Wannier-Mott Excitons in Nanoscale Molecular Ices

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The absorption of light to create Wannier-Mott excitons is a fundamental feature dictating the optical and photovoltaic properties of low band gap, high permittivity semiconductors. Such excitons, with an electron-hole separation an order of magnitude greater than lattice dimensions, are largely limited to these semiconductors but here we find evidence of Wannier-Mott exciton formation in solid carbon monoxide (CO) with a band gap of >8 eV and a low electrical permittivity. This is established through the observation that a change of a few degrees K in deposition temperature can shift the electronic absorption spectra of solid CO by several hundred wave numbers, coupled with the recent discovery that deposition of CO leads to the spontaneous formation of electric fields within the film. These so-called spontelectric fields, here approaching 4×10^7 V m^{-1}, are strongly temperature dependent. We find that a simple electrostatic model reproduces the observed temperature dependent spectral shifts based on the Stark effect on a hole and electron residing several nm apart, identifying the presence of Wannier-Mott excitons. The spontelectric effect in CO simultaneously explains the long-standing enigma of the sensitivity of vacuum ultraviolet spectra to the deposition temperature.

A fundamental step in the operation of photovoltaics may involve the formation of electron-hole pairs or excitons [1–4], rather than through the direct production of free charge carriers. Excitons are found in highly diverse materials. Recent examples include polymer:fullerene bulk heterojunctions [5] and lead halide inorganic-organic perovskite hybrids [6] such as methylammonium lead bromide perovskite [7]. The latter is reported to have an electron-hole separation of $\sim$4.38 nm, characteristic of Wannier-Mott excitons in low band gap, high electrical permittivity materials. Here we expand the diversity of materials showing Wannier-Mott excitons in a very simple species,

unexpectedly finding these excitons in solid CO, which is both a high band gap material (>8 eV) and of low electrical permittivity. The presence of Wannier-Mott excitons in solid CO may be identified through the spontelectric nature of thin films of dipolar materials [8–12], where the spontaneous polarization charge and the accompanying spontelectric field are generated through dipole orientation. Note that spontelectrics are radically different from ferroelectric species [13,14], in which spontaneous polarization results from a crystallographic phenomenon based on individual unit cells, whereas spontelectric polarization is due to a collective, long-range interaction extending throughout the film [9].

Raw data for the present work, showing remarkable spectral shifts with deposition temperatures differing by only a few K, are provided by the electronic spectroscopy of solid CO [15]. Absorption spectra of CO ices were measured using both the UHV InterStellar Astrochemistry Chamber, in Madrid, and the UHV Interstellar Photoprocess System at the High-Flux beam line (BL03A) at the National Synchrotron Radiation Research Center in Taiwan (NSRRC), yielding essentially identical spectra. The ice samples were grown by background vapor deposition on a MgF_2 window, connected to the tip of a closed-cycle He cryostat. During ice deposition, the ice thickness, of final value $\sim$17 nm, was monitored by FTIR and He-Ne laser interference measurements. Variation of the deposition rate of CO, using background pressures between 10^{-6} to 10^{-9} m bar, had no effect on the results of temperature-programmed desorption and by implication on the structure of the CO film. After measurement of the VUV absorption spectrum of each ice sample, the MgF_2 window was warmed and held at 200 K for 20 min. VUV absorption spectra of N_2 were obtained at NSRRC using the same techniques. Spectra have also been taken of solid N_2O and CO_2 at NSRRC and at the storage ring ASTRID2 at Aarhus University. N_2O, being spontelectric [9], shows strong spectral shifts as a function of deposition temperature and CO_2, lacking a dipole moment, shows no such shifts.

Figure 1, upper panel, shows the absorption spectrum of solid carbon monoxide (CO) at 14 K. For comparison, the absorption spectrum of isoelectronic N_2 is shown in the lower panel. The red curves show typical Gaussian fits to the data used to obtain the peak absorption wavelengths employed subsequently. Figure 2, left hand panel, illustrates the shift with deposition temperature in the electronic absorption spectrum of solid CO. For CO deposition temperatures between 20 and 26 K, a shift in peak spectral absorption of 406 cm^{-1} ($\sim$1 nm) to the red may be seen. Shifts in peak spectral absorption for films deposited at temperatures between 14 and 26 K, relative to the spectrum at 20 K, are shown in Table I. Note that 26 K is the highest temperature at which CO films can be deposited, lying close to the thermal desorption temperature of CO. The right hand panel of Fig. 2 shows spectra of solid N_2 at 14, 20, and 24 K, illustrating the absence of spectral shifts for a nondipolar film laid down at different temperatures.

