

# RECENT RESULTS ON THE VIBRATIONAL SPECTRA OF SOME INORGANIC COMPOUNDS

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During the past few years a considerable fraction of our research effort has been devoted to inorganic substances. This work has benefited greatly by the availability of two pieces of equipment:

- (i) a small grating infrared spectrometer capable of measurement down to about  $70\text{ cm}^{-1}$ ;
- (ii) apparatus for obtaining the Raman spectra of coloured compounds. This paper will describe some of the results of our studies.

## PCl<sub>5</sub> (Dr G. L. Carlson)

PCl<sub>5</sub> is an interesting substance because the structure of the solid is different from that of the vapour or liquid. It is well established that it is monomeric in the vapour and liquid states, and in solution in solvents of low dielectric constant, and has a trigonal bipyramid structure of symmetry D<sub>3h</sub>. In the crystal, however, it disproportionates to PCl<sub>4</sub><sup>+</sup> · PCl<sub>6</sub><sup>-</sup>. These ions have T<sub>d</sub> and O<sub>h</sub> symmetry respectively.

The Raman and infra-red spectra of the covalent form have been reported by others<sup>1</sup>. We have re-determined both, and have observed two of the low infra-red-active frequencies for the first time. This has led to changes in several of the assignments as shown in *Table 1*. The fundamentals for SbCl<sub>5</sub>, also re-determined by us, are included there for comparison.

If the vapour of PCl<sub>5</sub> is deposited on a cold window at  $\sim 90^\circ\text{K}$  in the

*Table 1.* Covalent PCl<sub>5</sub> and SbCl<sub>5</sub>

D <sub>3h</sub> species	Activity	No.	PCl <sub>5</sub>		SbCl <sub>5</sub>
			W. and B. <sup>1</sup>	This work	This work
a <sub>1</sub> '	R(p), —	1	394	393	356
		2	394	?	307
a <sub>2</sub> ''	—, i.r.	3	465	446	371
		4	[176]	299*	154
e'	R, i.r.	5	592	580	395
		6	335	273*	172
		7	100	100	(?)
e''	R, —	8	280	280	165

[ ] Calculated.

\* Differs from the assignment of Wilmshurst and Bernstein<sup>1</sup>.

Table 2. Observed frequencies for ionic  $\text{PCl}_6^-$ ,  $\text{PCl}_5\cdot\text{AlCl}_3$ ,  $\text{Na}\cdot\text{AlCl}_4$ , and  $\text{NO}\cdot\text{AlCl}_4$  (stronger bands only)

$\text{PCl}_4^+\cdot\text{PCl}_6^-$		$\text{PCl}_4^+\cdot\text{AlCl}_4^-$		$\text{Na}^+\cdot\text{AlCl}_4^-$		$\text{AlCl}_4^-$ (ref. 3)		$\text{NO}^+\cdot\text{AlCl}_4^-$		Assignment*		
Raman ( $\text{cm}^{-1}$ )	<i>I</i>	Raman ( $\text{cm}^{-1}$ )	<i>I</i>	Raman ( $\text{cm}^{-1}$ )	<i>I</i>	Raman ( $\text{cm}^{-1}$ )	<i>I</i>	Raman ( $\text{cm}^{-1}$ )	<i>I</i>	$\text{PCl}_6^-$	$\text{PCl}_4^+$	$\text{AlCl}_4^-$
Infrared ( $\text{cm}^{-1}$ )	<i>I</i>	Infrared ( $\text{cm}^{-1}$ )	<i>I</i>	Infrared ( $\text{cm}^{-1}$ )	<i>I</i>	Infrared ( $\text{cm}^{-1}$ )	<i>I</i>	Infrared ( $\text{cm}^{-1}$ )	<i>I</i>			
		<62	s									
150	2			147	3	146	2	136	3	4		
171	3	171	w	172	8	180	3 dp	182	3	5	2	2
251	4	251	m	252	8	253	s				4	4
281	4	282	w	352	3	347	vvw	349	20	2		1
360	10	449	vs	459	10	490	vs			1	3	3
458	3			495	0	658	vs	~495	br	3	1	3
658	1	584	m	656	0?	658	vs			?		
		653	s									
		'										
		'										
		'										

\* See Tables 3 and 4 for the meanings of the numbers.

