A Quantitative Approach to Host–Guest Interactions for Matrix-isolated Alkali-metal Salts of Hexafluoroanions and Perchlorates

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From matrix-isolation i.r. studies it is demonstrated that heavier alkali-metal salts of a number of hexafluoroanions can be vaporised as molecular species. In all cases there is some decomposition and this is particularly serious for the non-transition elements. The i.r. spectrum of $CsNbF_6$ in a range of matrix gases is reported in the Nb–F stretching region. It is found that for matrices where the host–guest interaction is expected to be weak (Ne, Ar) a characteristic doubling of ν_3 of the NbF_6^- ion is observed. This is interpreted as due to the presence of a tridentate (facial) interaction between the caesium ion and the NbF_6^- anion. For matrices where the host–guest interaction is expected to be stronger (CO, N_2) a characteristic triplet is observed and this is interpreted as due to a bidentate (edge) interaction between the caesium ion and the NbF_6^- ion. In an attempt to calibrate the host–guest interaction $CsClO_4$ is studied in a range of matrix gases. The separation between the 'terminal' stretching frequency and the 'bridge' stretching frequency is taken as a measure of the interaction between the $CsClO_4$ and the matrix. This leads to the following sequence in order of decreasing frequency separation: Ne > Ar > $O_2 \approx F_2$ > Kr > Xe > N_2 > CO. (Neon showing the greatest separation is assumed to have the smallest host–guest interaction.) When the above frequency separations for $CsClO_4$ are plotted against those for $CsNbF_6$ in the same matrix gases there is a close correlation between the two. Further, those *matrices in which a doublet behaviour is observed* for $CsNbF_6$ *are precisely the ones which interact weakly* in terms of the above sequence (Ne, Ar, O_2, F_2, Kr); *a triplet is found for matrices showing a stronger interaction* (CO, N_2). For xenon (and to a lesser extent krypton) both doublet and triplet forms are present. The spectrum of $CsNbF_6$ in a 1 : 1 mixture of argon and nitrogen is strikingly similar to that in xenon.

The study of molecules, ions, or fragments trapped in inert matrices has many advantages, in particular the ability to make spectroscopic measurements over an extended time-scale. The principal disadvantages are the loss of rotational information and the possible effect of the host matrix on the guest. For studies at low temperatures argon and nitrogen are two of the most frequently used matrix gases, which is perhaps surprising as nitrogen is known to co-ordinate to a variety of metal centres. Molecular beam experiments on van der Waals' molecules show analogies to matrix-isolation studies. It is therefore interesting to note that Leopold *et al.*[1] conjecture 'in principle there is no reason to expect an abrupt transition between 'covalent' and 'van der Waals' bonding as the donor molecule is varied.' They then go on to consider whether 'the van der Waals interaction may also be viewed in terms of a Lewis acid–base model.'

For metal atoms isolated in inert gas matrices there has recently been considerable interest in the case of Ni^0 where coexistence of $^3D_3$ and $^3F_4$ (separated by only about 200 cm^{-1} in energy) has been observed.[2] As Fortsmann and Kolb[3,†] point out the guest–host interaction varies with temperature because of increased vibrational motion, coupled with thermal expansion of the matrix. In the case of *molecules* both vibrational spectra and electronic spectra may be affected. The molecule may be considered to be immersed in a 'phonon bath.' In this connection it is important to remember the lowered symmetry in a matrix relative to a crystal.[4] Swanson and Jones[5] have probably carried out the most extensive studies of 'site structure and dynamics' for matrix-isolated molecules, including orientation effects. There is also an elegant paper by Horton-Mastin and Poliakoff[6] on the use of isotopically labelled $Cr(CO)_6$ as a probe of trapping sites. In addition to these 'cage' effects there is evidence that species such as $Cr(CO)_5$ can interact with an inert gas atom such as krypton.[7] For example bond energies in the range 10—40 kJ mol^{-1} have been suggested on the basis of calculation.[8]

Perutz[9] recently stated that there are 'no convincing cases in which molecular symmetry differs in gas and matrix phases.' This has also been discussed by Green and Ervin[10] who chose ozone as a test case to examine changes in geometry between gas and matrix. In their experiments it was shown that within the experimental accuracy the bond angle of ozone in Ar or Kr matrices is identical to that in the gaseous molecule.

