THE ELECTRET EFFECT IN POLAR MOLECULE CONDENSATES IN THE TEMPERATURE RANGE 90–230 K

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It was found that when polar molecules condense on a cold substrate an electric current is generated which can be measured by an electrometer coupled to the substrate. The direction of this current depends only on the temperature of the substrate. This electret effect is a consequence of the existence of a surface charge on the free surface of the condensate layer. No such electret effects were observed in the case of non-polar molecules. This phenomenon is caused by the polarization of dipole molecules which is induced by an electromagnetic resonance interaction between the condensing molecules and the substrate.

1. INTRODUCTION

In 1969 Elliot *et al.*[1] observed the phenomenon of surface charge generation during the condensation of gases on a substrate at a temperature of 78 K. In 1972 Kutzner[2] published a detailed paper on the electrification of condensing gases with a non-zero dipole moment, *e.g.* CO, NO and H_2O. Kutzner assigned this effect to the spontaneous polarization of polar gas molecules during the condensation of the gaseous phase on a substrate in the temperature range 3–100 K. In 1975 Sujak *et al.*[3] observed a similar effect during an investigation of some anomalies in the electron exoemission from MIM devices at low temperatures in a vacuum (about 10^{-3} Pa).

The results of a detailed investigation of the electrification of polar molecule condensates in the temperature range 90–230 K are presented in this paper. Most of the substances investigated were organic polar molecules containing hydrogen bonds and water as they showed particularly interesting properties.

2. EXPERIMENTAL

The electret effect in condensed vapours was investigated using a vacuum system which was able to sustain a vacuum of the order of 10^{-4} Pa. A "cold finger" which was part of a flow-through cryostat cooled with liquid nitrogen was situated inside the vacuum chamber. This cooling system ensured temperature regulation and stabilization in the range 90–300 K. The condensation chamber containing the parallel-plate measuring condenser and the heat exchanger is shown schematically

in Fig. 1. The lower electrode of the measurement condenser was used as a condensing panel. This electrode was fixed to the heat exchanger but was electrically isolated from it ($R \geqslant 10^{12}$ Ω at 300 K).
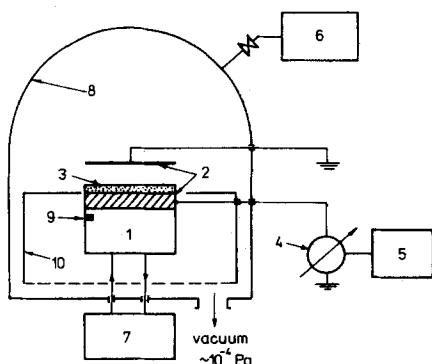

Fig. 1. The measuring system: 1, heat exchanger; 2, parallel-plate condenser; 3, condensate; 4, vibrating reed electrometer; 5, self-recording compensator; 6, dosimetric system; 7, heating–cooling system; 8, vacuum chamber; 9, resistance thermometer; 10, thermal screen.

A vibrating reed electrometer coupled to a self-recording compensator was connected to this electrode and recorded temporal changes $J(t)$ in the displacement current generated during the condensation of the gases under investigation. The head of the cryostat was completely shielded with a thermal screen (295 K) in order that condensation occurred on the measuring electrode only.

The proportioning unit attached to the vacuum chamber supplied a precisely determined mass of the vapour under investigation. A metering needle valve connecting the vacuum chamber to the vapour tank was used to regulate the vapour flow rate. The gases were produced from high purity liquids.

The method of integral measurement of the cumulative charge generated during the condensation of a constant mass of gas was used. The $J(t)$ curve was integrated over the condensation time to determine the total charge Q_m generated during the condensation process:

$$Q_m \approx \int_{\Delta t} J(t) \, dt \qquad (1)$$

where Q_m is the charge generated during the condensation of a constant mass m_0 of the vapour, $J(t)$ represents the curve of current *versus* time and Δt is the duration of the condensation process. In this way curves of Q_m *versus* T were obtained where T is the temperature of the substrate. The preliminary investigations confirmed Kutzner's results that, within the limits of experimental error, the current induced in the cooled electrode is independent of both the substrate material and the external electric field.

