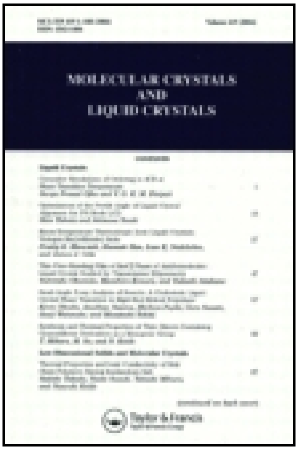

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Dielectric Behavior of Perchloryl Fluoride—An Unusual Rotator Solid

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Dielectric Behavior of Perchloryl Fluoride—An Unusual Rotator Solid

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Perchloryl fluoride possesses one of the lowest molecular electric dipole moments, yet the solid exhibits appreciable dielectric absorption with maxima at low temperatures (90–110 K) and 500 Hz–200 kHz frequencies from a Debye relaxation process. The dielectric properties and activation energy of 24.8 kJ mol^{-1} for molecular reorientation are somewhat unusual for a rotator solid and are discussed in terms of free-volume theory. In the clathrate hydrate condition there is no apparent dielectric dispersion from orientation of the guest ClO_3F, although the temperature dependence of the dielectric permittivity suggests possible contributions from dipole rotations and lattice vibrations at low temperatures.

INTRODUCTION

Perchloryl fluoride is a small near spherical molecule with C_{3v} symmetry,[1-3] and is thus expected to rotate within a volume similar to that of the molecule itself. Rotational energy barrier measurements from the n.m.r. technique reveal a rather high Arrhenius activation energy of 28.9 kJ mol^{-1} for solid ClO_3F.[4] This value has been explained in terms of a cooperative process involving a defect diffusion mechanism.[4] These results are in line with earlier thermodynamic investigations which revealed the presence of a residual entropy, possibly from reorientational disorder at temperatures as low as 0°K.[5,6] Furthermore, Mountfield and Weir interpreted their findings of a conductance maximum at 92.6°K and 1.598 kHz, and a rise in the dielectric permittivity and heat capacity of ClO_3F in the temperature region 80–126°K, as due to distortion polarization, vacancy formation and/or anharmonicity in the lattice prior to melting.[6]

In view of the uncertainty on the nature of the relaxation process in solid perchloryl fluoride, and the limited data on its electrical properties, a dielectric study covering wide frequency (5×10^2–2×10^5 Hz) and temperature (4.2–140 K) ranges was performed.

Perchloryl fluoride is known to form a type I clathrate hydrate,[7-9] that is, a nonstoichiometric inclusion compound in which the guest is held principally via van der Waals interactions in a metastable host lattice consisting of 46 water molecules per unit cell.[10-12] Each cubic cell contains two 12-hedral and six 14-hedral cages with average free diameters of ca. 5.0 and 5.8 Å, respectively. The perchloryl fluoride molecule has a maximum van der Waals diameter of around 5.3 Å and is anticipated to occupy only the 14-hedra resulting in a limiting composition of $ClO_3F \cdot 7\frac{2}{3}H_2O$.[7–9,13] It is, therefore, of interest to compare the relaxation behavior of ClO_3F in an inclusion compound to that of the pure solid, as rotational mobility is dependent to a large extent on the environment of the molecule. Perchloryl fluoride is also a challenging candidate for dielectric study, as it has the lowest permanent electric dipole moment known for any molecule.[14] It also has one of the highest resistances to electrical breakdown of any gas and, therefore, is used as an insulator in high voltage systems.

EXPERIMENTAL

Samples of perchloryl fluoride (Ozark–Mahoning) were prepared by solidifying the gas in a liquid nitrogen trap in a vacuum line, followed by evacuation, trap-to-trap distillation, and further evacuation of the residue to remove any impurities. The solid was melted and transferred into a teflon ring of 0.172 cm thickness and 1.587 cm inner diameter, mounted on a cold (77°K) low electrode plate of a capacitor cell in a nitrogen atmosphere. The purity of the perchloryl fluoride was checked from its mass spectrum.

Perchloryl fluoride clathrate hydrate was made as described in the literature by reacting a sufficient quantity of gas with enough degassed (via several freeze-pump-thaw cycles) distilled water to form $ClO_3F \cdot 7\frac{2}{3}H_2O$ clathrate.[8,13] Ice, from distilled water, and clathrate samples were first ground and then pressed at ca. 1.1 kBar in a precooled (77°K) die to form thin 1.905 cm diameter disks.

