THE PHOTOELECTRON SPECTRUM OF THIAZYL FLUORIDE

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The photoelectron spectrum has been observed using He 584 Å excitation. Assignments are made and compared with those for related molecules.

1. Introduction

Thiazyl fluoride, NSF, is isoelectronic with sulphur dioxide SO2. A comparison between the electronic structures of these molecules is of considerable theoretical interest since the bond stretching force constants are well represented by the very different valence-bond formulae N≡S−F and O=S=O. Work by Barrow et al. [1,2] on the electronic spectrum of NSF showed that the variations of the geometry on electronic excitation from the ground state are at variance with Walsh's rules [3]. It is suspected that in the corresponding SO2 transitions [4,p.605],

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which have not as yet been completely analysed, a similar discrepancy occurs. We have therefore compared the photoelectron (PE) spectra of NSF and SO2 to see what parallels can be drawn between the electronic structure of these molecules.

2. Results

The PE spectrum of NSF was obtained using a Perkin Elmer PS 16 spectrometer, the resolution of which was such that it just resolved two peaks of similar intensity separated by 20meV. The NSF was prepared by heating a sample of Hg(NSF2)2 in a copper vessel connected directly to the spectrometer. It was necessary to take this precaution, since NSF reacts

Fig. 1. The He 584 Å photoelectron spectrum of NSF.
Fig. 2. The second and third band systems of NSF on an expanded scale. The progressions indicated are: second system, (a) 000, 000, (b) 010, 000 and (c) 020, 000; third system, (d) ν1, 000 and ν1, 010, (e) ν1, 100 and ν1, 110 and (f) ν1, 200 and ν1, 210; (g) is a hot-band in the second system.

with pyrex to produce SO₂ - a serious contaminant which can mask the NSF spectrum. Traces of SO₂ in some spectra served as an internal calibrant. The PE spectrum of NSF consists of five well-defined band systems (figs. 1 and 2), of which three show considerable vibrational structure. The adiabatic ionisation energies associated with these bands are 11.49, 13.39, 13.78, 15.35, and ca. 16.3eV.

3. Assignments

The assignment of the bands to the states of the ion NSF⁺ was aided by an analysis of the vibrational structure, and a knowledge of ionisation potentials of related molecules [5]. The first band system observed at 11.49eV had little regular fine structure, and is assigned to ionisation to a 2A' state of the ion by analogy with the first band of the SO₂ spectrum, where ionisation is from the essentially non-bonding 4a₁ orbital, yielding a 2A'₁ state of SO₂⁺. In NSF the orbital involved is thought to be mainly a lone pair on the sulphur atom. The visible electronic transitions of NSF have been assigned to singlet and triplet excited states arising from (3a''→7a') one-electron excitations from this same orbital.

The vibrational analysis of the second and third band systems is a little uncertain, since the vibration frequencies of NSF⁺ are near multiples of one another. We have based our assignments on the expected pattern of relative intensities when two or more vibrations are simultaneously excited [4,p.145].

The first band in the second system is a weak band at 13.345eV. If this is assigned as the 0→0 transition, then there are serious difficulties in interpreting the intensity distribution of subsequent peaks, since the relative intensities of the first three bands would then imply very long progressions in each of two frequencies. We therefore assign the second band at 13.39eV as the 0→0 band, with subsequent peaks arising from up to two quanta in each of ν₂ ≈ 780 cm⁻¹ and ν₃ ≈ 460 cm⁻¹. Assignments, with estimated relative intensities compatible with the Franck-Condon principle, are given in table 1 and indicated in fig. 2. The weak band at 13.45eV is assigned to the hot-band 000→001 for the following reasons:

(i) the separation from the 0→0 band is equal to ν₃'' = 371 cm⁻¹ [2] within the errors of measurement;
(ii) the ratio of the populations of the 001 and 000 levels is ≈ 0.16 at room temperature, and
(iii) there is an approximate symmetry between the transition probabilities of 1→0 and 0→1 transitions.

The 0→0 transition of the third system is assigned to the band at 13.78 eV: this peak is too intense and too widely separated from the previous peaks to represent a continuation of the second system. In view of the uncertainties in the vibrational analysis, solutions to the problem are based on the expected pattern of relative intensities when two or more vibrations are simultaneously excited [4,p.145].

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Table 1

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Ionisation potential (eV)</th>
<th>Vibrational frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adia. vert. ν₁ ν₂ ν₃</td>
<td></td>
</tr>
<tr>
<td>7a'</td>
<td>11.49 11.98 - - -</td>
<td></td>
</tr>
<tr>
<td>6a'</td>
<td>13.39 13.53 - 780 460</td>
<td></td>
</tr>
<tr>
<td>2a''</td>
<td>13.78 13.9 1030 690 360</td>
<td></td>
</tr>
<tr>
<td>5a'</td>
<td>15.35 15.62 800 - -</td>
<td></td>
</tr>
<tr>
<td>1a''</td>
<td>ca. 16.3 ca. 16.6 - -</td>
<td></td>
</tr>
<tr>
<td>4a'</td>
<td>ca. 16.3 ca. 16.6 - -</td>
<td></td>
</tr>
</tbody>
</table>

a) Error limits on IP's = 0.02eV.
b) Error limits on vibration frequencies = ± 80 cm⁻¹.
of the intensities and spacing of the three subsequent peaks we are led to an analysis involving all three vibrational modes in which \( \nu_1, \nu_2 \) and \( \nu_3 \) are approximately in the ratio 3:2:1 being \( \nu_1 \approx 1030 \text{ cm}^{-1} \), \( \nu_2 \approx 690 \text{ cm}^{-1} \) and \( \nu_3 \approx 360 \text{ cm}^{-1} \). There is little intensity to transitions with \( \nu_3 > 1 \).

