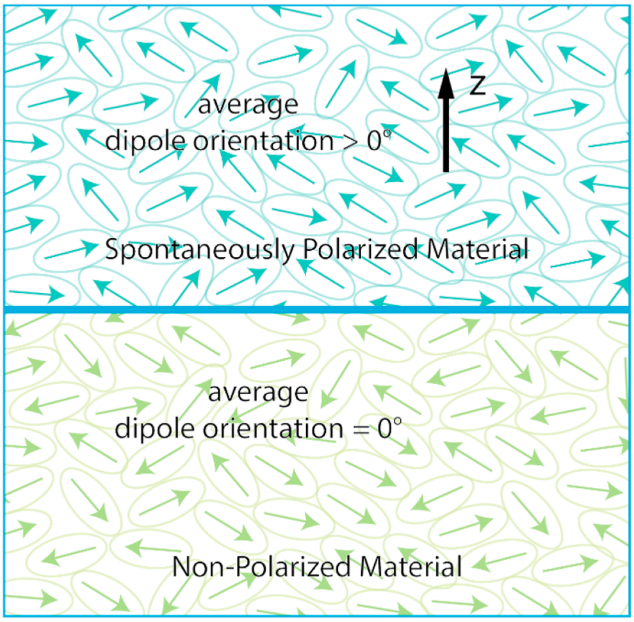

Figure 2. A representation of a dipole-oriented, polarized material (top), compared to a nonpolarized material (bottom). The oriented dipoles in the polarized material, show a tendency for dipoles to generate some average angle, $\theta > 0$, with the plane of the film. In a nonpolarized material, $\theta = 0$.

Heating a film prepared in the spontelectric state causes little change in internal electric field. However, sublimation apart, a critical temperature, a "Curie" temperature, is encountered at which the field decays abruptly. The spontelectric field is not reinstated by subsequent cooling of the film.[7]

The molecular materials of which spontelectric films are composed must possess a permanent dipole moment. The species include simple hydrocarbons, halocarbons, organic formates and alcohols,[5,9] benzene derivatives and such simple molecules as ammonia,[10] carbon monoxide and nitrous oxide. A list of materials studied in our own group is provided in Table 1. Films may be either crystalline, for example nitrous oxide[11] and ammonia[12] or noncrystalline and glassy, for example *cis*-methyl formate.[1] To underpin our observations, a mean-field model of spontelectrics, section 2, has been developed to model the electric field change with temperature.

Table 1. A list of species identified as spontelectric by means of experiments conducted in our own laboratories

Molecule	Gas phase dipole moment/Debye	Techniques used to identify spontaneous polarization
Nitrous oxide	0.166	Surface potential measurements[6]
		Stark shifts in IR spectroscopy[13]
		Stark shift in VUV spectroscopy[14]
Carbon monoxide	0.122	Stark shifts in IR spectroscopy[4]
		Stark shift in VUV spectroscopy[2]
Methyl formate	1.766	Surface potential measurements[15]
		Stark shifts in IR spectroscopy[16]
Ammonia	1.42	Stark shift in VUV spectroscopy[12]
Toluene	0.385	Surface potential measurements[6]
Freon 13 (CF_3Cl)	0.5	Surface potential measurements[17]
Freon 12 (CF_2Cl_2)	0.510	Surface potential measurements[17]
Freon 11 ($CFCl_3$)	0.45	Surface potential measurements[17]
2,5-dihydrofuran	1.320	Surface potential measurements[7]
Ethyl formate	1.980	Surface potential measurements[7]
Isoprene	0.252	Surface potential measurements[6]
Isopentane	0.130	Surface potential measurements[6]
Propane	0.08	Surface potential measurements[6]

1.2. Alternative Forms of Spontaneously Polarized Molecular Solids

Spontaneous polarization is best known in ferroelectrics, in which polarization through creation of a dipole generally arises locally through distortion of the unit cell, rather than globally and collectively as in spontelectrics. The characteristic property of ferroelectrics is that of hysteresis, a property not yet observed in spontelectrics. Spontaneous polarization is also encountered in ferroelectric liquid crystals.[18−20] Thin films of amorphous solid water have also been reported to be spontaneously polarized by several authors.[21−23] This has been linked to porosity in the films and the collective orientation of under-saturated hydrogen bond donors.[24] We note also that molecular dynamics simulations have indicated a tendency for net dipole orientation in condensing water films, qualitatively recreating the negative surface potential at the film surface that is measured experimentally.[25] In addition, there is an extensive group of molecular organic semiconductors, that demonstrate spontaneous polarization[26] and whose properties resemble those of spontelectric films. A notable example is Alq_3, in which bulk dipole orientation is responsible for the electric fields in this and related glassy materials.[27−30] Recent results have also demonstrated that ultrastable glasses[31] may in some cases be spontaneously polarized.[32−34]

A vital element in the spontelectric state is the feedback between dipole orientation and the electric field of which this orientation is the root. This fundamental aspect of the spontelectric state and the collective nature of polarization are both absent in any discussion of materials such as organic semiconductors.

1.3. The Potential Importance of Spontelectric Behavior

The immediate impact of this work has been in astrophysics and highlights the importance of the microscopic in controlling the macroscopic process of star formation in dense prestellar cores.[3,4,35] Dust grains accrete molecular films of almost pure CO at the low temperatures reported in dark molecular clouds, where stars form. This growing layer of CO ice presents a spontelectric mantle with a positive surface potential and so attracts gas phase electrons to collide with the grain, which in turn attracts positive ions to preserve electroneutrality. This leads to increased interaction between ions and electrons on the grain surface and reduces the degree of ionization in star-forming cores by a factor of between 5 and 6, facilitating the expulsion of magnetic fields and significantly increasing the predicted rate of star formation, removing a major inconsistency in the field of star formation.

Turning to applications in electronics, internal electric fields are known to impact on charge carrier flow in thin organic films, key contributors to technological advance in electronics and optoelectronics.[36,37] Oriented molecular dipoles in polar systems are a likely cause of these fields. This links directly to observations of spontelectric fields, noting the success of spectroscopic probes in revealing the presence, magnitude and distribution of such fields within organic semiconductor devices,[38−41] through the role of the Stark effect.

At the same time as integrating our knowledge of the spontelectric effect into the field of organic semiconductors, we may also be able to realize the Holy Grail proposed by Zare, that is, the manipulation of chemistry at surfaces through intense, localized electric fields of magnitude around 10^8 V m^{-1},[42] as in the active pocket of an enzyme.[43] Related behavior has been observed by application of external electric fields, using surface capacitors[44−46] and AFM tips.[47−49]

Several open questions need to be addressed to achieve these applications and are discussed in Section 5. We begin with an introduction to the spontelectric model.