The apparatus for dielectric studies is basically as described in References 15 and 16. A three-terminal, circular, parallel-plate, brass electrode assembly was used for dielectric measurements at frequencies in the range 5×10^2–5×10^4 Hz in conjunction with a General Radio 1615-A capacitance bridge. Frequencies $\leq 5 \times 10^4$ Hz were produced on a Hewlett-Packard model 203 A variable phase function generator which also supplied a reference signal to the X-sweep of a Tektronix type 564-B storage oscilloscope. A Rhode & Schwartz tunable indicating amplifier type UMB 12121/2 with output to the Y-sweep of the oscilloscope served as a null detector for the transformer ratio bridge. At frequencies of 10^4 to 2×10^5 Hz a Hewlett-Packard 4275A Multi-Frequency LCR meter was also used to measure the dielectric response of the sample. Frequencies applied across the dielectric cell were checked on a Hewlett-Packard 5223L electronic counter and with the timebase of the oscilloscope.

The sample cell was fitted into an Andonian Associates Inc. Variable Temperature Cryogenic System, 0-25/7 M series. Temperature control was via a proportional control circuit similar to that described in Reference 16. Measurements of temperatures $\geq$ 77°K were from the emf values of a copper-constantine thermocouple, whereas below 77°K the resistance of a four-wire calibrated CryoCal Inc. Germanium Cryogenic Temperature Sensor #4379 afforded the temperature.

RESULTS

The temperature dependence of the relative dielectric permittivity (ε') and loss factor (ε'') (corrected to zero loss from ε'' at $T \ll T_{max}$ and $T \gg T_{max}$) afforded estimates of the amplitude of the dielectric dispersion ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) and the maximum dielectric loss factor (ε''_{max} at temperature T_{max}) (see Figures 1–3). A relaxation process that is characterized by a single relaxation time (τ) has a dielectric absorption described by the Debye–Pellat equation[17,18]:

$$\varepsilon'' = \Delta\varepsilon\omega\tau/(1 + \omega^2\tau^2) \tag{1}$$

where ω is the angular frequency of the applied electric field. Equation (1) reduces to $\Delta\varepsilon/2$ at ε''_{max}, in which ε_0 and ε_∞ are the limiting values of the dielectric permittivity at low and high frequencies, respectively. If there is a symmetrical distribution of relaxation times about a mean value, τ, then the dielectric loss factor becomes:

$$\varepsilon'' = \frac{\Delta\varepsilon\cos(\alpha\pi/2)}{2\{\cosh[(1-\alpha)\ln\omega\tau] + \sin(\alpha\pi/2)\}} \tag{2}$$

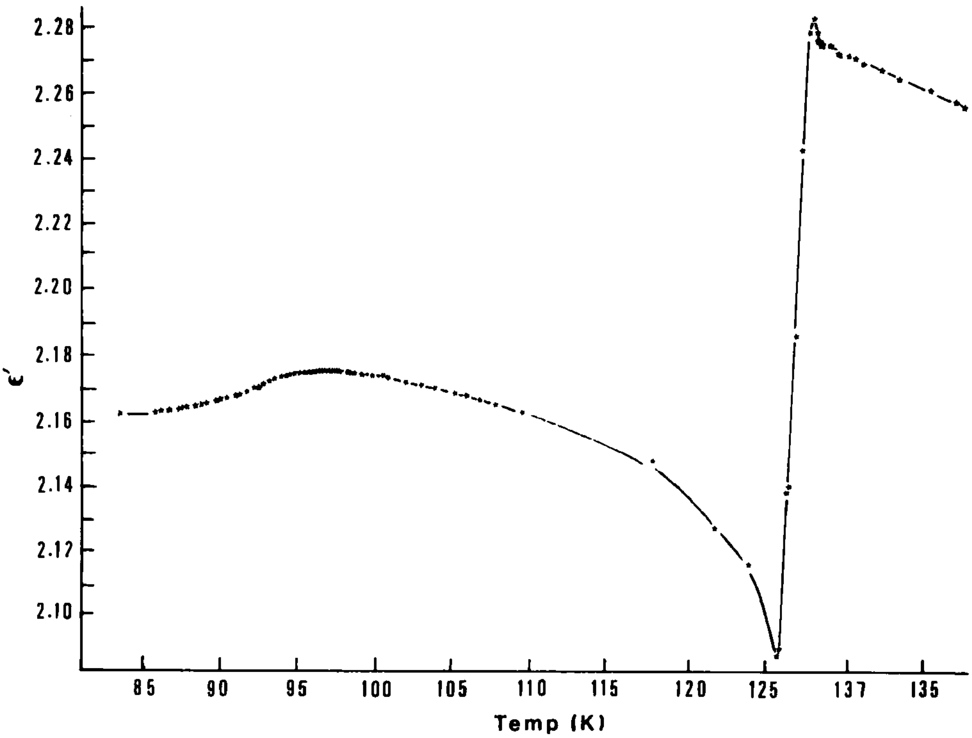

FIGURE 1 Dielectric permittivity of perchloryl fluoride as a function of temperature at 1 kHz.