In both these systems the lengths of the progressions excited are appropriate to the changes in frequency from those of the neutral molecule: \( \nu_1 = 1372 \text{ cm}^{-1} \) (N=S stretch), \( \nu_2 = 640 \text{ cm}^{-1} \) (S-F stretch) and \( \nu_3 = 371 \text{ cm}^{-1} \) (bend) [6]. (We have calculated normal coordinates and these are essentially localised as indicated.) The two states of the ion are assigned to the two components of a \( ^2\Pi \) state of linear NSF+, as in SO₂. The \( ^2\Delta'' \) component arises from ionisation from the highest occupied \( a'' \) orbital, which is out-of-plane \( \pi \)-bonding between N and S, but weakly anti-bonding between S and F. This ionisation would be expected to lead to little change in the angle or in \( \nu_3 \), an increase in \( \nu_2 \), and a substantial decrease in \( \nu_1 \). For the \( ^2\Delta' \) state the ionisation will be from an in-plane \( a' \) orbital, antibonding between N and F, and a moderate increase in \( \nu_2 \) is expected. The effect of this ionisation on the stretching frequencies is harder to predict because of \( \sigma-\pi \) mixing. On the basis of the vibrational structure we therefore assign the second system to a \( ^2\Delta' \) state of NSF+, and the third system to the \( ^2\Delta'' \) state.

The fourth band system, with origin at 15.35 eV, consists of a long progression with an initial spacing of 800 cm\(^{-1}\) decreasing to 700 cm\(^{-1}\) after 8 intervals. Were this associated with excitation of \( \nu_2 \) we would except only a short progression, as in the second system where \( \nu_2 = 780 \text{ cm}^{-1} \). We therefore assign this progression to \( \nu_1 \) (NS stretch) with a very reduced frequency from that of the neutral molecule. By the use of the Franck-Condon principle the elongation of the NS bond is calculated to be about 0.17 Å, which corresponds to a change in NS bond length from that characteristic of a triple bond to that of a double bond. We interpret this as indicating ionisation from an \( a' \) orbital with strong NS sigma-bonding character.

On the basis of the IP's of other fluorine containing molecules the fifth band system is assigned to the two unresolved systems corresponding to removal of electrons from \( a' \) and \( a'' \) orbitals which are located mainly on the fluorine atom. We presume that the three remaining \( a' \) valence shell orbitals lie too deep to be detected with HeI radiation.

We therefore propose that the configuration of NSF is

\[
\text{KKKL}(1a')^2(2a')^2(3a')^2(4a')^2(1a'')^2
\]

\[
(5a')^2(2a'')^2(6a')^2(7a')^2.
\]

4. Discussion

Despite the very different force fields of O=O=S=O and N=S—F there is a remarkable similarity between their photoelectron spectra. The most marked differences are the shift of the ionisation potential of the sulphur "lone pair" \(-4a_1(12.29\text{eV})\) of SO₂ to \( 7a' \) (11.49 eV) of NSF — and the detection of \( 5a' \) of NSF. Molecular orbital calculations [7,8] suggest that the \( 2b_2 \) orbital of SO₂, corresponding to \( 5a' \) of NSF, is almost degenerate with \( 3a_1 \), and it now appears probable that the complex structure between 16 and 17 eV in the SO₂ spectrum represents ionisation from the

![Fig. 3. A correlation between ionisation energies of CO₂, SO₂, NSF and OCS. Orbital labels are appropriate to the valence shell.](image-url)
three orbitals 2b₂, 3a₁, and 1b₁. Superposition of the fourth and fifth band systems of the NSF spectrum would give a very similar vibrational structure to this SO₂ system. Fig.3. gives a correlation between the ionisation energies of CO₂, OCS (16 valence electrons), SO₂ and NSF (18 valence electrons). The 2π orbital of OCS must be formally correlated with 2a'' and 6a' of NSF. However, the first ionisation potentials of OCS and NSF are very similar in magnitude. McLean and Yoshimine [9] have shown that the 2π molecular orbital of OCS is largely a 3p sulphur orbital, but with some weak antibonding to the other atoms, and we suggest that 7a' of NSF has a similar character.

While this paper was in preparation a paper was published by Cowan et al. [10] on the photoelectron spectrum of NSF. Our interpretation differs from theirs in part, both with regard to vibrational assignments and assignments of electronic states. We consider that our assignments are in accord with the Franck-Condon principle, whereas theirs are at variance with this in some respects. We have also based our electronic assignments on comparison with related molecules, rather than on semi-empirical calculations, which have been shown to be unreliable for the IP's of sulphur-containing molecules such as OCS and CS₂ [11].

References