The gas flow rate varied during the condensation process and so a mean flow rate $\langle S \rangle = m_0 / \Delta t$ was introduced. It was found that Q_m did not depend on $\langle S \rangle$ and therefore was independent of the actual flow rate. This means that the measured charge depends only on the mass of the condensing vapour if the depolarization

processes are sufficiently slow. The curves of Q_m *versus* T obtained in this work are equivalent to Kutzner's reduced curves because

$$f(T) = \frac{J(T)}{\dot{m}} = \frac{J(T)\mathrm{d}t}{\mathrm{d}m} = \frac{\mathrm{d}Q_m}{\mathrm{d}m} = \frac{Q_m(T)}{m} \tag{2a}$$

and hence

$$f(T) = \hat{Q}_m(T) \tag{2b}$$

where $f(T)$ represents the reduced current curves presented in ref. 2, $\dot{m}$ is the flow rate of the condensing vapour, $J(T)$ represents the current intensity measured during the condensation process *versus* temperature and $\hat{Q}_m$ is the reduced charge.

3. RESULTS

High purity polar and non-polar liquids were used to produce the gases to be condensed. The polar substances were water (H_2O), acetone (CH_3COCH_3), chloroform ($HCCl_3$), trichloroethylene ($CHCl=CCl_2$), toluene ($C_6H_5CH_3$), *ortho*-dichlorobenzene (o-$C_6H_4Cl_2$), methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH) and isobutanol (($CH_3)_2CHCH_2OH$). The non-polar substances were benzene (C_6H_6) and carbon tetrachloride (CCl_4).

The dependence on T of the charge Q_m generated during condensation of the vapour was in general non-monotonic. The shape of the $Q_m(T)$ curve is characteristic and completely reproducible in the low temperature range. In the high temperature range (150–230 K) depolarization processes affect the shapes of the $Q_m(T)$ curves[4]. Nevertheless the curves retain the character typical of a given condensing substance.

The special properties of water vapour condensates were studied first. The $Q_m(T)$ curve for water vapour condensates is presented in Fig. 2. The measured charge for these condensates is positive throughout the temperature range 90–230 K except in the narrow interval 190–205 K where it is negative. This means that in this interval the free surface of the condensate is positive relative to earth. According to
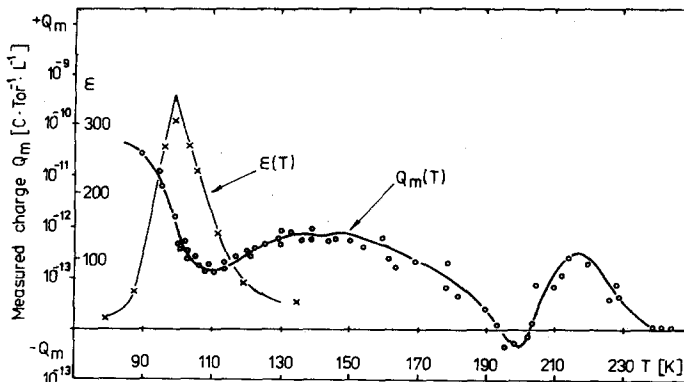

Fig. 2. The $Q_m(T)$ curve for water vapour condensates. $\varepsilon(T)$ is the temperature dependence of the dielectric constant of ice reported in ref. 5.

Kutzner[2] the electret effect does not occur in water vapour condensates above 100 K and anomalous effects are observed in the range 100–120 K. In our experiments the $Q_m(T)$ curve for water vapour condensates exhibits a minimum in the measured charge near 110 K, *i.e.* at the temperature where ice undergoes a ferroelectric phase transition[5]. The surface charge density near 90 K is 10^{-7}–10^{-8} C cm^{-2}, and the electric field intensity inside the condensate is estimated to be 10^4–10^5 V cm^{-1} (ref. 4).