2. A PHYSICAL MODEL FOR THE SPONTELECTRIC STATE

The model of spontelectrics addresses how the spontaneous orientation of molecules within a film depends on the temperature of the surface on which material is deposited (Figure 1). The degree of orientation of dipoles in a field is expressed using the textbook Langevin expression,[50] and is given in atomic units by,

$$\frac{\langle \mu_z \rangle}{\mu} = m = \coth\left(\frac{E_z\,\mu}{T}\right) - \left(\frac{E_z\,\mu}{T}\right)^{-1} \tag{1}$$

where E_z is the local field normal to the film (z-axis), noting that fields in the $x-y$ plane of the film average to zero, μ is the dipole moment of the molecule in the solid state and T is the deposition temperature. The model formulates the local electric field, E_z, which any molecule experiences at any site, where this electric field itself contains the degree of orientation.[7] Net molecular orientation makes the film slightly positive or negative on one side, relative to the other, giving rise to the spontelectric field. The local field, E_z, is described by

$$E_z = [E_s[1 + \zeta m^2] - E_A m] \tag{2}$$

The E_s term arises from polarization, dispersion, and covalent interactions; the second and anisotropic term, involving the parameter ζ, explicitly involves the dipole—dipole interaction; and the third term involving the parameter E_A, that is, $E_A m$, represents the spontelectric field itself. We define the degree of orientation, m, as the spatially averaged proportion of the total solid-state dipole, pointing in the z-direction. Combining eqs 1 and 2, the expression governing the relationship between m and T may be expressed as $m = f(T,m)$. This equation is not analytically soluble and is an implicit equation containing feedback, through which the behavior of orientation with T depends on the degree of orientation itself. The mean orientation, which determines the spontelectric field, will itself contribute to the mean orientation of the molecules, which itself affects the value of the spontelectric field and so on. Numerical solutions are sought for which the molecules agree in their degree of orientation, through a mutual global consensus.

We use two examples, nitrous oxide and *cis*-methyl formate, one straightforward and one pathological, showing how the model reproduces observed m versus T. The two parameters, E_s and ζ, are obtained by fitting to observations. The proportionality constant between the value of m and the parameter E_A, may be shown to take the value of the total dipole in the solid state, divided by the molecular volume and the permittivity of free space, as described in ref 7.

Experimental data, derived from Figure 1, for the measured spontelectric field versus deposition temperature,[6,11] are shown in Figure 3 for nitrous oxide [black squares]. Data in Figure 3 reveal the subtlety that there is a phase change at 48 K. The phase change was confirmed separately using reflection-absorption infrared absorption spectroscopy, neutron scattering and temperature-programmed desorption experiments.[11] The fitting parameters of the model vary accordingly (Table 2).

Turning now to *cis*-methyl formate, we enter the realm of disorganized glasses.[1] The observed variation of m with deposition temperature for *cis*-methyl formate is shown in Figure 4.[15] Above 77.5 K, an increase in polarization is observed with increasing temperature. The data go smoothly through a numerical minimum and the model yields the observed result that m versus T is not monotonic.

However, the form of $m = f(T,m)$ is such that its total derivative can never be zero for any physically realizable values of the parameters governing $f(T,m)$. Thus, the total differential does not represent the slope. The region of the minimum in m versus T is in fact characterized by the differential becoming infinite, negative to the low T side and positive to the high T side, in this case. Examples also exist of a maximum in m versus T, for example, for 1-pentanol,[9] where the differential is positive on the low T side and negative on the high T side.[51]

The outstanding current problem is that we do not have insight into how the system becomes caught in the spontelectric state or, further, how the behavior in Figure 4 can arise. In earlier work, we made a qualitative suggestion that librational fluctuations were an underlying cause of the

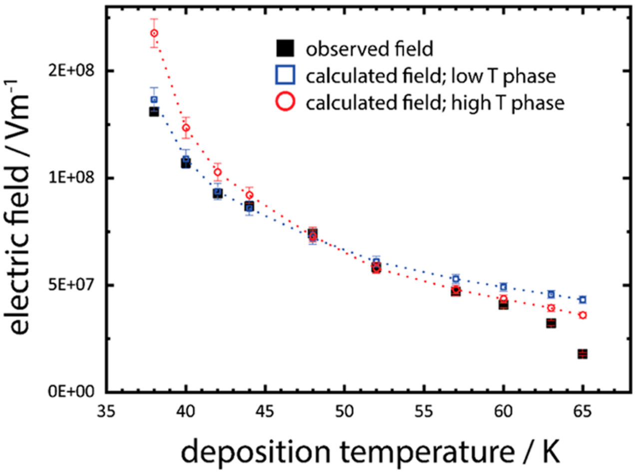

Figure 3. Measured electric field in nitrous oxide as a function of film deposition temperature (black squares), with the calculated fields for the low temperature (blue squares) and high temperature phase (red circles) superimposed. The dotted lines act as a guide to the eye. The fields shown are those derived from the data given in Figure 1. Nitrous oxide is close to sublimation at temperatures around 60 K causing the model to fail for $T > 63$ K. Systematic errors in the film thicknesses, and therefore in the spontelectric field, are estimated at 20%. Adapted with permission from ref 11. Copyright 2016 American Chemical Society.

Table 2. Nitrous Oxide: Parameters of the Model Used to Create the Fits Shown in Figure 3[a]

N_2O: low temperature phase < 48 K	N_2O: high temperature phase > 48 K
Layer separation 0.2855 ± 0.002 nm	Layer separation 0.2905 ± 0.002 nm
$E_s = 7.79 \pm 0.28 \times 10^8$ V m^{-1}	$E_s = 6.01 \pm 0.28 \times 10^8$ V m^{-1}
$E_A = 6.69 \pm 0.24 \times 10^8$ V m^{-1}	$E_A = 6.92 \pm 0.25 \times 10^8$ V m^{-1}
$\zeta = 26.8 \pm 1.8$	$\zeta = 57.5 \pm 3.9$

[a] The mean field in the z-axis, E_z, is given for each phase by eq 2, where m varies between 0.199 at 38 K to 0.046 at 63 K. Layer separations are derived from neutron scattering data.

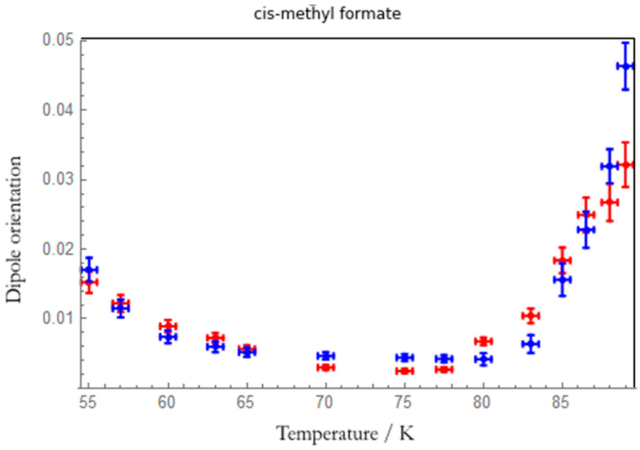

Figure 4. Variation of the degree of dipole orientation, m, with deposition temperature for *cis*-methyl formate. Experimental data are shown as red points, derived from direct measurement of film surface potentials. Fits to experiment, blue points, are for $E_s = 1.37 \pm 0.27 \times 10^7$ V m^{-1}, $E_A = 1.27 \pm 0.19 \times 10^9$ V m^{-1}, and $\zeta = 12200$. Adapted with permission from ref 15. Copyright 2012 Royal Sociey of Chemistry.

spontelectric effect, as supported by recent large scale simulations of *cis*-methyl formate films.[52] Strikingly, the molecular dynamics simulations in 52, based on *ab initio* potentials, reproduced the variation in net orientation in *cis*-methyl formate versus temperature of deposition, giving a value of deposition temperature for the minimum of around 70 K, close to that observed at 77.5 K.