The presence of an electric field within ices engenders a corresponding deposition temperature dependent vibrational Stark shift [16]. Reflection-absorption infrared spectroscopy (RAIRS) was therefore used to establish the presence of spontelectric fields as a function of deposition temperature in thin films of CO [8]. Spontelectric fields derived from experimental data for solid CO as a function of deposition temperature are shown in Table II.

The series of vibronic bands observed in CO, Fig. 1, is attributed to the $A^1\Pi \leftarrow X^1\Sigma$ transition [15]. Bands show a redshift as a function of increasing deposition temperature above 20 K (Fig. 2 and Table I). For brevity, we consider here only the (0,0) band near 156.4 nm. Data are available
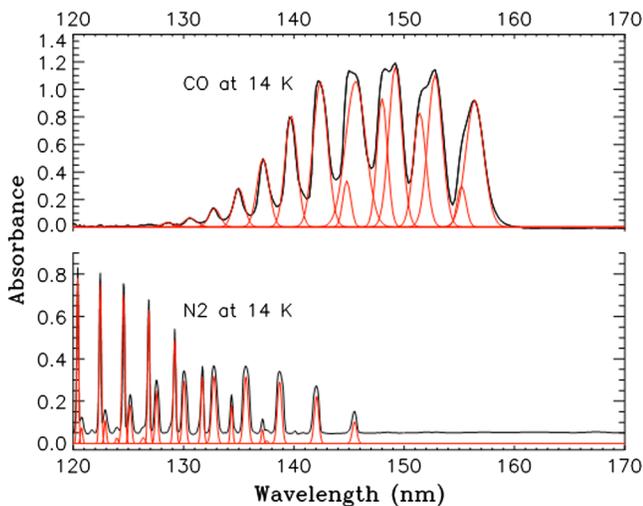

FIG. 1.   Upper panel: VUV absorption spectra of solid CO in the $A^1\Pi \leftarrow X^1\Sigma$ transition at 14 K. The splitting of lines, most clearly seen in the $v' = 1$ and 2 vibronic bands may be attributed to the Davydov effect (see text). Lower panel: similar data for solid N_2 at 14 K. All spectra were taken with a resolution of 0.1 nm. Red curves show Gaussian fits to spectra used to establish peak absorption wavelengths, the technique used to establish peak shifts shown in Table I for spectra taken over the range of temperatures of film deposition shown in Fig. 2, left hand panel.
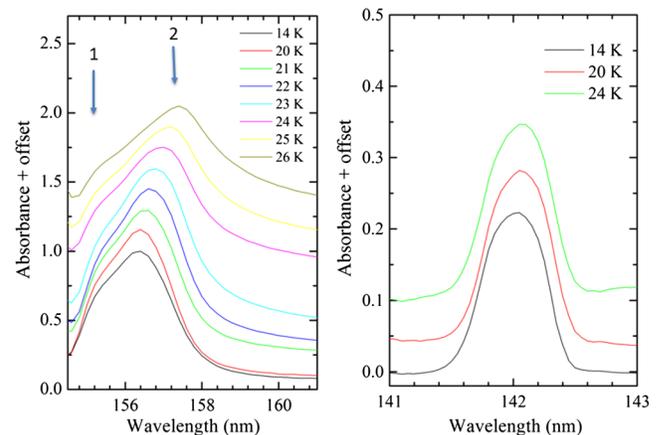

FIG. 2.   Left hand panel: VUV absorption spectra of solid CO in the (0,0) band of the $A^1\Pi \leftarrow X^1\Sigma$ transition at a succession of deposition temperatures 14, 20, 21, 22, 23, 24, 25, and 26 K (data taken from Ref. [15]), showing the marked shifts in spectra associated with these deposition temperatures. The broadening of the absorption lines may be attributed to Davydov splitting, components of which are labeled 1 and 2. Right hand panel: similar data for solid N_2 at 14, 20, and 24 K, illustrating that spectra of this nonpolar species show that the spectrum remains unchanged over this temperature range. All spectra were taken with a resolution of 0.1 nm and are vertically offset from one another for ease of viewing.