The $Q_m(T)$ curves for the other condensates investigated are shown in Figs. 3–6 where it can be seen that in most cases a change in the temperature of the substrate induces a change in the sign of Q_m. This means that the current generated during the condensation of a molecular beam changes direction as the temperature of the substrate changes.
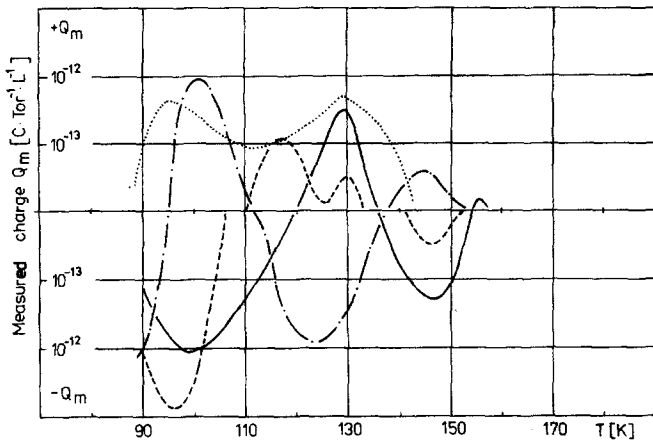

Fig. 3. The $Q_m(T)$ curves for the alcohols investigated: ——, methanol ($\times 10^{-2}$); —·—, ethanol ($\times 2 \times 10^{-2}$); ···, propanol ($\times 1.0$); – – –, isobutanol ($\times 1.7$). The numbers in parentheses are the conversion factors required to obtain the effective value of $Q_m(T)$.
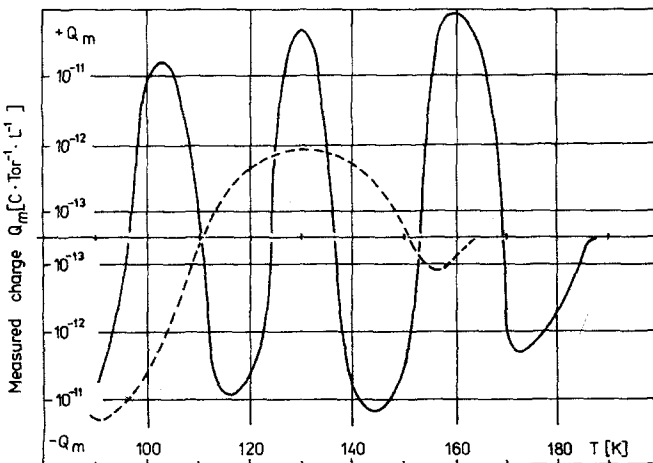

Fig. 4. The $Q_m(T)$ curves for acetone (– – –) and trichloroethylene (——) condensates.
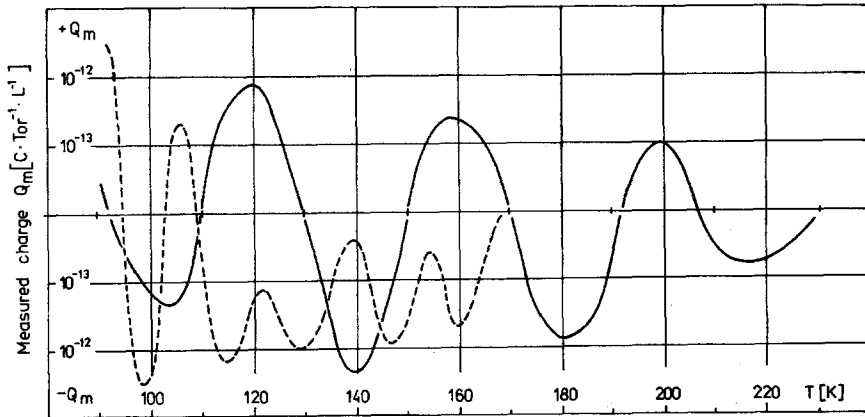
Fig. 5. The $Q_m(T)$ curves for *ortho*-dichlorobenzene (———) and toluene (– – –) condensates.
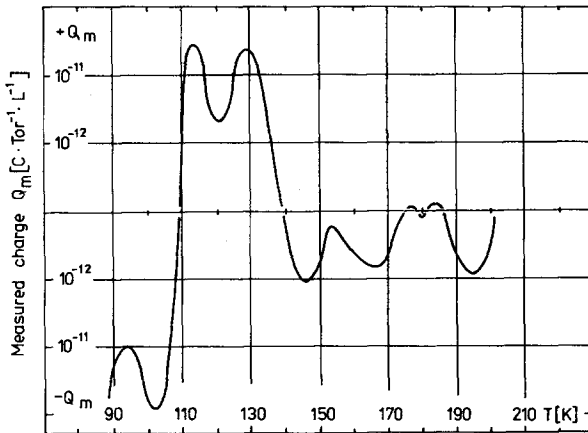