2.1. The broader Context of Dipolar Films: Collective Behavior and a Comparison with Spin Glasses

Surface potential measurements for thin films of N_2O diluted in Xe indicate that films persist in exhibiting a spontelectric field until the N_2O molecules are at least 1.25 nm apart, some four times the separation in solid N_2O.[53] The field drops as the degree of dilution of N_2O in the nonpolar Xe matrix increases. These observations support the hypothesis that the spontelectric effect is a concerted many-body phenomenon.

Consequently, the standard picture, that properties of a solid can be described by individual species, or individual unit cells, and their local interactions, must be abandoned for spontelectrics. Thus, spontelectrics bear a strong resemblance to the large family of spin glasses whose properties again arise from the collective agency of many species.[54] A spin glass ceases to exist in the spin glass state if the degree of dilution of the magnetic moments is such that they are too far apart to interact, analogous to the dilution-induced decay in the spontelectric field just described.[53] There are two explicit differences between spin glasses and spontelectric materials: (i) the dipoles involved in a spin glass are magnetic dipoles and (ii) spin glasses, having zero spontaneous net magnetic dipole orientation, do not generate a spontaneous magnetic field.

Consider first glassy spontelectrics, that is, noncrystalline materials, in relation to spin glasses. Glassy spontelectrics are composed of randomly oriented species, save for the residual orientation associated with the spontaneous electric field. The energy landscape is craggy with deep minima. This feature is quenched into the system, prepared at any temperature, and leads to complex decay patterns in glassy spontelectrics. This behavior is observed in methyl formate (section 4).[1] Both spin glasses and glassy spontelectrics are nonergodic, due to the deep minima in the energy landscape, and therefore are not strictly thermodynamic objects. In general, for both glassy and crystalline spontelectrics, the measured properties of any film are not independent of the route by which it was formed,[7] violating a fundamental tenet of a thermodynamic system. For example, a film of crystalline nitrous oxide formed by deposition at 40 K displays a spontelectric field of 1.09×10^8 V m^{-1} field. If ostensibly the same film is prepared by deposition at higher temperature, say, 60 K, and cooling to 40 K, the spontelectric field is ~2.66 times lower.[6]

In the spontelectric model described above we have used statistical mechanics to understand a nonergodic system. For example, we define temperature independent parameters to describe observed phenomena. Since the model provides a useful description of spontelectric properties in a wide variety of contexts we feel justified in this approximation and our classical approach. We acknowledge that further insight into the spontelectric effect will be gained by the application of more accurate quantum chemical methods.

3. SPECTROSCOPIC STUDIES OF SPONTELECTRIC MATERIALS

3.1. Vibrational Spectroscopy, Spontelectric Behavior, and the Vibrational Stark Effect (VSE)

We now turn to the spectroscopic investigation of spontaneous dipole orientation in thin solid films by IR spectroscopy. Sufficiently thick and ordered molecular films will exhibit Longitudinal Optical (LO)−Transverse Optical (TO) splitting of the molecular modes in the solid state. Such LO-TO splitting arises through electrostatic interactions coupling the individual molecular vibrations with the collective vibrational motions of the solid. In a spectroscopic measurement from a thin film, with the incident beam at grazing incidence, LO vibrations can only be measured when they occur perpendicular to the surface of the film and TO vibrations can only be measured when they occur parallel to the surface of the film. In reflection−absorption infrared spectroscopy (RAIRS),[55] used here, only the LO mode would have the necessary symmetry to be observed following the metal surface selection rule and the TO band should be suppressed.[56] Fortuitously, burying the reflective substrate under a few hundred nanometers of rough amorphous silica[57] allows us to circumvent the metal surface selection rule while still benefiting from the enhanced sensitivity described in refs 55 and 56. This is illustrated in measurements reported in Figure 5 on thin solid films of N_2O.[13]

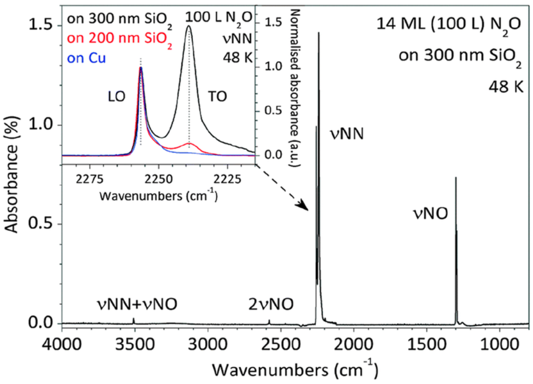

Figure 5. RAIR spectrum of 100 Langmuirs (L) or 14 monolayers of N_2O deposited at 48 K on a copper plate coated with 300 nm of amorphous silica. The inset shows the *ν*NN region of the RAIR spectra of 100 L of N_2O on bare copper (blue), on copper coated with 200 nm (red) or 300 nm (black) of amorphous silica at 48 K. The intensity of each spectrum has been normalized to that of its LO mode. Dotted lines indicate the positions of the LO and TO modes. Adapted with permission from ref 13. Copyright 2015 Royal Society of Chemistry.

The simultaneous observation of both LO and TO modes provided us with a platform to explore the temperature dependence of the vibrational spectroscopy of spontelectric films of N_2O, and Figure 6 illustrates our reported observations on the *ν*NN band of solid N_2O on our substrate. The LO-TO splitting decreases with increasing deposition temperature, that is, with decreasing spontelectric field. In this context, we also note the observations of Hama et al. on amorphous N_2O solid films using infrared multiple-angle incidence resolution spectrometry (IR-MAIRS).[58]

Shifts in vibrational frequency are a necessary consequence of the presence of the spontelectric field, through the

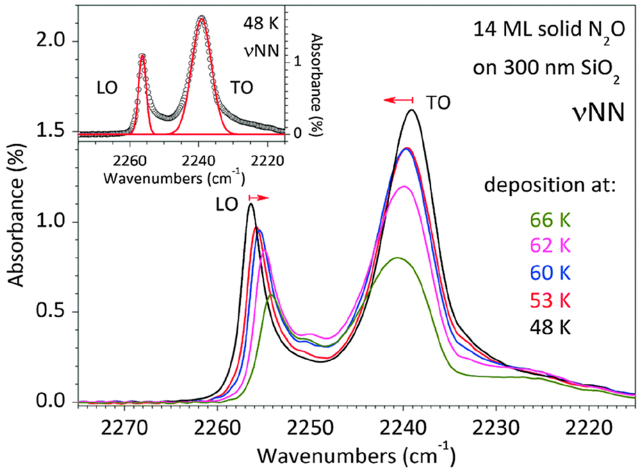

Figure 6. RAIR spectra showing the νNN band of 14 ML N_2O films deposited at 48, 53, 60, 62, and 66 K on 300 nm silica. The red arrows highlight the shift of the LO and TO modes with increasing deposition temperature of the films. The inset presents the RAIR spectrum of the film deposited at 48 K (open symbols) and the Gaussian fits to the LO and TO modes (full lines). Adapted with permission from ref 13. Copyright 2015 Royal Sociey of Chemistry.