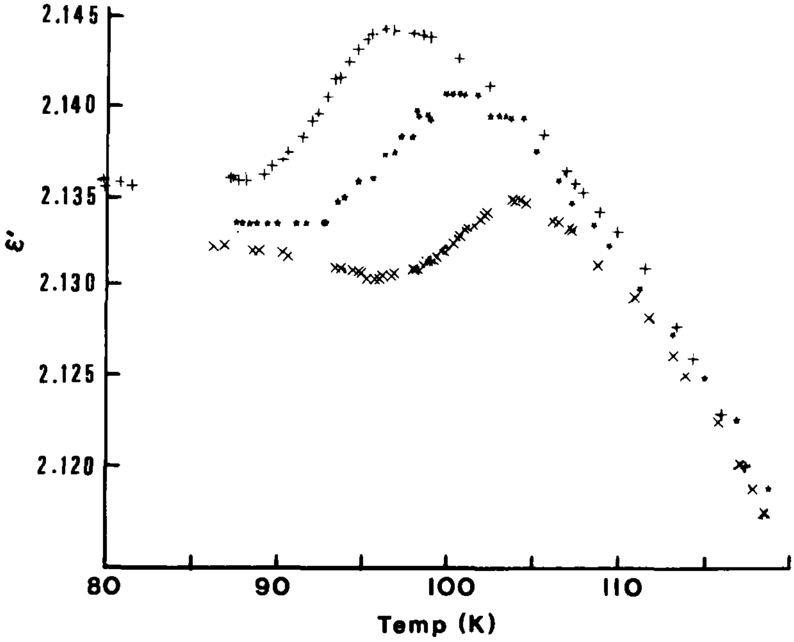

FIGURE 2 Dielectric dispersion of solid perchloryl fluoride; +, 1 kHz; *5 kHz; X, 20 kHz.

In Equation (2) the Cole–Cole distribution parameter ranges $0 \leq \alpha < 1$ and is 0 for a Debye absorption.[19] It is possible to determine α from the interval $0.1 < (\nu/\nu_{\max}) < 10$ in the plot of $ln\ \varepsilon''$ against $\ln \nu$ by use of the following expressions[20]:

$$\varepsilon'' = \Delta\varepsilon(\nu/\nu_{\max})^{1-\alpha}\ (\nu << \nu_{\max}) \tag{3}$$

$$\varepsilon'' = \Delta\varepsilon(\nu/\nu_{\max})^{-1-\alpha}\ (\nu >> \nu_{\max}) \tag{4}$$

The frequency (ν) at which the dielectric loss is a maximum is denoted by $\nu_{\max}$, which also affords the Arrhenius activation energy (E_a)

$$ln\ \nu_{\max} = ln\ A - (E_a/\mathrm{RT}) \tag{5}$$

from its temperature dependence (see Table I and Figure 4). The constant A in the above equation is a pre-exponential term.

A direct measure of the magnitude of the dielectric dispersion is available from the isochronal temperature dependence of ε' (Figure 2). Once ε_0 and ε_∞ are obtained, then the molar polarization (P_o) and the molar refraction (R) can be estimated.

$$P_o = \left(\frac{\varepsilon_o - 1}{\varepsilon_0 + 2}\right)\frac{\rho}{M} \quad \text{and} \quad R = \left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right)\frac{\rho}{M} \tag{6}$$

In the above equations, ρ is the density of a dielectric material of molecular weight