Fig. 6. The $Q_m(T)$ curve for the chloroform condensates investigated.

It was also observed in a number of cases that there is a correlation between the moment of inertia I_0 of the condensed molecules and the temperature range in which the depolarization effects occur. For molecules in which I_0 is small a weak current flowing in the opposite direction to the condensation current appears after the condensation process even in temperature ranges where the saturated vapour pressures of the condensates are low (10^{-5}–10^{-8} Pa). Particularly strong depolarization processes were observed near the triple point (about 30 K) where intense vaporization occurred. Therefore the depolarization processes at low temperatures are probably due to the reorientation of polarized molecules inside the condensates.

Since the external constant electric fields and the flow rate of the molecular beam have no observed effect on Q_m the ion processes are at most of secondary importance. Trace impurities in the polar sources had no observable effect on the shapes of the $Q_m(T)$ curves except in a few cases[6]. Pure vapour condensates of benzene and carbon tetrachloride were also investigated for electric effects.

The results presented here show that the electret phenomenon is essentially due to the polarization of polar molecules during the condensation process and that the model of the polarized condensate proposed in refs. 2, 4 and 7 is reasonable.

If the effective surface charge of the polarized condensate is Q_s then the charges induced on the electrodes of a parallel-plate condenser are

$$Q_u = -Q_s\left(1 - \frac{x}{\varepsilon d}\right) \tag{3a}$$

$$Q_l = -Q_s\frac{x}{\varepsilon d} \tag{3b}$$

where Q_u and Q_l are the charges induced on the upper and lower electrodes respectively, x is the thickness of the condensate layer, d is the separation between the electrodes in the measurement condenser and ε is the dielectric constant of the condensate. Equations (3a) and (3b) are valid if it is assumed that $x \ll d$. The current $J(t)$ flowing during the condensation of the polar molecular beam onto the substrate is given by

$$J = J_1 \approx -\frac{Q_s}{\varepsilon d}\frac{dx}{dt} \tag{4}$$

Integration of this expression over the time Δt during which condensation occurs gives

$$\int J\, dt = \int J_1 dt \approx -\frac{Q_s}{\varepsilon d}\int dx \tag{5}$$

If it is assumed that $x(t = 0) = 0$ and $x(t = \Delta t) = x_0$, we have

$$Q_m = \int_{\Delta t} J(t)\, dt \approx -\frac{Q_s x_0}{\varepsilon d} \tag{6}$$

where $J_1(t)$ is the current intensity induced on the lower electrode (the substrate) and x_0 is the total thickness of the condensate layer.

The results presented here generally agree with Kutzner's observations, and it has also been shown that the electret phenomenon can occur in any temperature range where solidification of a gaseous phase on a cold substrate is possible. However, the stability of the surface charge of the condensates at temperatures of the order of 200 K is much less than that in the liquid helium temperature range.