Vibrational Stark Effect (VSE). Since the 1990s, Boxer and co-workers have demonstrated the importance of the VSE in quantifying the impact of electric fields on molecular vibrations in a wide variety of environments.[59−61] We have coupled the model of spontelectric behavior, outlined in section 2, and detailed in ref 13, with a simple linear VSE. This procedure reproduces the observed experimental shifts in LO-TO splitting as a function of deposition temperature shown in Figure 7.

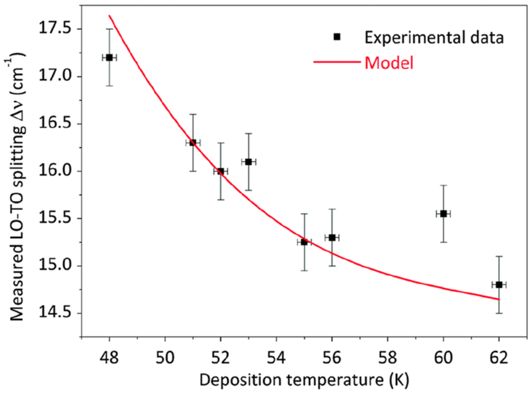

Figure 7. Comparison between the spontelectric model (red curve), using known values of parameters of the model, Table 2, involving no additional fitting, and experimental values of LO-TO splitting in N_2O films grown at different deposition temperatures. Adapted with permission from ref 13. Copyright 2015 Royal Sociey of Chemistry.

We have also studied the spontelectric effect in CO[35] and in *cis*-methyl formate[16] using RAIRS. The former confirmed that films of CO ice are spontelectric, Section 3.2, and the latter confirmed the anomalous and counterintuitive behavior of *cis*-methyl formate with increasing deposition temperature, Figure 4.[16]

3.2. Electronic Spectroscopy, Spontelectric Behavior, and Wannier−Mott Excitons

When a solid material absorbs a photon of sufficient energy to give rise to an electronic excitation, the excited electron and newly formed hole can remain bound through Coulombic attraction. This gives rise to a quasi-particle called an *exciton*. The electron and hole are spatially separated in the exciton and the quasi-particle can diffuse through the material. The conduction properties and lifetimes of excitons govern much of the physics of photovoltaics.[62−64] If the radius of the quasi-particle is larger than the unit cell dimensions, then the exciton is described as delocalized, and the term Wannier−Mott exciton is used. The spontelectric effect has revealed that Wannier−Mott excitons, considerably larger than the dimensions of the unit cell, are prevalent in condensed molecular ices.[2] An electric field influences the separation of the hole and electron in a Wannier−Mott exciton and, thus, the energy of formation of the exciton and the accompanying wavelength of absorption of light by a solid film. The field introduces a Stark shift in the position of absorption peaks in the electronic spectra of spontelectric materials, through the spontelectric field pushing the hole and electron apart.[2] Since the field depends on the temperature of film deposition, so the absorption spectrum changes with this temperature. An example is the $A^1\Pi \leftarrow X^1\Sigma$ transition in thin CO films condensed between 20 and 26 K. This shows a series of absorptions peaks, which are blue-shifted by up to 400 cm^{-1} as the growth temperature is decreased from 26 to 20 K.[65,2] This observation and the associated temperature range match the increasing spontelectric field in CO thin films, measured through LO-TO splitting in RAIRS (section 3.1).

Using the ASTRID2 synchrotron storage ring at Aarhus, we have measured the variation of absorption wavelength with film deposition temperature in the vacuum ultraviolet (VUV) range for a series of spontelectric molecular solids, including nitrous oxide, ammonia and methanol.[14,12] The large size of Wannier−Mott excitons, typically several nm, results in a binding energy of electron and hole in the meV range, with accompanying sensitivity to spontelectric fields in the 10^7 to 10^8 V m^{-1} regime. Figure 8 compares changes in the peak position in the VUV absorption spectra for the isoelectronic species CO_2 and N_2O[14]. The nonpolar CO_2 molecule, Figure 8a, produces an ice that does not harbor an electric field and the absorption features appear at the same wavelength regardless of growth temperature. In contrast, VUV absorption spectra for the polar molecule, N_2O, demonstrate a clear temperature dependence.

The shift in peak position by 65 meV, from 137.95 nm at 40 K to 138.96 nm at 60 K for the lower energy peak associated with the C-band transition, allowed us to compare the observed Stark shift in films of N_2O with a calculated shift. This calculated shift was based on the temperature dependent strength of the electric field known to exist in this material from our previous independent experiments involving electron beam surface potential measurements and RAIR spectroscopy.[6,13,14] The comparison between observed and calculated values of absorption wavelength, shown in Figure 9, indicates that the energy that the spontelectric field contributes to the expansion of the exciton matches the experimental observations of the wavelength accurately over most of the temperature range, save close to sublimation at 64 K. This simple Coulombic model however breaks down as the growth temperature approaches that of the known phase transition for

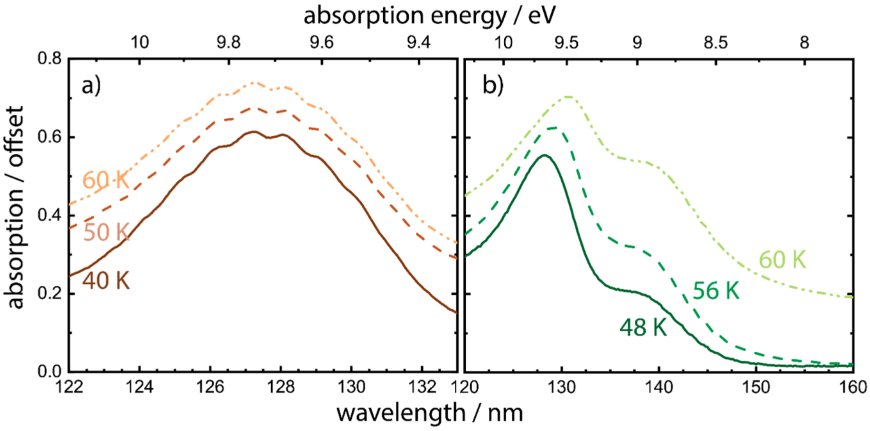

Figure 8. VUV absorption spectra for (a) CO_2 and (b) N_2O recorded for films prepared at the different temperatures indicated. Data have been offset on the *y*-axis to ease comparison. Data were obtained on the ASTRID2 synchrotron radiation source at Aarhus. Adapted with permission from ref 14. Copyright 2019 Royal Society of Chemistry.

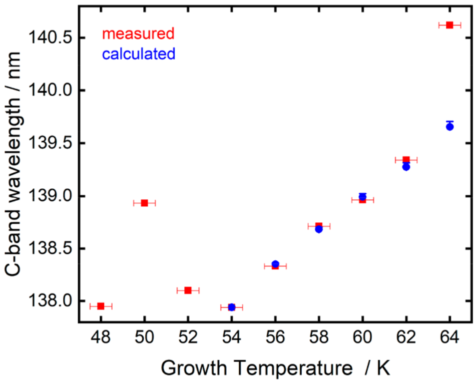

Figure 9. Observed peak absorption wavelength for the C-band in the VUV spectrum for films of N_2O, shown in red. Calculated shifts, based on the Stark shift induced by the spontelectric field from the peak position at 54 K, are shown in blue. Adapted with permission from ref 14. Copyright 2019 Royal Society of Chemistry.