TABLE I.   Column 1: CO ice deposition temperature. Column 2: the measured energy separation, or redshift, between the peak absorption, marked 1 in Fig. 2 (left hand panel), in the envelope of the spectra in the (0,0) $A^1\Pi \leftarrow X^1\Sigma$ transition in CO for ices deposited at 20 K and the temperature shown in the first column. Column 3: as for column 2 but for the peak marked 2 in Fig. 2. Note the large redshifts for very small changes in ice deposition temperatures. All data are taken from Ref. [15], with additional data at 23 and 25 K.

T/K	Measured energy shift to the red/cm^{-1}: peak 1	Measured energy shift to the red/cm^{-1}: peak 2
14	0	0
20	0	0
21	0	82
22	0	82
23	83	163
24	83	245
25	124	325
26	124	406

for higher vibronic bands, as seen in Fig. 2, upper panel, of Ref. [15] and these will be analyzed in future work. Returning to the (0,0) band, no redshift is observed between 14 and 20 K, illustrated by inclusion of these data in Fig. 2 and Table I. In this connection, CO molecules do not become increasingly oriented when grown at temperatures below 20 K [15]. We therefore focus only upon data between 20 and 26 K, for which we have values of the spontelectric field in CO (Table II).

There are four possible mechanisms involving the spontelectric effect in solid CO that could contribute to the redshifts in spectra between 20 and 26 K shown in Fig. 2 and in Table I: (i) the permanent dipole moment change, $\Delta\mu$, and associated Stark shift between the X and A states of CO; (ii) the induced dipole moment change, $\Delta\mu_I$, through polarizability differences between the X and A states;

TABLE II.   First column: deposition temperature of CO ice. Second column: spontelectric fields in solid CO, taken from reference [8] with interpolation for values at $T = 23$ and 25 K. Third column: calculated displacements of hole and electron, $\Delta r_{i,j}$ [Eq. (2)] under the influence of the temperature dependent spontelectric field for data referring to the Davydov component peak 1 in Fig. 1. Fourth column: as for column 3, but for peak 2.

Deposition temperature/K	Spontelectric field /V m^{-1}	Displacement Δr_1/au	Displacement Δr_2/au
20	3.78×10^7	16.2	49.1
21	3.75×10^7	16.0	48.1
22	3.72×10^7	15.7	47.1
23	3.69×10^7	15.6	46.1
24	3.66×10^7	15.4	45.2
25	3.62×10^7	15.1	44.0
26	3.58×10^7	14.9	42.9

(iii) the change in degree of dipole orientation associated with a change in deposition temperature between 20 and 26 K; and (iv) electron-hole formation in the excited state of solid CO.

Our purpose initially is to show that the first three mechanisms cannot account for the observed magnitudes of the shifts.

Turning to (i), the permanent dipole moment of the $A^1\Pi$ state of CO is 0.335 D [17] with $C^{\delta+}O^{\delta-}$ and the ground state CO has a value of 0.122 D $C^{\delta-}O^{\delta+}$. Thus the energy shift for material deposited between 20 and 26 K would be of the order of $\Delta E_S \, \Delta\mu \sim 0.15$ cm^{-1}, where ΔE_S is the change in the spontelectric field between 20 and 26 K [8], that is, 3.78×10^7 to 3.58×10^7, or 2.0×10^6 V m^{-1} (Table II) and $\Delta\mu = 0.457$ D.

Referring to (ii), induced dipole moment differences $\Delta\mu_I$ in the fields of 3.78×10^7 and 3.58×10^7 V m^{-1} depend on the unknown polarizability of the $A^1\Pi$ state. This state has a molecular volume $\sim 30\%$ greater than the X state using values given in Ref. [18]. Relating molecular volume to polarizability and ignoring here the correction due to solid-state depolarization [9,19], $\Delta\mu_I$ becomes $\sim 5 \times 10^{-5}$ D and contributes negligibly to the observed shifts.

Finally and with regard to (iii), the change with deposition temperature in the degree of dipole orientation, we note that the energy of interaction between two dipoles, each of value μ, at an angle θ to one another and at a distance r_{12} apart, may be expressed in SI as $-[\mu^2/(4\pi\varepsilon_0 \, r_{12}^3)](1 - 3\cos^2\theta)$. With $r_{12} = 0.339$ nm, $\mu_{CO} = 0.0786$ D in the solid state, values of θ at 20 and 26 K are, respectively, 86.4° and 88.0° to the normal to the surface [8]. This leads to interaction energies between adjacent CO species of 1.62 cm^{-1} at 20 K and 1.5 cm^{-1} at 26 K, implying a shift of ~ 0.12 cm^{-1}.