Although the phonon resonance hypothesis proposed by Kutzner[2] seems reasonable, the application of Debye's linear approximation for temperatures greater than the boiling point of helium is invalid. It is well known that Debye's approximation is correct at very low temperatures only, particularly in the case of molecular crystals. If the concept of the polarization of dipole molecules is applied the mean temperature difference ΔT between adjacent maxima of the $Q_m(T)$ curve can be taken as a measure of the energy difference between two resonant states of the system, i.e. the condensing molecule and the condensation surface, which appear at temperatures T_1 and T_2.

The relation between ΔT and $(\mu^2/I_0)^{1/2}$, where μ is the permanent dipole moment of the molecule and I_0 the mean moment of inertia of the molecule, is shown

in Fig. 7 for the condensates investigated. There is an obvious linear correlation between ΔT and the dipole moment μ of the condensed molecules. This correlation suggests that electromagnetic interactions may affect the generation of surface charge on the polar molecule condensates.
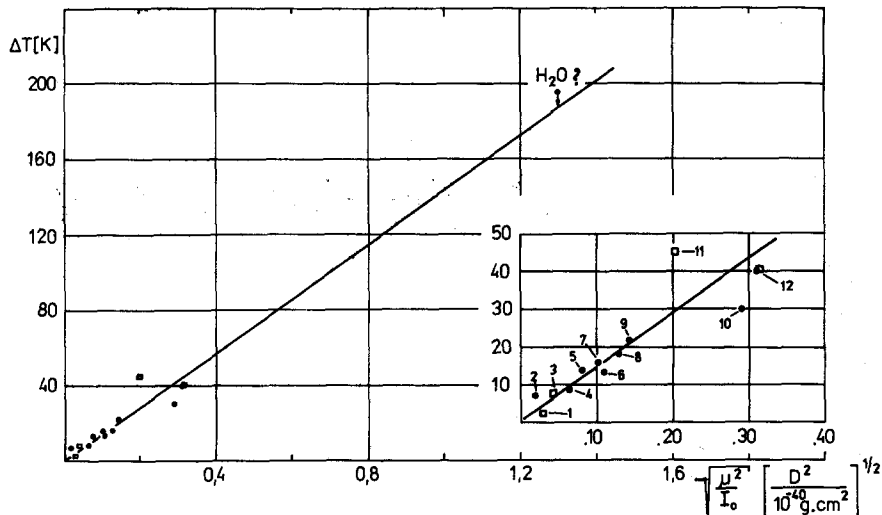

Fig. 7. The correlation between ΔT and $(\mu^2/I_0)^{1/2}$ obtained for the condensates investigated. For comparison the points ($\square$) for CO, NO, SO_2 and acetone calculated from the ΔT values reported in ref. 2 are also presented. The μ and I values were obtained from spectroscopic measurements. The numbers denote the points for the condensates: 1, CO; 2, toluene; 3, NO; 4, chloroform; 5, trichloroethylene; 6, isobutanol; 7, propanol; 8, ortho-dichlorobenzene; 9, ethanol; 10, methanol; 11, SO_2; 12, acetone.

The relation between $(L/I)^{1/2}$, where L is the heat of vaporization of the condensate and I is the moment of inertia of the molecule, and ΔT given in ref. 2 is not straightforward in the physical sense. The straight line obtained when ΔT is plotted against $(L/I)^{1/2}$ does not pass through the origin of the coordinate system and ΔT does not show any correlation with the dipole moments of the molecules.

A more exact model of the electret effect is required which must take into consideration the electromagnetic quantum effects which probably occur during accommodation and "freezing" of the molecule[4, 8].

4. ELECTROMAGNETIC RESONANCE HYPOTHESIS

Recent investigations have mainly been devoted to thermostimulated depolarization in water condensates and do not satisfactorily explain the electret effect observed during the condensation of polar molecules[7, 9].

The influence of the permanent dipole moment on ΔT suggests that the electromagnetic field, e.g. the thermal electromagnetic field emitted from each substance and also from the substrate*, may be an important factor in molecular polarization.

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* An additional source of electromagnetic radiation is provided by the molecules striking the substrate.

