of the face : $F = 0$ ($E \varepsilon a^2$). Thus the interface couples will be no greater than $\chi \leqslant 0$ ($E \varepsilon a$). For the gradients of the couples to be of the same order as the shear stresses, so that, from equation 1, $\sigma_{xy} - \sigma_{yx} = 0$ (σ_{xy}) $= 0$ (σ_{xx}), the difference of the shear stresses is of the magnitude of the stresses themselves :

$$\frac{\partial \chi}{\partial x} = 0 \left(Ea \frac{\partial \varepsilon}{\partial x} \right) = 0 \; (E \varepsilon)$$

$$\text{or} \quad \frac{\partial \varepsilon}{\partial x} = 0 \left(\frac{\varepsilon}{a} \right)$$

Such high gradients of strain would be expected only around singularities such as cracks and dislocations.

Interface couples may also be of importance in laminated plastics reinforced by fibre. If alternate plies are laid with the fibres perpendicular to each other, and the whole assembly pulled at $45°$ to both fibre directions, there will be couples acting on the interfaces between plies wherever fibres cross over each other. The sign of these interface couples changes from one side of a ply to the other, so that there would be large gradients of the interface couples and hence $\sigma_{xy} \neq \sigma_{yx}$.

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Molecular Orbitals and Vibrational Potential Function of Nitryl Fluoride

IN their work on the electronic structure of the N_2O_4 molecule, in which the N—N bond was found to be a π-only bond, Coulson and Duchesne[1] were led to consider the structure of a single NO_2 molecule. This can be represented using in particular two nitrogen lone-pair electrons, three π-electrons associated with the whole O—N—O framework and four σ-electrons. The aim of this communication is to see to what extent this picture may be used as a basis for the study of NO_2F in terms of molecular orbitals. In this molecule, contrary to what occurs in N_2O_4, N_2O_3 and N_2O_2, we should expect a normal σ-bond for NF. Such a bond should be obtained by promoting one of the lone-pair electrons to the π-orbital labelled Q by Coulson and Duchesne[1]. This gives rise to a total of four π-electrons, distributed in the P and Q molecular orbitals, whereas the remaining lone-pair σ-electron is coupled with the $2p_z$ electron of fluorine.

Let us now consider the effects which can be expected from this redistribution of electrons on the properties of the NO_2 group. As the Q orbital may be assumed to be $O \leftrightarrow O$ anti-bonding, the ONO angle has to be larger in NO_2F than in NO_2, whereas the corresponding bending force constant should be smaller. On the other hand, as the Q orbital is $N \leftrightarrow O$ non-bonding (or perhaps very slightly anti-bonding), the change in the NO bond-lengths ought to be insignificant, though the variation of the hybridization character at the nitrogen atom caused by the angle opening might give rise to a small bond shortening.

Table 1

Force constants	NO$_2$F	NO$_2$*	NF$_3$†
f_{NF}	4·3– 5·3		4·28–5·27
f_{NO}	11·0–11·8	10·42	
f_{ONO}	0·2– 0·5	1·099	
f_{FNO}	1·5– 1·6		

* From ref. 5.
† From values given in ref. 6.

The validity of this model must be tested, and a comparison with the vibrational potential function is valuable. (It is to be noted that. the molecular dimensions reported[2] for NO_2F are affected by the fact that the value for the ONO angle had to be assumed.)

In Table 1 are given the limits between which the force constants of NO_2F (expressed in 10^5 dynes/cm.), which is of C_{2v} symmetry[2][4], are found to vary when making reasonable assumptions of the values of the coupling constants. (The accuracy for the values of the interaction terms is too low to make any suggestion here. It is, however, fairly certain that $f_c(NO/NF)$ and $\gamma_c(NF/ONO)$ are respectively positive and negative.) The results have been deduced from a general potential function, introduced earlier by Duchesne[3]. The infra-red and Raman data have been taken from the work of Dodd, Rolfe and Woodward[4]. For comparison, the corresponding constants for NO_2 and NF_3 are also given in the table.

First, it is seen that the NF stretching constants are almost the same in NO_2F and NF_3, in agreement with our model. Secondly, on going from NO_2 to NO_2F a large weakening of the bending constant (about 65 per cent) and a small strengthening of the NO bonds (about 10 per cent) are observed. This also was to be expected on the basis of the general properties of the Q orbital, the anti-bonding character of which is now estimated. The extension of these results to the discussions of molecules such as NO_2Cl and NO_2Br is premature, due to lack of experimental data. It is to be hoped that the present work, which may be compared with Duchesne's work on the electronically excited molecules[3], may indicate a fruitful way for testing and evaluating the properties of the molecular orbitals.

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An Oxidation Reaction Highly Dependent on Pressure

THE rates of oxidation of metals in gases at high temperatures are frequently influenced by the pressure of the gas. The dependence on pressure, which has in some cases been theoretically explained[1], is gener-