A change of structure with matrix gas has been proposed for the molecule $CsUF_6$ between argon and nitrogen matrices.[11] This cannot be considered to be a difference from the gas phase as the bonding there is almost certainly polytopic[12] at high temperatures,‡ and no molecular beam studies have been carried out. It appeared to us that these results were of sufficient interest to warrant further experimental work. It also suggested that the shapes of 'high temperature' molecules might be influenced by their matrix environment, notably where the molecules could be regarded as having a high degree of ionic character and as 'highly co-ordinatively unsaturated.' The lattice energy of argon or nitrogen is of the order of 6 or 7 kJ mol^{-1}. Nonetheless there is the possibility that during the isolation process a particular configuration of the vibrating molecule may be frozen-in due to the nature of the matrix site or to specific interactions between the matrix and the host. A striking observation is that although $CsClO_3$ showed a tridentate interaction[13,14] between the anion and the cation in a

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[†] See also, M. G. Ruffolo and S. Ossicini, *J. Chem. Phys.*, 1985, **82**, 3988; 1985, **83**, 6145.

[‡] A polytopic bond 'has essentially the same energy when it connects atoms in very different positions.'[12]

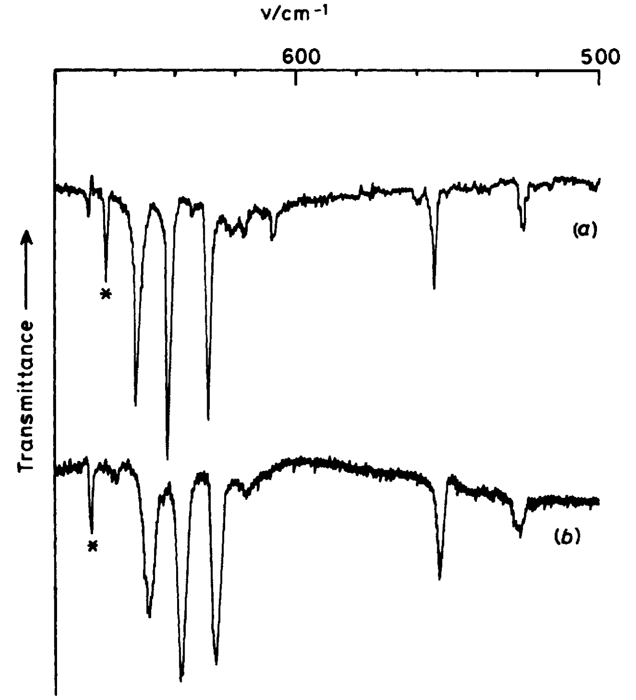


Figure 1. The i.r. spectrum of $CsNbF_6$ (500—680 cm^{-1}) isolated in (*a*) nitrogen, (*b*) carbon monoxide. * Matrix-isolated CO_2

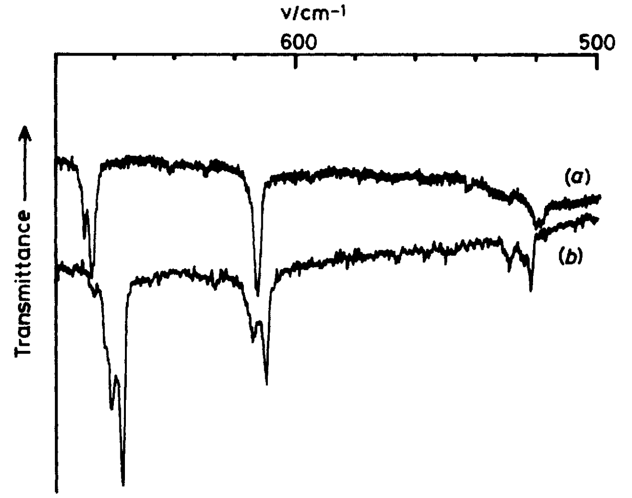


Figure 2. The i.r. spectrum of $CsNbF_6$ (500—680 cm^{-1}) isolated in (*a*) neon, (*b*) argon

nitrogen matrix, the corresponding perchlorate[15] showed a bidentate interaction.