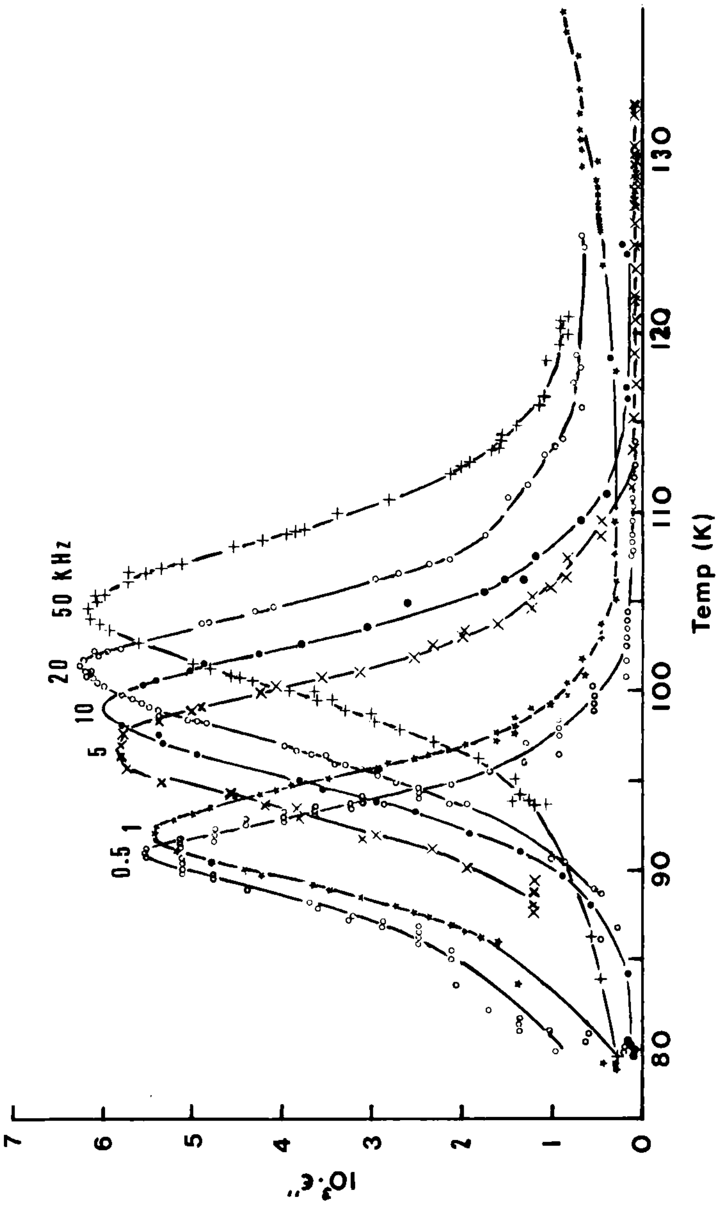

FIGURE 3 Dielectric absorptions of solid perchloryl fluoride.

TABLE I

Temperature of dielectric loss maxima (ε''_{max}), relaxation time (τ), and electric dipole moment data for solid perchloryl fluoride

Temp (K)	τ(s)	$10^3\varepsilon''_{max}$	μ (D)
90.6	3.30×10^{-4}	5.5	0.023
91.6	1.62×10^{-4}	5.5	0.032
92.0[a]	1.59×10^{-4}	7.6	0.026
97.2	3.29×10^{-5}	5.8	0.030
98.5[a]	1.73×10^{-5}	6.2	0.031
99.2	1.62×10^{-5}	6.0	0.026
101.5	8.05×10^{-6}	6.2	0.026
105.0	3.20×10^{-6}	6.2	0.010
110.2	7.96×10^{-7}	4.9	0.021

[a] Sample #2.

M. The electric dipole moment (μ) is then available from the Debye–Clausius–Mossotti relation (N_A is Avogadro's number)[18]:

$$\mu^2 = 9kT(P_o - R)/(4\pi N_A) \tag{7}$$

A Chebyshev polynomial ($\varepsilon' = \Sigma AT^i$)[21] was used to fit the apparent dielectric permittivity data as a function of temperature (see Table III).

DISCUSSION

In the solid state molecular motion is often hindered because of the local force fields and steric constraints of the lattice. However, many spherical and cylindrical molecules which form rotator phases, can effectively rotate in a small volume with little displacement of neighbours. The ability of some molecules to relax in the solid state has been correlated to molecular size, shape, polarity, and free-volume factors.[22-26]

The pseudospherical substituted methane rotators, such as 1,1,1-trichloroethane, 2,2-dichloropropane, and tert-nitrobutane are classic examples of molecules which display liquid-like rotational freedom below their freezing points.[24,25] This is reflected in the similarity of the relaxation times and activation energy for molecular reorientation in the solid and liquid states. When the shape of the molecule is somewhat aspherical, *e.g.*, t-amyl chloride,[22] or when there are large dipole interactions as for tert-cyanobutane,[25] then reorientation becomes difficult in the solid. On the basis of size, shape, and dipole moment, perchloryl fluoride is expected to be a facile rotator in its solid state.

Perchloryl fluoride does indeed show dielectric activity in the solid as exemplified by the variation of the dielectric permittivity with temperature (Figure 1). The main features to note are: (i) the sharp change in ε' at 125.5°K from melting of the sample, *i.e.*, dominance of the density and dipole terms in the dispersion equations; and (ii) the rapid recovery followed by dielectric dispersion of the ε' at