N_2O at 48 K (Figure 3 and Table 2).[11,14] As the growth temperature decreases toward 50 K, the crystallite size drops below that necessary to allow the exciton to reach its full expansion, commensurate with the increasing strength of the electric field. This gives an upper limit on the physical size of crystallites in the N_2O film of 3.12 nm at 54 K, and decreasing as the temperature drops toward 50 K.

The restriction on the size of the exciton imposed by shrinking crystallites as a material approaches a phase change was also suggested through similar studies of the VUV absorption spectrum of solid NH_3.[12,66] This material is known to exist in 2 phases, with a transition at ~52 K.[67,68] VUV data then enable us to estimate the spontelectric fields in ammonia and place a lower limit of 1.58 nm on the size of crystallites for $T < 52$ K, representing 16 unit cells or 64 species. For higher deposition temperatures, minimum crystallite sizes are 4.73, 3.62, and 2.45 nm, containing 1688, 756, and 236 molecules of ammonia, ±20%, at deposition temperatures of 65, 60, and 55 K respectively.

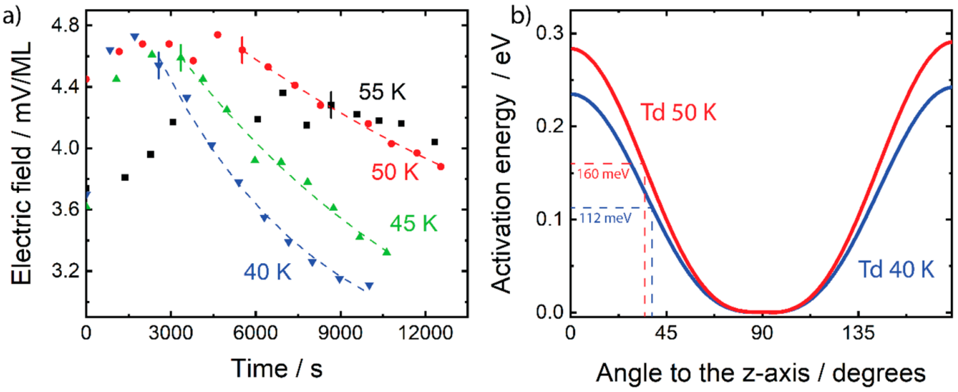

Figure 10. (a) Electric fields per ML in thin films of *cis*-methyl formate, measured as a function of time, for deposition temperatures of 40, 45, 50, and 55 K. Offset times, defined as the time before electric field decay begins, are indicated with short vertical lines, and were used to calculate the activation barriers used in panel b. Dashed lines are exponential fits to subsequent decay of field strength. (b) The spontelectric model was used to calculate the barrier to rotating a molecular dipole when the dipole lies in an electric field of different strengths. Two curves, representing the field strength at deposition temperatures of 40 K (blue) and 50 K (red) are shown. The dashed vertical lines indicate the barriers to rotation derived from panel (a) and show that rotations of approximately 50° from the resting position are required. Adapted with permission from ref 69. Copyright 2021 Royal Societ of Chemistry.

4. THE SPONTELECTRIC EFFECT AS A PROBE OF DYNAMICS IN GLASSES

Time-dependence of the magnitude of the spontelectric field in films has been observed and can be attributed to a net rotation of the average direction and thus decay of orientation of molecular dipoles. The example of *cis*-methyl formate is shown in Figure 10a. This behavior has pioneered a new technique for the study of relaxation by molecular rotation in supercooled molecular glasses.[1,69] Neutron scattering has been used to quantify molecular translational diffusion and to differentiate it from rotation, in these materials.[1] Layering isotopically labeled spontelectric films generates a sample with multiple interfaces. Blurring and loss of these interfaces, observed through neutron scattering, indicates translational diffusion and mixing of the isotopically labeled materials. The interrogating neutron beam is sensitive to the isotopic interfaces so generated, thus allowing the measurement of self-diffusion. Neutron scattering data therefore allow us to exclude diffusion[1,11] below a deposition temperature of 55 K. Decay of the spontelectric effect at $T \leq 55$ K (Figure 10a) can therefore be attributed wholly to rotationally induced loss of orientation.

Films of *cis*-methyl formate undergo a glass transition at 90 K to form a crystalline material which desorbs above 135 K.[70,71] Only the glassy state of methyl formate is spontaneously polarized.[70] At $T \leq 55$ K, well below the glass transition temperature, the strength of the electric field in deeply supercooled films of *cis*-methyl formate decreases with time, with a higher rate for lower growth temperature, Figure 10a. In addition, a decreasing time delay was observed before decay begins, at lower temperatures. This behavior suggests that films become less stable and more prone to molecular rotation, and hence loss of spontelectric field, as the growth temperature decreases.

To understand this counterintuitive behavior of relaxation of the glass at deeply supercooled temperatures of 40 to 55 K, we used the spontelectric model described in section 1, to estimate the extent of molecular rotation required to overcome the energy barriers suggested by the rates of decay of orientation, employing data shown in Figure 10a. This established that individual molecules should rotate by as much as 50° at a deposition temperature of 40 K, say, to overcome the energy barrier of 112 meV, estimated from the kinetic data in Figure 10a. This barrier rises to 160 meV at 55 K. The results from the model are shown in Figure 10b. To move out of a potential well, the dipole must rotate against the spontelectric field. We estimate the extent of this rotation using Figure 10b, where rotations of ~50° correspond to the activation energies estimated from data in Figure 10a, for example 112 and 160 meV, as shown in Figure 10b. Films prepared at increasingly lower deposition temperatures produce correspondingly less relaxed and thus less stable glassy materials, and these materials decay faster, through this rotation mechanism. The spontelectric effect, therefore, gives insight into the elusive dynamical processes that take place far below the molecular glass transition temperature.

5. SUMMARY AND OUTLOOK

The observation of spontelectric fields in nanofilms rests upon electron beam and Kelvin probe measurement of surface potentials, and vibrational and electronic Stark effects. We have chained techniques together, for example using the results of the electron beam method for nitrous oxide[5] to verify the RAIRS Stark method of detection.[13] The RAIRS technique was then used to infer electric fields in solid carbon monoxide,[4] for which there were no electron beam data. These results were in turn used to interpret VUV data, showing that the energy of Wannier−Mott excitons in solid CO would vary with film deposition temperature in the manner observed.[2] Additional structural and diffusion measurements from neutron scattering data have allowed us to apply the spontelectric effect to quantify aging in a glass.

The dynamical processes through which the spontelectric effect asserts itself remain unclear. The mechanism by which symmetry in the *z*-axis is broken and through which dipoles find a particular direction with which to align remains unanswered and we may only conjecture at present that the formation of the spontelectric state is fluctuation driven.[53] There is evidence to suggest that in some cases the symmetry breaking may be driven by the chemistry at the film-vacuum interface,[72] and future experiments can explore the potential of this to tune the sign of the electric field generated. This, in turn, could be used to increase the field strength that can be obtained at a given growth temperature and to identify molecules which show the spontelectric effect at ever higher deposition temperatures, presently limited to 90 K. Data may be used in conjunction with established machine learning techniques for low-data problems to efficiently explore chemical space. The goal here would be to identify room temperature spontelectrics, with a view to their practical use, for example for energy storage and electrostatic-enhanced catalysis. In regard to practical energy storage, large scale deposition of (near) room temperature material may for example be speculatively envisaged to store ~10 MJ in a spontelectric field of 10^8 Vm^{-1} in a 1 mm thick (say), 30 × 30 m^2 area of material. Turning to chemical reactivity, there is a well-established literature that supports electric field enhancement of reactivity[44−49] derived from our knowledge of such effects in the active pockets of enzymes.[61] The ability to prepare polymer substrates from spontelectric monomers expressing similar fields to those measured within the active pockets of enzymes may open pathways to explore novel heterogeneous or heterogeneodized homogeneous catalytic systems, especially in flow environments.