Results and Discussion

(a) *Vaporisation of Alkali-metal Salts of Hexafluoroanions.*— The effect of an alkali-metal cation interacting with an octahedral MF_6^- species is to reduce the symmetry of that species below octahedral. An edge or bidentate interaction (such as that found for many tetrahedral oxoanions[16] and for AlF_4^- [17]) leads to

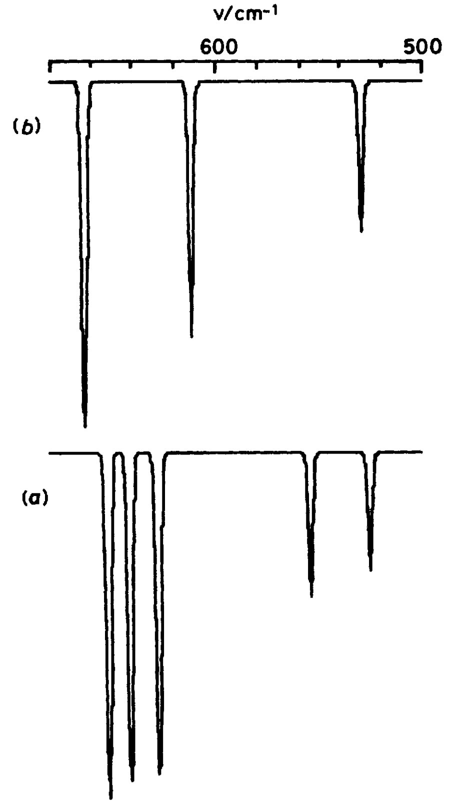
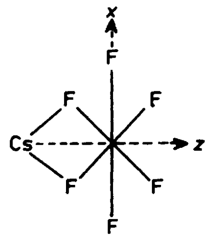


Figure 3. Calculated spectra for (*a*) bidentate, (*b*) tridentate interaction. Bridge force constants are of the order of 3 mdyn $Å^{-1}$ and terminal of the order of 4 mdyn $Å^{-1}$. Interaction force constants had values of the order of one tenth of the primary constants; 1 dyn = 10^{-5} N

a symmetry of C_{2v} or lower. The stretching modes are shown below. The b_1 component deriving from ν_3 (t_{1u}) (the i.r.-active

$$\begin{array}{ll} O_h & C_{2v} \\ t_{1u} \longrightarrow & a_1 + b_1 + b_2 \\ a_{1g} \longrightarrow & a_1 \\ e_g \longrightarrow & a_1 + b_2 \end{array}$$



stretching vibration of the original octahedron) is the axial stretch which, being pure 'terminal,' is expected to occur at the highest frequency of the resolved triplet. The other components deriving from ν_3 involve both terminal and bridging modes in the *yz* plane of the molecule; Figure 1(*a*) shows the resolution of ν_3 into a triplet for $CsNbF_6$ isolated in nitrogen. A similar effect is seen for carbon monoxide in Figure 1(*b*). In both cases ν_2 (e_g) is split into a doublet as expected.

The alternative† 'face' or tridentate interaction leads to C_{3v} symmetry (see below). In this case the ν_3 (t_{1u}) mode would be

$$\begin{array}{ll} O_h & C_{2v} \\ t_{1u} \longrightarrow & a_1 + e \\ a_{1g} \longrightarrow & a_1 \\ e_g \longrightarrow & e \end{array}$$

resolved into a doublet with an approximately 2:1 intensity ratio (e:a_1) depending on the degree of interaction with other adjacent vibrations of the same symmetry, while the original ν_2

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† The less likely apical interaction leads to C_{4v} symmetry which resolves t_{1u} into $a_1 + e$, but also resolves e_g into a doublet $a_1 + b_1$. The mode of symmetry b_1 is i.r. inactive.