We conclude that these three simple electrostatic effects contribute shifts in the energy separation of the ground and excited states of solid CO, with deposition temperature, of at least 2 orders of magnitude less than those observed.

Turning to contribution (iv), we propose that electronic excitation of solid CO creates a molecular exciton, that is, an electron-hole pair. The observation of Davydov splitting in spectra of solid CO [15,20,21], characteristic of molecular excitons in general [4], lends support to this proposal. The splitting, into peaks labeled 1 and 2 in Fig. 2, may readily be observed in the spectra. Davydov splitting arises through a force field imposed by the lattice, of cubic symmetry in the case of CO, which separates the energy levels of the exciton into three components. Transitions to two of these, both of irreproducible representation T, hereafter T_1 and T_2, are allowed from the $X^1\Sigma$ state of CO. The Davydov effect may therefore be viewed as an effect analogous to that found in crystal field or ligand field theory for transition metal complexes. The standard theory of Davydov splitting [4] shows that the splitting of the two T components should be essentially independent of the temperature of deposition of the CO film. However, here

we find that the splitting, estimated by fitting a pair of Gaussian profiles to each vibronic band in spectra similar to that in the upper panel of Fig. 1, varies significantly with temperature. For example, analysis of the (0,0) band in Fig. 2 shows that the splitting varies between 450 and 750 cm^{-1} for CO deposited at 20 and 26 K, noting that the value of 450 cm^{-1} at 20 K agrees with that reported in Ref. [20].

In the model of spontelectrics based upon dipole orientation [9], we introduce the concept of the symmetrical part of the electrical field. The crystal field, associated with the cubic lattice of CO, the origin of the Davydov effect as just mentioned and invoked in Refs. [20,21] is directly related to this symmetrical part of the field, $\langle E_{sym} \rangle$. This we have shown, in setting out the model of the spontelectric state [9], may be represented by $\langle E_{sym} \rangle [1 + \zeta(\langle \mu_z \rangle/\mu)^2]$, where $\langle \mu_z \rangle/\mu$ is the average degree of dipole orientation in a mean field description and "z" represents the axis orthogonal to the plane of the film. For solid CO, $\zeta = 43.8$, values of $\langle \mu_z \rangle/\mu$ at, say, 20 and 26 K are 0.0645 and 0.0349, respectively, and $\langle E_{sym} \rangle$ is $4.48 \pm 0.21 \times 10^7$ V m^{-1} [8]. Thus between 20 and 26 K, the symmetrical part of the field drops from $5.3 \pm 0.25 \times 10^7$ to $4.7 \pm 0.22 \times 10^7$ V m^{-1}. While the general shift of both T_1 and T_2 components is ascribed to the change of spontelectric field with deposition temperature (Table II), the observed temperature dependence of the Davydov splitting and marked broadening of the envelope of absorption lines for CO in the left-hand panel of Fig. 2, with increasing deposition temperature, is viewed as a consequence of the temperature dependence of the crystal field. In support of this qualitative explanation, the temperature of deposition shows no effect on the solid N$_2$ spectra. Thus solid N$_2$, while well known to demonstrate the Davydov effect [20], has a splitting independent of deposition temperature as expected in the absence of a spontelectric field.

We present below a simple electrostatic description for the shifts in the absorption spectra, without specific treatment of the Davydov effect. We note that, since the dipole orientation changes as the deposition temperature increases, it is intuitive to suggest that the Davydov splitting must also adjust accordingly. However, our subsequent analysis shows that the coupling between the two may be set aside for the purpose of treating the spectral shifts. Thus the two Davydov components are considered independently of one another, recording the shifts of each, shown in Table I, and treating these shifts as indicative of Stark shifts. Only the relative position of the electron and hole in the spontelectric field is relevant in the subsequent analysis: the dynamics of the system is not considered and the electron-hole pair is regarded in the normal manner as a unit weakly bound by Coulomb attraction. A simple electrostatic model is now introduced in which the spontelectric field acts as an applied field, causing the electron to move in one direction and the hole in the other. The spontelectric field causes a change in their mutual attraction by $1/[\varepsilon(r + \Delta r)^2] - 1/(\varepsilon r^2)$, using

atomic units. This change must be equal to $2E_S$, where E_S is the spontelectric field, and thus,

$$1/(\varepsilon(r + \Delta r)^2) - 1/(\varepsilon r^2) = 2E_S. \tag{1}$$

We now consider two temperatures T_i and T_j. The energy change associated with change in position of both charges by Δr_i is $2\Delta r_i E_i$, where E_i is the spontelectric field at temperature T_i. Therefore, the observed spectral shift $\Delta \mathcal{E}_{ij}$ in spectra taken at T_i and T_j, substituting for $\Delta r = [r/(1 - 2E_S \varepsilon r^2)^{1/2}]E_S$ from Eq. (1), is given by

$$2(\Delta r_i E_i - \Delta r_j E_j) = \Delta \mathcal{E}_{ij} = 2\{[r/(1 - 2E_i \varepsilon r^2)^{1/2}]E_i \\ - [r/(1 - 2E_j \varepsilon r^2)^{1/2}]E_j\}. \tag{2}$$