The interaction between the cold substrate and the condensing molecule, in which the dipole moment of the molecule is preferred, may not be of the electrostatic (coulombic) type because other types of intermolecular forces usually predominate[10]. It appears that the resonance type of interaction may lead to a preference for one species of interaction. The suggestion that the energy exchange between the accommodating molecule and the cold substrate is of the resonance type was originally made by Dawson and Haygood[11].

In the IR and microwave regions the majority of substances emit electromagnetic radiation similar to that of a perfect radiator[12]. This means that the spectral density of the emitted photons is given by an expression of the type

$$v_{\mathrm{m}} = \alpha T \tag{7}$$

where v_{m} is some fundamental frequency which represents the maximum in the photon spectral density, $\alpha \approx 1.56 k_{\mathrm{B}}/h \approx 3.3 \times 10^{10}$ Hz K^{-1} is a constant, h being Planck's constant and k_{B} Boltzmann's constant, and T is the temperature of the substance[4]. The intensity of this electromagnetic field at a short distance (10 Å or less) from the condensing surface may be very large. The substrate contains many oscillators near which the intensity of the fundamental frequency v_{m} of radiation reaches about 10^6 V cm^{-1} (quasi-static oscillator zone).

The assumption that during the accommodation process the molecules are able to perform vibrations or librations around different points of equilibrium in the same way as the harmonic oscillator seems correct. Therefore overtones and combination vibrations should also occur.

Away from resonance, *i.e.* when the eigenfrequencies v_{e} of the molecules on the surface and the maximum of the spectral photon density of the electromagnetic field emitted from the condensation surface have different values, the interaction between the molecule and the field is weak. When the temperature of the substrate surface reaches the appropriate value resonance coupling may occur between the electromagnetic field and the condensing molecule, and then v_{m} of the field is approximately equal to one of the eigenfrequencies v_{e}' of the molecule appropriate to the given orientation of the dipole to the substrate surface. This interaction may be intense.

Many types of interaction between the vibrating molecule and the condensing surface probably appear. Therefore resonance curves that are not of the classical shape may be produced. In addition this electromagnetic field contains many quanta and the maximum spectral photon density is rather large. The spectrum of this electromagnetic field may also be more complicated than for a perfect radiator at thermal equilibrium.

In the case of quantum electromagnetic resonance the processes of absorption and emission are equally probable and both processes induce changes in the angular momentum of the molecules in the IR and microwave regions. The remainder of the molecules which have other orientations to the substrate and hence have vibrational eigenfrequencies $v_{\mathrm{e}}'' \neq v_{\mathrm{e}}'$ due to the different moments of inertia do not interact with this electromagnetic field. This or a similar mechanism may generate a surface charge on the polar molecule condensates as a consequence of a change in orientation of one of the accommodating molecules. Statistically, the different orientations are equally probable, and when there is no ordering mechanism no

polarization should occur over the liquid helium temperature range. The change in the condensation temperature from T_1 to T_2 induces the same mechanism for another part of the population with another dipole moment orientation and eigenfrequency v_e''. In general many eigenfrequencies exist for polyatomic molecules (rotary isomers and dimers) and hence the $Q_m(T)$ curves presented in this paper are probably the sums of the different resonances which occur in the various temperature ranges.

The dependence of the parameter ΔT on the dipole moment of the molecules investigated seems rather clear because in the dipole approximation of radiation the probability of a quantum transition is closely related to the presence of a vibrating dipole moment. Strictly, it is dependent on $|\mu_{12}|^2$, i.e. the matrix element of the transition between states $|1\rangle$ and $|2\rangle$. In this case $|\mu_{12}|^2$ is probably of the form

$$|\mu_{12}|^2 \approx \mu^2 \frac{K^2}{J(J+1)} + \text{a vibrational term}$$

where μ is the dipole moment and J and K are the angular momentum and magnetic quantum numbers for the rotator[13]. The observed maxima in $Q_m(T)$ should be situated near the extreme values of the absorbance index for given condensates, particularly in the far IR and microwave radiation regions*. The intensities of the $Q_m(T)$ maxima depend on many factors including the coupling power, the electromagnetic field and the vibrating dipole moment of the molecule.