Table 1. The i.r. spectra of some alkali-metal MF_6^- species isolated in low-temperature matrices (frequencies in cm^{-1}, range 500—680 cm^{-1})

Matrix[a]	ν_3 Components[b]			$\Delta\nu_3$	ν_2 Components[b]		Cation	Anion	Unassigned minor features
Ne (D)	667.4	612.4	—	55.0	520.0	—	Cs	NbF_6^-	
Ar (D)	658.0	610.5	—	47.5	523.1	—	Cs		
	(661.0)	(615.0)			(530.0)				
Ar (D)	664.0	612.5	—	51.5	530.0	—	Rb		
Ar (D)	667.1	612.0	—	55.1	528.1	—	K		
	(662.0)				(519.0)				
O_2 (D)	657.8	613.2	—	44.6	527.0	—	Cs		629
O_2 (D)	662.0	615.0	—	47.0	528.5	—	Rb		630.7, 677.0
Kr (D)	656.8	614.0	—	42.8	530.5	—	Cs		
(T)	659.0[c]	644.5	627.5	31.5					
Xe (D)	652.0[c]	612.5	—	39.5	526.5	—	Cs		
(T)	649.0	639.0	622.0	27.0	551.5	513.5			
CH_4 (D)	656.0	613.0	—	42.9	528.9	—	Cs		630, 626.2
CH_4 (D)	657.0	614.0	—	43.0	528.6	—	Rb		
N_2 (T)	651.8	641.3	628.1	23.7	554.3	525.3	Cs		
N_2 (T)	654.3	642.9	628.4	25.9	555.5	523.9	Rb		
N_2 (T)	657.8	645.2	628.0	29.8	555.2	519.5	K		
	(654.0)	(643.0)							
CO (T)	648.0	637.8	626.0	22.0	552.8	527.0	Cs		617
CO (T)	650.5	638.8	626.1	24.4	553.5	525.0	Rb		
Ar (D)	638.4	583.1	—	55.3	532.0	—	Cs	TaF_6^-	
	(641.0)[d]	(587.6)			(539.2)				
N_2 (T)	633.6	616.4	607.2	26.4	560.0	537.0	Cs	TaF_6^-	624.0, 590.4, 549.0
CO (T)	630.2	614.0	603.6	26.6	558.7	536.0	Cs	TaF_6^-	588.0
O_2 (D)	537.5	522.1	—	15.4			Cs	UF_6^-	617.0, ν_1?
	(541)[c]								
F_2[e] (D)	537.0	522.5	—	14.5			Cs	UF_6^-	618.5, ν_1?
	(542)[c]								
N_2[f] (T)	721.8	719.9	714.5	7.3			Cs	AsF_6^-	670.0, ν_1?

[a] D = Doublet, T = triplet. [b] Weaker features in parentheses. [c] Present as a shoulder on an adjacent band. [d] Complex absorption. [e] Weak band due to CF_4 observed at 630 cm^{-1} (ν_4). [f] Strong bands due to AsF_3 observed at 728 and 683 cm^{-1} (ν_1 and ν_3). Range 600—750 cm^{-1}.

(e_g) mode would formally appear as a *single* absorption. Figure 2(*a*) shows such behaviour for $CsNbF_6$ isolated in neon. (The apparent doubling of the main band is due to an inverse CO_2 band from air in the i.r. spectrometer.) A similar pattern occurs for argon and this is shown in Figure 2(*b*). (The slight doubling of all bands in this spectrum is assumed to be due to a matrix site effect). A doublet (from ν_3) was also observed in oxygen and a rather poor quality spectrum in methane suggested similar behaviour. For xenon both doublet- and triplet-type spectra were present in roughly equal amounts and we shall return to this point later. Finally krypton gave a rather poor quality spectrum indicating a principal doublet, but with some evidence of a small amount of the triplet. Figure 3 shows the corresponding calculated spectra for (*a*) a bidentate and (*b*) a tridentate interaction.