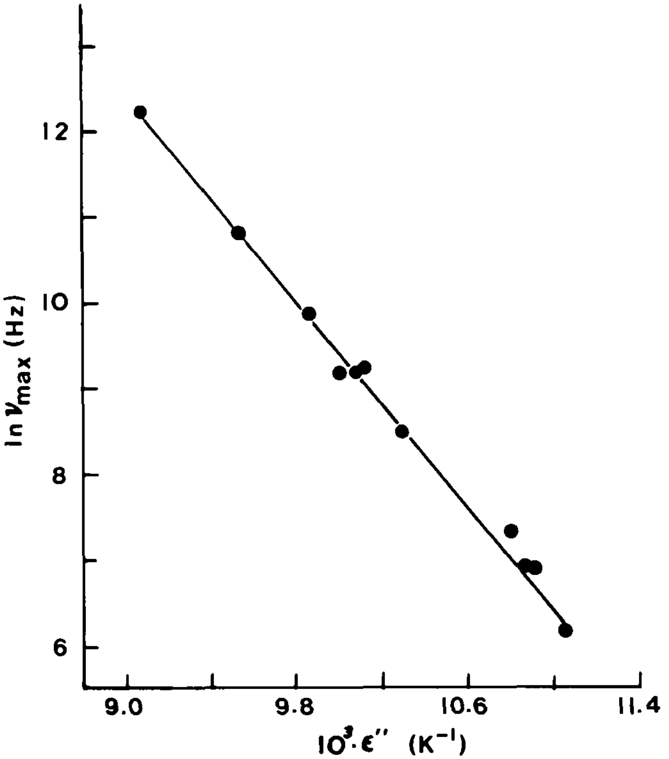

FIGURE 4 Arrhenius plot for solid perchloryl fluoride (x, Reference 6).

the low temperatures. The amplitude of the latter feature corresponds to an orientation polarization process involving a dipole moment of ca. 0.025 Debye (Table I).

Even though most measurements of the electric dipole moment of ClO_3F have been from the microwave absorption of the gas (μ = 0.023 to 0.025 ± 0.003 D),[1,27,28] a Stark effect study, by De Leon and Muenter,[29] on ClO_3F, from the same supplier as in this work, gave μ = 0.0228 D for the gas expanded through a nozzle cooled to 195°K. Rotational modes are dielectrically inactive if there is a zero electric dipole moment component perpendicular to the axis of rotation. In the case of perchloryl fluoride any reorientations around axes which intersect at the centre of mass (0.151 Å from the centre of the Cl atom along the Cl—F bond[3]) and are perpendicular to the axis of the three-fold symmetry will give rise to a small dielectric absorption, as the molecular dipole moment resides along the Cl—F bond.

Other important observations to consider are: (i) the empty teflon ring sample holder exhibited no dielectric absorption and constant dielectric permittivity over the range of temperatures where ClO_3F solid relaxes dielectrically; (ii) ClO_3F possesses only one set of dielectric absorption peaks in the temperature range 4.2–140 K (Figure 3); and (iii) there is a rise in the dielectric loss factor above ca. 120°K at 1 kHz, possibly from dipolar relaxation in the liquid.

Mountfield and Weir have previously reported the dielectric dispersion of solid perchloryl fluoride, but for the sample in a coaxial cell at a single frequency.[6] They measured only one conductance maximum at 92.6°K and 1.598 kHz. Their results, however, show appreciable overlap of the dielectric permittivity from the solid $\rightleftharpoons$ liquid phase transition, with that for dispersion in the solid. Further, they suggest that there is no permanent dipole moment in the solid and negligible orientation polarization in the temperature range 4 to 160°K. Any change in ε' is attributed to electronic and distortion polarization. From the present study, the two regions of dielectric permittivity are clearly separated and the apparent electric dipole moment is associated with molecular rotation in the solid.

Dielectric loss curves related to the low temperature dispersion process (Figures 3 and 5) provide a measure of the average Arrhenius activation energy for dipole rotation (E_a = 24.8 kJ mol^{-1}). This value compares to that of 28.9 kJ mol^{-1} from ^{19}F-n.m.r. spin-lattice relaxation times.[4] The n.m.r. data yielded the relaxation time as $\tau = 6.27 \times 10^{-21} \exp(3455/T)$, whereas the present dielectric study affords:

$$\tau_{\text{diel}} = 1.40 \times 10^{-18} \exp(2986/T) \tag{8}$$

The lack of anisotropy in the ^{19}F-n.m.r. lineshapes[4] suggested reorientation between sites of tetrahedral or higher symmetry, and this is consistent with the symmetrical