If it is assumed that at resonance the eigenfrequencies of oscillation of the condensing molecules are equal to the fundamental frequency of the electromagnetic field and μ^2 is the quasi-potential of these oscillations, we can write

$$\Delta T = T_2 - T_1 \propto h(v_e'' - v_e')$$
$$\propto (\mu^2/I_2)^{1/2} - (\mu^2/I_1)^{1/2} \tag{8}$$

and to a first approximation

$$\Delta T \propto (\mu^2/I_0)^{1/2} \tag{9}$$

where T_1 and T_2 are the temperatures at which adjacent extrema occur on the $Q_m(T)$ curve, v_e' and v_e'' are the resonance frequencies at temperatures T_1 and T_2 respectively, I_1 and I_2 are the moments of inertia of the molecule at two different orientations to the substrate and I_0 is the mean moment of inertia of the molecule about its centre of mass. It has been shown[4] that the difference $(\mu^2/I_2)^{1/2} - (\mu^2/I_1)^{1/2}$ for the molecules investigated can be taken as $(\mu^2/I_0)^{1/2}$ to a first approximation. This simplification was indispensable because it is very difficult to find points of equilibrium for polyatomic molecules during surface oscillations.

5. DISCUSSION

The hypothesis presented here is reasonable but the real picture of the phenomenon may be more complicated. We do not yet know what the connection is between the electret effect and the phase transitions which occur in the condensates.

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* For some condensates it was observed in the visible range[14].

In some cases the ferroelectric phase transformations produce a large perturbation in the electret effect.

The source of the electromagnetic radiation may be the coupling of preferred lattice modes, *e.g.* transverse optical modes, to an electromagnetic wave spreading inside the crystal medium, *i.e.* polaritons[15]. At some temperatures the intensity of these vibrations may become very large and then the mode may become unstable. This mode may interact with the condensing polar molecule by photon exchange. The existence of some type of feedback seems possible.

These exciting resonance states may accompany some types of phase transformation. This is suggested by the fact that in some cases (ethanol and acetone) the $Q_m(T)$ maxima and some phase transitions in the condensates occur at the same temperatures[4,16]. Therefore some types of phase transition inside the condensate layers may be induced by large amplitude lattice modes (non-local resonance states) in a similar manner as proposed by Cochran[17] for some ferroelectric materials.

In the very low temperature range (below 4.2 K) the third law of thermodynamics may have an important influence on polarization phenomena. The condensate, which is in a nascent state at helium temperatures, is a thermodynamic ensemble in which the spontaneous reduction of configuration entropy could occur. It is generally observed that for crystals composed of asymmetric molecules, *e.g.* CO, NO and H_2O, the experimental value of the entropy at the zero point (about 0 K) is lower than that theoretically predicted[18,19]. This proves that strong polarization forces which induce an additional degree of order occur at the zero point. Hence at very low temperatures the resonance effect discussed earlier may be masked by other intense processes. This may explain why there are no changes in the sign of the surface charge in this temperature range.

The temperature difference ΔT between two adjacent $Q_m(T)$ maxima for water vapour condensates obtained from the relation $\Delta T \propto (\mu^2/I_0)^{1/2}$ is about 185 K. This means that the next extremum in $Q_m(T)$ should appear near 10 K but unfortunately no anomaly in the polarization curve for ice films was observed by Kutzner[2].

At a given resonance temperature the polarized condensate has an excess energy $\Delta E = E(\uparrow, \uparrow, \ldots) - E(\uparrow, \downarrow, \ldots)$ due to the existence of an internal electric field inside the condensate. This excess energy is given by $\Delta E = \int \varepsilon F^2 dv$, where ε is the dielectric constant of the condensate, F is the intensity of the electric field and v is the volume of the condensate.

After some time has elapsed the surface charge disappears in the temperature range investigated owing to depolarization processes. It is possible that an ensemble of such polarized dipoles will show some unusual optical properties particularly in the IR and microwave regions.

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