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usual way, it gives the infrared spectrum of the covalent form. If the film is allowed to warm up, an irreversible change occurs in which certain bands disappear and new ones appear. The end result is the spectrum of the ionic solid,  $\text{PCl}_4^+ \cdot \text{PCl}_6^-$ . Gerding and Houtgraaf<sup>2</sup> have made an assignment for both ions, but had only the Raman spectrum available. We have repeated the Raman work, have added the infrared results, and have been able to separate the frequencies for the two ions in the following way. The complex  $\text{PCl}_5 \cdot \text{AlCl}_3$  is known to actually be  $\text{PCl}_4^+ \cdot \text{AlCl}_4^-$ . It was prepared and its spectrum measured. The Raman bands due to  $\text{AlCl}_4^-$  are known from work on  $\text{Na}^+ \cdot \text{AlCl}_4^-$  and  $\text{NO}^+ \cdot \text{AlCl}_4^-$  (ref. 3). The relevant spectral data for (a)  $\text{PCl}_4^+ \cdot \text{PCl}_6^-$ , (b)  $\text{PCl}_4^+ \cdot \text{AlCl}_4^-$ , and (c)  $\text{Na}^+ \cdot \text{AlCl}_4^-$  and  $\text{NO}^+ \cdot \text{AlCl}_4^-$  are assembled in Table 2. Bands found only in (a) must belong to  $\text{PCl}_6^-$ , those which are common to (a) and (b) must belong to  $\text{PCl}_4^+$ , and those common to (b) and (c) must be due to  $\text{AlCl}_4^-$ . Having attributed the frequencies to the proper ions, it is a simple matter to make the assignments for each individual ion. They are summarized in Tables 3 and 4. It is remarkable how well this works out.

 Table 3. Assignments of the fundamentals for  $\text{AlCl}_4^-$ ,  $\text{SiCl}_4$ , and  $\text{PCl}_4^+$  ( $T_d$  symmetry)

Species	Activity	No.	$\text{AlCl}_4^-$	$\text{SiCl}_4$ (ref. 4)	$\text{PCl}_4^+$
$a_1$	R(p), —	1	349	424	459
e	R, —	2	146	150	171
$f_2$	R, i.r.	3	490*	608	658
		4	180	221	252

\* Gerding and Houtgraaf<sup>2</sup> assigned this to  $575 \text{ cm}^{-1}$ .

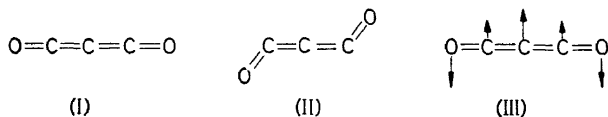
 Table 4. Assignments of the fundamentals for  $\text{PCl}_6^-$  ( $O_h$  symmetry)

Species	Activity	No.	( $\text{cm}^{-1}$ )
$a_{1g}$	R(p), —	1	360
$e_g$	R, —	2	281
$f_{1u}$	—, i.r.	3	449
		4	<62(?)
$f_{2g}$	R, —	5	150
$f_{2u}$	—, —	6	(?)

## CARBON SUBOXIDE (Dr W. G. Fateley)

This molecule presents one of the most interesting unsolved problems in molecular structure. In 1954, Long, Murfin, and Williams<sup>5</sup> published a re-determination of the infrared and Raman spectrum which they interpreted on the basis of a linear structure (I). Almost simultaneously Rix<sup>6</sup> published similar data which he claimed were incompatible with a linear molecule. Specifically, the infrared band contours were wrong. He proposed a bent *trans* structure (II). Electron diffraction did not really settle

the question<sup>7</sup>. Stoicheff<sup>8</sup> then measured the pure rotational Raman spectrum. If the molecule is linear, the line spacing would be  $\sim 0.56 \text{ cm}^{-1}$ , which would be easily resolved on his instrument. If it is non-linear the spacing would be  $\sim 0.28 \text{ cm}^{-1}$ , which would probably not be resolved. Actually an unresolved spectrum was obtained.