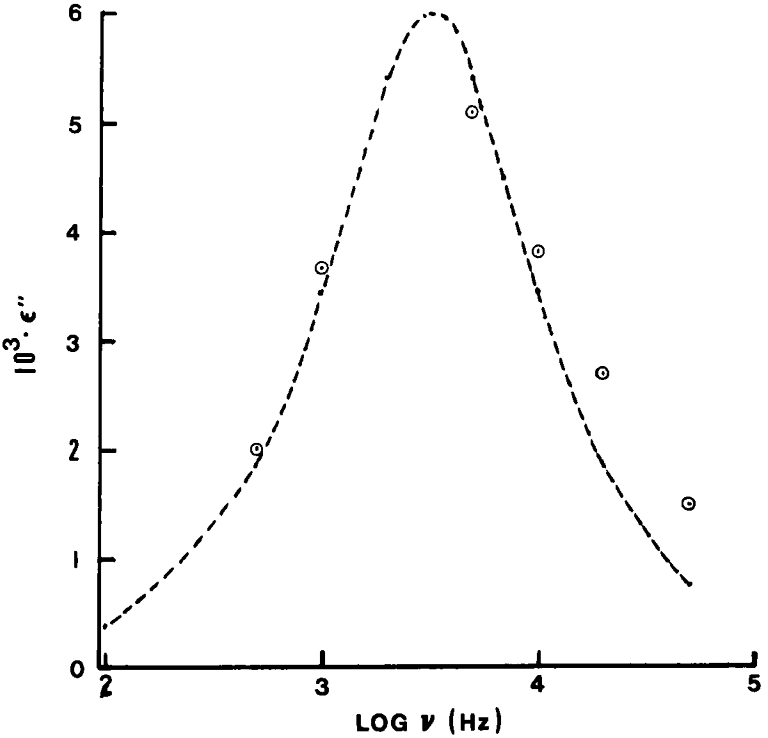

FIGURE 5 Dielectric loss factor (--- calc.) versus frequency for solid perchloryl fluoride at 95°K.

and narrow dielectric absorption curves (Figures 3 and 5) of perchloryl fluoride.

In contrast to perchloryl fluoride, larger and more polar molecules, *e.g.*, 1,2-dichloropropane and nitro tert-butane, in their rotator phases exhibit low rotational energy barriers in the range 2 to 6 kJ mol^{-1} along with short relaxation times which are similar to those of their liquids.[25] Perchloryl fluoride is, therefore, an unusual rotator solid and is more akin to the intermediate or pseudorotator solids, *e.g.*, pyrole, pyridine, and γ-picoline, even though they are not spherical.[24]

The question arises as to why ClO_3F is not a normal rotator solid. Clemett and Davies consider that two prime factors, free-volume and molecular interaction energies, are important in the characterization of the rotator phase.[26] Free-volume theory is dealt with in Hill's model of rotational mobility.[24] When the difference between the free-volume for viscous flow (b) and the free volume of rotation (b′) is greater than ca. 10%, then a rotator phase should exist.[24] If η, ζ, and ρ are the viscosity, friction constant ($\zeta = 2kT\tau$) and density of the liquid, respectively, then the free volumes are available from the equations:

$$\eta = A/(v - b) \quad \text{and} \quad \zeta = A'/(v - b') \tag{9}$$

where v is the specific volume.[24] Literature values of density,[30] viscosity,[31] and orientational correlation times[32] of liquid perchloryl fluoride were used to calculate b and b' (*vide infra*). A comparison of some physical properties and relaxation parameters of ClO_3F with a typical rotator solid, 1,1,1-trichloroethane, (see Table II) reveals the unusual rotator behaviour of the former molecule.

The substituted methane rotators with van der Waals diameters of ca. 6.1 Å have $b' \sim 10\%$ less than b while ClO_3F has b' (79.3 Å^3) only 2.8% less than b (81.6 Å^3) and very close to the molecular volume (77.95 Å^3). It is interesting that the intermediate rotators, such as pyrole, have b' 3.8–4.3% less than b, and rigid solids have $b \sim b'$.[24] When the dipolar interaction energies (μ^2/d^3; d is the molecular van der Waals diameter[25]) of the substituted methane rotators (ca. 1.4×10^{-21}–3.4×10^{-21} J per molecule[25] are compared to that of ClO^3F (3.6×10^{-25} J per molecule) one predicts a low potential barrier to rotation in the latter case.

It is likely that the small free-volume, from the packing of the ClO_3F molecules in the solid, accounts in large part for the observed high Arrhenius activation energy of 24.8 kJ mol^{-1}, at least for rotation about axes perpendicular to the Cl—F bond. The close-packing of the perchloryl fluoride molecules is reflected in the rather high density (2.128 – 2.19 g/c.c.) of the solid.[6] There is also an unusually high

TABLE II

Comparison of density of liquid (ρ), molecular volume (V_{mol}), dipole moment (μ), relaxation times (τ), and Arrhenius activation energy (E_a) of ClO_3F with 1,1,1-trichloroethane, a normal rotator solid