Understanding charge transport in molecular films is a key step to integrating molecular solids into optoelectronic devices. The spontelectric effect will influence the ability to inject charge into polarized films and conduct that charge to an electrode. Indeed, surface potentials have been reported to generate interfacial charge-migration barriers in photovoltaics and molecular orientation, that is, anisotropic molecular packing, has been reported to influence the efficiency of these devices. These effects are usually linked to anisotropy in vapor-deposited materials but the role of the spontelectric effect, the feedback between dipole orientation and the spontaneous electric field, has not yet been included. Our work, so far, has focused on low molecular weight, volatile species well-suited to surface science experiments in ultrahigh vacuum setups but future research will have to find the means to study the spontelectric effect in the larger molecules typically encountered in organic semiconducting materials. Stark shifts in spectroscopic measurements, particularly in the IR, may be the best means to characterize these species.

So-called "volcano peaks" that occur when two species with different desorption temperatures are layered and then heated, forcing the more volatile species to remain adsorbed until the materials with the higher desorption temperature is reached, are of particular interest to the astrochemical community.[73,74] Questions about the phase and diffusion of the trapped species remain unanswered and the combination of neutron scattering and surface potential measurements will help address these issues.[75]

At all events, new physics is encountered in the very familiar and outwardly simple system of vacuum-deposited thin films, with potential application in many chemical environments.

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CRediT: **Andrew Martin Cassidy** conceptualization (equal), data curation (equal), formal analysis (equal), investigation (equal), methodology (equal), project administration (equal), writing-original draft (equal), writing-review & editing (equal); **Martin R. S. McCoustra** conceptualization (equal), data curation (equal), formal analysis (equal), funding acquisition (equal), investigation (equal), methodology (equal), writing-original draft (equal), writing-review & editing (equal); **David Field** conceptualization (equal), data curation (equal), formal analysis (equal), investigation (equal), methodology (equal), writing-original draft (equal), writing-review & editing (equal).

Notes

The authors declare no competing financial interest.

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Martin McCoustra holds the founding chair in Chemical Physics in Scotland, at the Institute of Chemical Sciences in the School of Engineering and Physical Sciences, Heriot-Watt University. His principal research interests relate to exploring the surface science of complex systems relevant to astrochemistry and polymer science.

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REFERENCES

(1) Cassidy, A.; Jørgensen, M. R. V.; Glavic, A.; Lauter, V.; Plekan, O.; Field, D. A Mechanism for Ageing in a Deeply Supercooled Molecular Glass. *Chem. Commun.* **2021**, *57* (52), 6368–6371.

(2) Chen, Y.-J.; Muñoz Caro, G. M.; Aparicio, S.; Jiménez-Escobar, A.; Lasne, J.; Rosu-Finsen, A.; McCoustra, M. R. S.; Cassidy, A. M.; Field, D. Wannier–Mott Excitons in Nanoscale Molecular Ices. *Phys. Rev. Lett.* **2017**, *119* (15), 157703.

(3) Rosu-Finsen, A.; Lasne, J.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Enabling Star Formation via Spontaneous Molecular Dipole Orientation in Icy Solids. *Astrophys. J.* **2016**, *832* (1), 1.

(4) Lasne, J.; Rosu-Finsen, A.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Spontaneous Electric Fields in Solid Carbon Monoxide. *Phys. Chem. Chem. Phys.* **2015**, *17* (44), 30177–30187.

(5) Balog, R.; Cicman, P.; Jones, N. C.; Field, D. Spontaneous Dipole Alignment in Films of N2O. *Phys. Rev. Lett.* **2009**, *102* (7), 073003.

(6) Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. C.; Field, D. A New Form of Spontaneously Polarized Material. *Phys. Chem. Chem. Phys.* **2011**, *13* (47), 21035–21044.

(7) Field, D.; Plekan, O.; Cassidy, A.; Balog, R.; Jones, N. C.; Dunger, J. Spontaneous Electric Fields in Solid Films: Spontelectrics. *Int. Rev. Phys. Chem.* **2013**, *32* (3), 345–392.

(8) Kutzner, K. Spontaneous Polarization of Condensing Carbon Monoxide and Other Gases with an Electrical Dipole Moment. *Thin Solid Films* **1972**, *14* (1), 49–61.

(9) Pilidi, A. N.; Gavra, I. K.; Tsekouras, A. A. Spontaneous Polarization of Cryo-Deposited Films for Five Normal Saturated Monohydroxy Alcohols, CnH2n+1OH, n = 1–5. *J. Phys. Chem. B* **2019**, *123* (40), 8505–8511.

(10) Sagi, R.; Akerman, M.; Ramakrishnan, S.; Asscher, M. Spontaneous Polarization of Thick Solid Ammonia Films. *J. Chem. Phys.* **2020**, *153* (12), 124707.

(11) Cassidy, A.; Jørgensen, M. R. V.; Rosu-Finsen, A.; Lasne, J.; Jørgensen, J. H.; Glavic, A.; Lauter, V.; Iversen, B. B.; McCoustra, M. R. S.; Field, D. Dipole-Oriented Molecular Solids Can Undergo a Phase Change and Still Maintain Electrical Polarization. *J. Phys. Chem. C* **2016**, *120* (42), 24130–24136.

(12) Cassidy, A.; James, R. L.; Dawes, A.; Field, D. Crystallites and Electric Fields in Solid Ammonia. *ChemistryOpen* **2020**, *9* (10), 983−990.

(13) Lasne, J.; Rosu-Finsen, A.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Spontaneously Electrical Solids in a New Light. *Phys. Chem. Chem. Phys.* **2015**, *17* (32), 20971−20980.

(14) Cassidy, A.; James, R. L.; Dawes, A.; Lasne, J.; Field, D. The Optical Absorption Spectra of Spontaneously Electrical Solids: The Case of Nitrous Oxide. *Phys. Chem. Chem. Phys.* **2019**, *21* (3), 1190−1197.

(15) 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* (28), 9972−9976.

(16) Roman, M.; Taj, S.; Gutowski, M.; McCoustra, M. R. S.; Dunn, A. C.; Keolopile, Z. G.; Rosu-Finsen, A.; Cassidy, A. M.; Field, D. Non-Linear and Non-Local Behaviour in Spontaneously Electrical Solids. *Phys. Chem. Chem. Phys.* **2018**, *20* (7), 5112−5116.

(17) Cassidy, A.; Plekan, O.; Balog, R.; Jones, N. C.; Field, D. Spontaneous Electric Fields in Films of CF3Cl, CF2Cl2 and CFCl3. *Phys. Chem. Chem. Phys.* **2013**, *15* (1), 108−113.