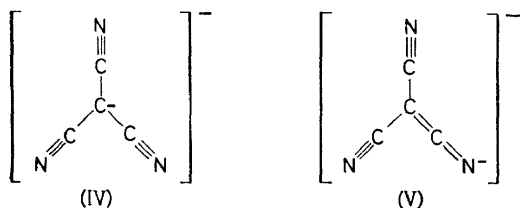
Stoicheff pointed out that this does not necessarily eliminate the linear structure. If the molecule were linear, but had a  $\pi_u$  fundamental which is sufficiently low to be well populated at room temperature ( $< 200 \text{ cm}^{-1}$ ), rotational transitions between the levels in this state would give the smaller  $0.28 \text{ cm}^{-1}$  spacing with considerable intensity.

This  $\pi_u$  fundamental should be very intense in the infrared spectrum, since it is due to the bending of the entire molecule as illustrated in (III). We have searched the far infrared spectrum for such a fundamental, covering the range  $70\text{--}300 \text{ cm}^{-1}$  with pressures of at least 200 mm (usually more), and with a path length of 7.5 m. Nothing was found. We conclude that there is no low-lying infrared-active fundamental in this range, and that the lowest one is  $550 \text{ cm}^{-1}$ . Thus Stoicheff's suggestion is not tenable, and the rotational Raman spectrum is incompatible with a linear structure.

We have also remeasured the entire infrared spectrum of  $\text{C}_3\text{O}_2$  on a Beckman IR-7 instrument, and have confirmed Rix's findings. Our somewhat better resolution has revealed a few more details, but he is correct in emphasizing that the infrared band contours do not fit a linear structure. At present we believe that his suggestion of a *trans* bent form (II) best fits the evidence.

### $\text{C}(\text{CN})_3\text{-ION}$ (Dr W. K. Baer)

This ion presents an interesting question: is it planar or pyramidal? If the extra negative charge resides mainly on the central carbon atom (IV),



One of 3 equivalent forms

this atom becomes isoelectronic with nitrogen. One would then expect the ion to be pyramidal. If the extra electron resides mainly on the three nitrogen atoms (V), the ion would be expected to be planar. One would predict

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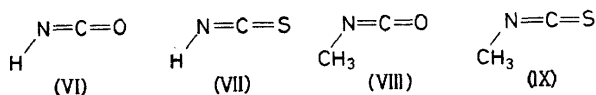
the latter because (V) is favoured by the higher electronegativity of nitrogen compared to carbon, and by the possibility of writing three equivalent structures.

The infrared and Raman spectra of  $\text{KC}(\text{CN})_3$  have been obtained as both solid and aqueous solution. They support the planar trigonal structure. Similar data were obtained for  $\text{ClC}(\text{CN})_3$ .

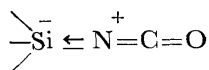
### $\text{Si}(\text{NCO})_4$ , $\text{Si}(\text{NCS})_4$ , $\text{P}(\text{NCO})_3$ , $\text{PO}(\text{NCO})_3$

(Drs G. L. Carlson, W. K. Baer)

It is known that the following compounds have bent skeletons, with an angle at the nitrogen atom of 125 to 150°:



On the other hand  $\text{Si}(\text{NCO})_4$  has been shown to be a tetrahedral molecule, with *linear*  $\text{Si}-\text{N}=\text{C}=\text{O}$  groups<sup>9</sup>.  $\text{H}_3\text{SiNCS}$  also has a linear skeleton<sup>10</sup>. This difference can be rationalized by postulating that in the latter compounds there is considerable double bonding between the nitrogen and the silicon. Presumably this involves the non-bonding pair of electrons on the nitrogen and an empty *3d* orbital on silicon. It can be represented schematically by



Formally this makes the nitrogen atom isoelectronic with carbon, and a linear configuration results. The double bonding does not occur when the  $-\text{NCO}$  or  $-\text{NCS}$  group is attached to H or C because the latter have no suitable *d* orbitals. Compounds (VI) to (IX) are therefore bent.

Further examples of this effect have now been established.  $\text{Si}(\text{NCS})_4$  has been re-examined and is tetrahedral.  $\text{P}(\text{NCO})_3$  and  $\text{PO}(\text{NCO})_3$  have been studied spectroscopically for the first time, and seem to be  $\text{C}_{3v}$  trigonal pyramids as expected. Unfortunately, this does not establish whether or not the  $\text{P}-\text{N}=\text{C}=\text{O}$  group is linear, for if they were bent symmetrically in the  $\sigma_v$  planes the symmetry would still be  $\text{C}_{3v}$ .

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