	ρ^{200}	V_{mol}	μ	$10^{12}\tau_{liq.}$(s)	$10^{12}\tau_{solid}$	E_a
	(g/c.c.)	(Å^3)	(D)	(at f.p.)		(kJ mol^{-1})
ClO_3F	1.945	77.95	0.025	3.9	30400	24.8
CH_3CCl_3[a]	1.041	119	1.78	11.0	12.4	4.6

[a] Reference 25.

density of ClO_3F (ρ = 1.945 g/c.c. at 200°K) in the liquid as compared to the substituted methane rotators ($\rho \sim 0.6$ to 1.04 at 220°K).[25] Perchloryl fluoride is also lower in molecular weight and smaller in size than many of the classical rotator solids. Any reorientation of the ClO_3F molecule will consequently involve considerable resistance from adjacent molecules in the lattice, which has been described as a primitive tetragonal unit cell.[33]

Garg *et al.* have proposed that defect diffusion leading to a cooperative relaxation of the ClO_3F molecules is the source of the high activation barrier.[4] Another possible mechanism for dielectric relaxation in amorphous solids is the β- or secondary process from localized regions where tunneling occurs.[34] These are loosely packed sites where limited rotational and translational motion of particles takes place at high temperatures. It has been stated that there is no exception to the universal occurrence of the β-process which also involves a wide distribution of relaxation times.[34,35] In the preceding context it is important to notice that the dielectric absorption of solid perchloryl fluoride fits a Debye curve (Figure 5). The low value of the Cole–Cole distribution parameter, $\alpha = 0.067$, reflects the very narrow symmetrical spread of relaxation times and activation energies about mean values. Molecular rotation, therefore, appears to be in an isotropic environment. Conductivity and microwave absorption measurements on ClO_3F also reveal a Debye relaxation process.[6,36] These results are in line with the dominance of a single relaxation process involving dipole reorientation in a rotator solid or plastic crystalline phase. Recent dielectric measurements on some almost spherical dipolar organic molecules revealed wide distributions of relaxation times for the α- and β-relaxation processes.[37]

If perchloryl fluoride behaved like a classical rotator solid it should exhibit fast relaxation as for guests in a clathrate hydrate.[11,38] ^{19}F-n.m.r. spin-lattice relaxation time measurements have shown the rotation of ClO_3F in the cavities of the clathrate at ca. 40°K.[39] Dielectric measurements on $ClO_3F \cdot 7\frac{2}{3}H_2O$, however, have failed to detect absorption from guest motion. It is likely that the low number density (N_1) of relaxing dipoles (μ) results in a very small dielectric dispersion as can be calculated from Equation (10). At 40°K $\Delta\varepsilon$(calc.) = 0.009

$$\Delta\varepsilon = 4\pi N_1 \mu^2 / 3kT \tag{10}$$

and $\varepsilon''_{max} = 0.0045$, which within the experimental error, is near the limit of resolution of the instruments. Other low polarity species such as iso-butane (μ = 0.132 D)[14] and *n*-propane (μ = 0.085 D)[14] possess $\Delta\varepsilon$ = 0.02 and 0.01, respectively, for molecular rotation in a clathrate hydrate at low temperatures (5–50°K) at audio and radio frequencies.[15]

One indication that a weak dielectric dispersion may exist for perchloryl fluoride clathrate hydrate at low temperatures ($\lesssim$ 120°K) comes from the temperature dependence of the dielectric permittivity ($d\varepsilon'/dT$). Above 150°K the rapid rise of the permittivity originates from the relaxation of the water molecules in the ice and clathrate samples (see Figure 6). If there is a contribution of the orientation polarization of ClO_3F to the dielectric permittivity, then $d\varepsilon'/dT$ of the clathrate should differ from that of ice. A look at Figure 6 suggests that below ca. 150°K