(18) Lagerwall, J. P. F.; Giesselmann, F. Current Topics in Smectic Liquid Crystal Research. *ChemPhysChem* **2006**, *7* (1), 20−45.

(19) Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. Ferroelectric Liquid Crystals. *J. Phys., Lett.* **1975**, *36* (3), 69−71.

(20) Clark, N. A.; Lagerwall, S. T. Submicrosecond Bistable Electro-optic Switching in Liquid Crystals. *Appl. Phys. Lett.* **1980**, *36* (11), 899.

(21) Iedema, M. J.; Dresser, M. J.; Doering, D. L.; Rowland, J. B.; Hess, W. P.; Tsekouras, A. A.; Cowin, J. P. Ferroelectricity in Water Ice. *J. Phys. Chem. B* **1998**, *102* (46), 9203−9214.

(22) Sagi, R.; Akerman, M.; Ramakrishnan, S.; Asscher, M. The Role of Thermal History on Spontaneous Polarization and Phase Transitions of Amorphous Solid Water Films Studied by Contact Potential Difference Measurements. *J. Chem. Phys.* **2020**, *153* (14), 144702.

(23) Shi, J.; Famá, M.; Teolis, B. D.; Baragiola, R. A. Ion-Induced Electrostatic Charging of Ice at 15−160 K. *Phys. Rev. B* **2012**, *85* (3), 035424.

(24) Bu, C.; Shi, J.; Raut, U.; Mitchell, E. H.; Baragiola, R. A. Effect of Microstructure on Spontaneous Polarization in Amorphous Solid Water Films. *J. Chem. Phys.* **2015**, *142* (13), 134702.

(25) Hashemi, S. R.; McCoustra, M. R. S.; Fraser, H. J.; Nyman, G. A Theoretical Study on Spontaneous Dipole Orientation in Ice Structures. *Phys. Chem. Chem. Phys.* **2022**, *24* (21), 12922−12925.

(26) Tanaka, Y.; Matsuura, N.; Ishii, H. Self-Assembled Electret for Vibration-Based Power Generator. *Sci. Rep.* **2020**, *10* (1), 6648.

(27) Ito, E.; Washizu, Y.; Hayashi, N.; Ishii, H.; Matsuie, N.; Tsuboi, K.; Ouchi, Y.; Harima, Y.; Yamashita, K.; Seki, K. Spontaneous Buildup of Giant Surface Potential by Vacuum Deposition of Alq3 and Its Removal by Visible Light Irradiation. *J. Appl. Phys.* **2002**, *92* (12), 7306−7310.

(28) 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* (11), 114508.

(29) Friederich, P.; Rodin, V.; von Wrochem, F.; Wenzel, W. Built-In Potentials Induced by Molecular Order in Amorphous Organic Thin Films. *ACS Appl. Mater. Interfaces* **2018**, *10* (2), 1881−1887.

(30) Jäger, L.; Schmidt, T. D.; Brütting, W. Manipulation and Control of the Interfacial Polarization in Organic Light-Emitting Diodes by Dipolar Doping. *AIP Adv.* **2016**, *6* (9), 095220.

(31) Swallen, S. F.; Kearns, K. L.; Mapes, M. K.; Kim, Y. S.; McMahon, R. J.; Ediger, M. D.; Wu, T.; Yu, L.; Satija, S. Organic Glasses with Exceptional Thermodynamic and Kinetic Stability. *Science* **2007**, *315* (5810), 353−356.

(32) Dalal, S. S.; Walters, D. M.; Lyubimov, I.; de Pablo, J. J.; Ediger, M. D. Tunable Molecular Orientation and Elevated Thermal Stability of Vapor-Deposited Organic Semiconductors. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (14), 4227−4232.

(33) Bishop, C.; Thelen, J. L.; Gann, E.; Toney, M. F.; Yu, L.; DeLongchamp, D. M.; Ediger, M. D. Vapor Deposition of a Nonmesogen Prepares Highly Structured Organic Glasses. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116* (43), 21421−21426.

(34) Rodriguez-Tinoco, C.; Gonzalez-Silveira, M.; Ramos, M. A.; Rodriguez-Viejo, J. Ultrastable Glasses: New Perspectives for an Old Problem. *Riv. Nuovo Cimento* **2022**, *45*, 325.

(35) Rosu-Finsen, A.; Lasne, J.; Cassidy, A.; McCoustra, M. R. S.; Field, D. Spontaneous Polarization of Solid CO on Water Ices and Some Astrophysical Implications. *Phys. Chem. Chem. Phys.* **2016**, *18* (7), 5159−5171.

(36) Organic and Printed Electronics Association. *White Paper OE-A Roadmap for Organic and Printed Electronics*, 7th ed.; VDMA Verlag.

(37) Innovate UK. *Electech Sector: A Roadmap for the UK*; 2019.

(38) Stampor, W. Internal Electric Fields in Vacuum-Evaporated Organic Films as Studied by Electroabsorption Spectroscopy. *Chem. Phys.* **2007**, *334* (1), 216−223.

(39) Lim, E.; Shibata, Y.; Manaka, T.; Iwamoto, M. Probing the Electric Field in Organic Double Layer-System by Optical Second Harmonic Generation. *Thin Solid Films* **2009**, *518* (2), 893−895.

(40) Celebrano, M.; Sciascia, C.; Cerullo, G.; Zavelani-Rossi, M.; Lanzani, G.; Cabanillas-Gonzalez, J. Imaging the Electric-Field Distribution in Organic Devices by Confocal Electroreflectance Microscopy. *Adv. Funct. Mater.* **2009**, *19* (8), 1180−1185.

(41) Siebert-Henze, E.; Lyssenko, V. G.; Fischer, J.; Tietze, M.; Brueckner, R.; Schwarze, M.; Vandewal, K.; Ray, D.; Riede, M.; Leo, K. Built-in Voltage of Organic Bulk Heterojuction p-i-n Solar Cells Measured by Electroabsorption Spectroscopy. *AIP Adv.* **2014**, *4* (4), 047134.

(42) Zare, R. N. The Quest to Control Chemical Reactions Using Interfacial Electric Fields. *Chem. World*, 2020. https://www.chemistryworld.com/holy-grails/views/a-new-grail.

(43) Stuyver, T.; Danovich, D.; Joy, J.; Shaik, S. External Electric Field Effects on Chemical Structure and Reactivity. *WIREs Comput. Mol. Sci.* **2020**, *10* (2), No. e1438.

(44) Shin, S.; Kim, Y.; Moon, E.; Lee, D. H.; Kang, H.; Kang, H. Generation of Strong Electric Fields in an Ice Film Capacitor. *J. Chem. Phys.* **2013**, *139* (7), 074201.

(45) Shin, S.; Kim, Y.; Kang, H.; Kang, H. Effect of Electric Field on Condensed-Phase Molecular Systems. I. Dipolar Polarization of Amorphous Solid Acetone. *J. Phys. Chem. C* **2015**, *119* (27), 15588−15595.

(46) Shin, S.; Park, Y.; Kang, H.; Kang, H. Electric Field Effect on Condensed-Phase Molecular Systems. IV. Conformational Change of 1,2-Dichloroethane in a Frozen Molecular Solid. *J. Phys. Chem. C* **2017**, *121* (45), 25342−25346.