In order to determine r, the separation of the hole and electron in the absence of the spontelectric effect, pairs of temperatures are now taken and Eq. (2) then yields a value of r of 58.1 ± 1.9, that is, 3.08 ± 0.10 nm, for the peak 2 data and 46.4 ± 2.64 or 2.46 ± 0.14 nm for peak 1 data, where errors are 1σ in each case. Here we have used an
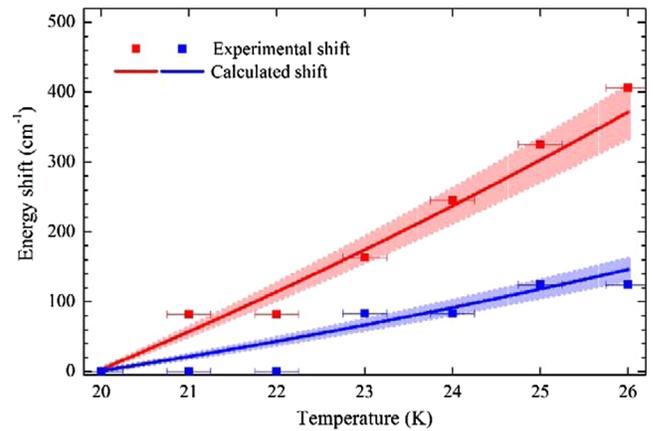

FIG. 3. The experimental shift of the peak of the absorption in the (0,0) band of the A$^1\Pi \leftarrow X^1\Sigma$ transition in solid CO, relative to the peak at 20 K deposition temperature, as a function of deposition temperature at 21, 22, 23, 24, 25, and 26 K (blue squares peak 1, red squares peak 2) versus the results obtained from expression 2 for $\Delta \mathcal{E}_{ij}$, the calculated shift (solid blue and red lines). Peaks 1 and 2 refer to the two Davydov components, which may be identified in Fig. 2, left hand panel. Errors arising in the determination of r, the separation of the hole and electron in the absence of the spontelectric effect, and uncertainties quoted in the spontelectric fields in CO [8], the major sources of error in our estimates, lead to an overall uncertainty in the calculated values of shifts of $\pm 10\%$. The continuous lines in each case were obtained by fitting the variation of the spontelectric field versus temperature of deposition, Table II, to a quadratic form in this temperature range. An uncertainty in the value of the temperature of ± 0.25 K has been included. Uncertainty in measured peak shifts are ± 4 cm^{-1}.

electrical permittivity ε of 1.4211 [22], where the use of a bulk value of ε is justified since hole-electron distances are much greater than the intermolecular separation of 0.339 nm for α-CO [8]. Equation (1) also yields the values of physical displacement Δr_i versus temperature, shown in Table II, giving a size $r + \Delta r_i$ of the hole-electron pair of the order of 5.5 nm for the Davydov state associated with peak 2 and 3.3 nm for peak 1, both values typical of a conventional Wannier-Mott exciton [7]. Values of displacement Δr_i are seen to drop with increasing temperature, reflecting the decreasing spontelectric field. Figure 3 shows the results for calculated redshifts for each case, obtained using Eq. (2), compared with the experimental values given in Table I.

The agreement in Fig. 3, without parametrization, between calculated and measured shifts in solid CO, though far from perfect, supports the presence of Wannier-Mott excitons in the A state of solid CO. It is further a proof of principle that the spontelectric field acting upon a Wannier-Mott exciton lies at the heart of why the electronic absorption spectra of thin films of CO and, by implication, of polar species in general are deposition temperature dependent to an extraordinary degree. The current work may also be seen as additional independent evidence for the presence of the spontelectric effect in films of dipolar species laid down by gas phase adsorption. The presence of spontelectric fields in nanofilms now rests upon measurement of surface potentials and both vibrational and electronic Stark effects, including qualitatively the temperature dependence of Davydov splitting.

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