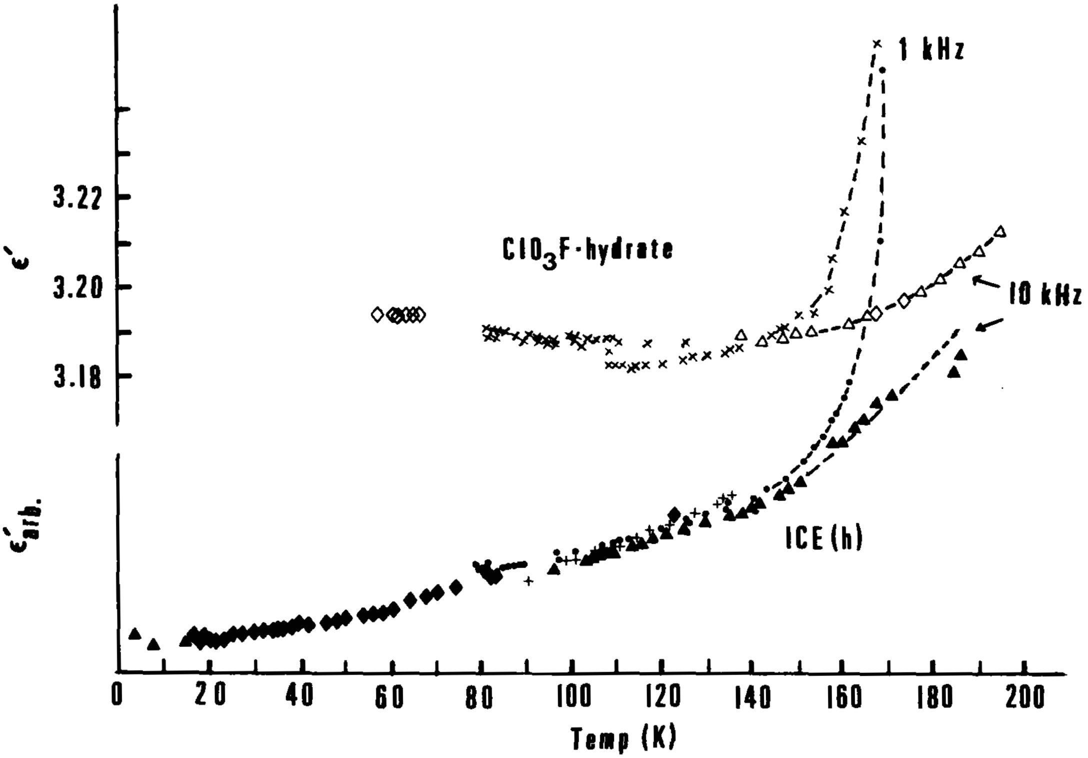

FIGURE 6 Plots of apparent dielectric permittivity versus temperature for hexagonal ice and perchloryl fluoride clathrate hydrate.

TABLE III

Polynomial fit ($\varepsilon' = A + BT + CT^2$) of the apparent dielectric permittivity versus temperature data of hexagonal ice and perchloryl fluoride clathrate hydrate.

Sample	Freq. (kHz)	Temp. Interval (K)	A	B	C
Ice #1	1	7–34	3.185	2.885×10^{-4}	4.613×10^{-6}
1	1	36–119	3.186	1.117×10^{-4}	1.278×10^{-6}
2	1	99–135	2.936	-5.381×10^{-4}	4.123×10^{-6}
2	10	96–151	2.899	-1.132×10^{-4}	1.844×10^{-6}
$ClO_3F \cdot \frac{23}{3} H_2O$[a]	10	4–77	2.510	-7.559×10^{-6}	1.295×10^{-6}
	1	80–125	3.139	-6.920×10^{-4}	3.038×10^{-6}
	1	108–229	2.419	-0.303	1.052×10^{-3}

[a] Sample #2.

the dielectric permittivity of the clathrate does vary somewhat differently with temperature than that of hexagonal ice. Polynomial fits of the ε' versus temperature data below ca. 120°K (see Table III) give good approximations to the expression derived by Gough[40] for hexagonal ice down to 4°K; $\varepsilon_\infty = 3.093 \pm 0.003 + (0.72 \pm 0.60)10^{-4}\,T + (0.11 \pm 0.2)^{-5}T^2$, but a poorer one for ClO_3F clathrate hydrate.

Distortion polarization is a main component of ε_∞ so that the lattice vibration modes may appreciably affect this parameter. It is expected that the ε_∞ will differ for ice and the clathrate hydrate, as does $d\varepsilon'/dT$ which may reflect the energy required for lattice vibration. Another point to consider is that the thermal expansivity of clathrate hydrates is greater than for hexagonal ice,[41] with the consequence that the apparent dielectric permittivity will vary as the sample thickness changes with temperature.

CONCLUSION

Solid perchloryl fluoride exhibits a Debye dielectric absorption (*e.g.*, $\alpha \approx 0.07$ at 95°K) associated with a higher than expected Arrhenius activation energy of 24.8 kJ mol^{-1} for such a small symmetric top molecule. The amplitude of the dielectric dispersion may be accounted for predominantly by the hindered rotation of the ClO_3F molecule around axes perpendicular to that of three-fold symmetry. This corresponds to an apparent electric dipole moment of ca. 0.025 D as compared to the gas phase value of 0.023 D at 298°K. Although perchloryl fluoride displays qualitatively many features of a rotator solid, it does not correspond quantitatively to the classical rotators, and in some respects is more like the intermediate class of rotators. The unusual dielectric behaviour of ClO_3F in its rotator phase may be related to the small free-volume and dense packing of the molecules.

Acknowledgments

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