(47) Park, Y.; Kang, H.; Field, R. W.; Kang, H. The Frequency-Domain Infrared Spectrum of Ammonia Encodes Changes in Molecular Dynamics Caused by a DC Electric Field. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116* (47), 23444−23447.

(48) Shaik, S.; Ramanan, R.; Danovich, D.; Mandal, D. Structure and Reactivity/Selectivity Control by Oriented-External Electric Fields. *Chem. Soc. Rev.* **2018**, *47* (14), 5125−5145.

(49) Shaik, S.; Danovich, D.; Joy, J.; Wang, Z.; Stuyver, T. Electric-Field Mediated Chemistry: Uncovering and Exploiting the Potential of (Oriented) Electric Fields to Exert Chemical Catalysis and Reaction Control. *J. Am. Chem. Soc.* **2020**, *142* (29), 12551−12562.

(50) Kittel, C. *Introduction to Solid State Physics*, 3rd ed.; New York, 1966.

(51) Cassidy, A.; Pijpers, F. P.; Field, D. Hidden Singularities in Spontaneously Polarized Molecular Solids. *J. Chem. Phys.* **2023**, *158* (14), 144501.

(52) Kexel, C.; Solov'yov, A. V. Predicting Dipole Orientations in Spontelectric Methyl Formate. *Eur. Phys. J. D* **2021**, *75* (3), 89.

(53) Cassidy, A.; Plekan, O.; Dunger, J.; Balog, R.; Jones, N. C.; Lasne, J.; Rosu-Finsen, A.; McCoustra, M. R. S.; Field, D. Investigations into the Nature of Spontelectrics: Nitrous Oxide

Diluted in Xenon. *Phys. Chem. Chem. Phys.* **2014**, *16* (43), 23843−23853.

(54) Stein, D. L.; Newman, C. M. *Spin Glasses and Complexity*; Princeton University Press, 2013.

(55) Greenler, R. G. Infrared Study of Adsorbed Molecules on Metal Surfaces by Reflection Techniques. *J. Chem. Phys.* **1966**, *44* (1), 310−315.

(56) Greenler, R. G.; Snider, D. R.; Witt, D.; Sorbello, R. S. The Metal-Surface Selection Rule for Infrared Spectra of Molecules Adsorbed on Small Metal Particles. *Surf. Sci.* **1982**, *118* (3), 415−428.

(57) Thrower, J. D.; Collings, M. P.; Rutten, F. J. M.; McCoustra, M. R. S. Laboratory Investigations of the Interaction between Benzene and Bare Silicate Grain Surfaces. *Mon. Not. R. Astron. Soc.* **2009**, *394* (3), 1510−1518.

(58) Hama, T.; Ishibashi, A.; Kouchi, A.; Watanabe, N.; Shioya, N.; Shimoaka, T.; Hasegawa, T. Quantitative Anisotropic Analysis of Molecular Orientation in Amorphous N_2O at 6 K by Infrared Multiple-Angle Incidence Resolution Spectrometry. *J. Phys. Chem. Lett.* **2020**, *11* (18), 7857−7866.

(59) Boxer, S. G. Stark Realities. *J. Phys. Chem. B* **2009**, *113* (10), 2972−2983.

(60) Fried, S. D.; Boxer, S. G. Measuring Electric Fields and Noncovalent Interactions Using the Vibrational Stark Effect. *Acc. Chem. Res.* **2015**, *48* (4), 998−1006.

(61) Fried, S. D.; Boxer, S. G. Electric Fields and Enzyme Catalysis. *Annu. Rev. Biochem.* **2017**, *86* (1), 387−415.

(62) Nelson, J. A. *The Physics Of Solar Cells*; World Scientific Publishing Company, 2003.

(63) Scholes, G. D.; Rumbles, G. Excitons in Nanoscale Systems. *Nat. Mater.* **2006**, *5* (9), 683−696.

(64) Schwoerer, M.; Wolf, H. C. *Organic Molecular Solids*; John Wiley & Sons, 2007.

(65) Muñoz Caro, G. M.; Chen, Y.-J.; Aparicio, S.; Jiménez-Escobar, A.; Rosu-Finsen, A.; Lasne, J.; McCoustra, M. R. S. Photodesorption and Physical Properties of CO Ice as a Function of Temperature. *Astron. Astrophys.* **2016**, *589*, A19.

(66) Zheng, W.; Kaiser, R. I. An Infrared Spectroscopy Study of the Phase Transition in Solid Ammonia. *Chem. Phys. Lett.* **2007**, *440* (4), 229−234.

(67) Cassidy, A.; James, R. L.; Dawes, A.; Field, D. The Rise of an Exciton in Solid Ammonia. *Chem. Commun.* **2022**, *58*, 815.

(68) Dawes, A.; Mukerji, R. J.; Davis, M. P.; Holtom, P. D.; Webb, S. M.; Sivaraman, B.; Hoffmann, S. V.; Shaw, D. A.; Mason, N. J. Morphological Study into the Temperature Dependence of Solid Ammonia under Astrochemical Conditions Using Vacuum Ultraviolet and Fourier-Transform Infrared Spectroscopy. *J. Chem. Phys.* **2007**, *126* (24), 244711.

(69) Cassidy, A.; Jørgensen, M. R. V.; Glavic, A.; Lauter, V.; Plekan, O.; Field, D. Low Temperature Aging in a Molecular Glass: The Case of Cis -Methyl Formate. *Phys. Chem. Chem. Phys.* **2021**, *23* (29), 15719−15726.

(70) Roman, M.; Dunn, A.; Taj, S.; Keolopile, Z. G.; Rosu-Finsen, A.; Gutowski, M.; McCoustra, M. R. S.; Cassidy, A. M.; Field, D. Assigning a Structural Motif Using Spontaneous Molecular Dipole Orientation in Thin Films. *Phys. Chem. Chem. Phys.* **2018**, *20* (46), 29038−29044.

(71) Burke, D. J.; Puletti, F.; Brown, W. A.; Woods, P. M.; Viti, S.; Slater, B. Glycolaldehyde, Methyl Formate and Acetic Acid Adsorption and Thermal Desorption from Interstellar Ices. *Mon. Not. R. Astron. Soc.* **2015**, *447* (2), 1444−1451.

(72) Tanaka, M.; Auffray, M.; Nakanotani, H.; Adachi, C. Spontaneous Formation of Metastable Orientation with Well-Organized Permanent Dipole Moment in Organic Glassy Films. *Nat. Mater.* **2022**, *21* (7), 819−825.

(73) Smith, R. S.; Huang, C.; Wong, E. K. L.; Kay, B. D. The Molecular Volcano: Abrupt CCl_4 Desorption Driven by the Crystallization of Amorphous Solid Water. *Phys. Rev. Lett.* **1997**, *79* (5), 909−912.

(74) Akerman, M. S.; Sagi, R.; Asscher, M. Inverse Volcano: A New Molecule-Surface Interaction Phenomenon. *Phys. Rev. Lett.* **2023**, *130* (8), 086203.

(75) Cassidy, A.; Plekan, O.; Balog, R.; Dunger, J.; Field, D.; Jones, N. C. Electric Field Structures in Thin Films: Formation and Properties. *J. Phys. Chem. A* **2014**, *118* (33), 6615−6621.