Table 1 summarises our matrix-isolation i.r. data on alkali-metal salts of hexafluoroniobate(v). As is usual in such experiments the bands of the anion were characterised by their cation sensitivity. This Table illustrates the increased splitting between the components of ν_3 on moving from caesium as the counter ion through rubidium to potassium. Similarly for the same cation the separation between the doublets follows the order Ne > Ar > Kr > Xe. No data are given for ν_1 in this Table since this region is partially obscured by niobium pentafluoride which is present as a decomposition product. As is normally the case the smaller the alkali-metal cation the greater the degree of decomposition observed. Data for ν_2 generally follow the behaviour expected by inspection of the more intense bands deriving from ν_3. Where ν_3 is split into a doublet, ν_2 is unsplit. Where ν_3 is split into a triplet, ν_2 is split into a doublet. It is also relevant that MoF_6 (isoelectronic with NbF_6^-) isolated in an argon matrix shows molybdenum isotope structure on a band centred at 737.7 cm^{-1} compared with a gas-phase value of 741 cm^{-1}, indicating very little perturbation of this species by the matrix environment.[18]

Similar results were obtained for salts of TaF_6^-, with rather less decomposition to the pentafluoride.

Because such studies are important in understanding vapour-phase transport we examined a number of other hexafluoroanion salts. We also hoped that species with lighter central atoms (PF_6^-) would show larger splittings. However this was not realized. We were able to vaporise $CsPF_6$ (with considerable decomposition to PF_5) but the observed splittings were less than those for NbF_6^-. Smaller splittings were recorded for AsF_6^- and SbF_6^-, also with extensive decomposition to the *lower* fluorides AsF_3 and SbF_3. These hexafluoroanion salts and their decomposition products are extremely reactive at the temperatures required for vaporisation. Even though we tried a variety of experimental techniques the results suggested that in all cases reaction with the containing material occurred. In the case of $CsAsF_6$, for example, heating in copper led exclusively to matrix isolation of AsF_3. Finally with $CsVF_6$ the only product observed in the matrix was VOF_3. The quality of the spectra in all these cases was poor and vibrational data are only reported for $CsAsF_6$.

(b) *Possible Reasons for Geometry Changes.*—The principal question arising from these observations is the reason for change in the i.r. spectrum between the extremes of neon and argon on the one hand (showing a doublet from ν_3) and nitrogen and carbon monoxide on the other (showing a triplet from ν_3). Carbon monoxide and nitrogen have similar structures[19] at the temperatures and pressures appropriate to a matrix-isolation experiment. (The structure of α-N_2 may be approximately described as based on a face-centred cubic close packing of the molecular centres. The molecular axes are oriented in such a way that the four molecules in the resulting primitive cell each lie along one of the cell diagonals.) The inert gases[20] and methane[21] crystallise in a face-centred cubic structure. The structures of solid oxygen[22] and fluorine[23] are similar. They differ from those of carbon monoxide and nitrogen in that the molecular axes exhibit close to parallel alignment leading to an approximately tetragonal unit cell.

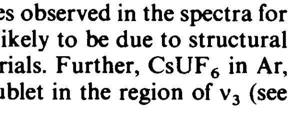
As we have shown ν_3 of NbF_6^- is resolved into a triplet for $CsNbF_6$ isolated in carbon monoxide and nitrogen (but not in oxygen). This behaviour is also present in xenon (together with the doublet pattern) but not in krypton to an appreciable extent, nor in argon or neon. In view of the similarities between the molecules N_2 and O_2 (apart from the paramagnetism of O_2) and the large differences in radii between neon and krypton,[24] for example, we felt that the changes observed in the spectra for the different matrix gases were unlikely to be due to structural differences between the pure materials. Further, $CsUF_6$ in Ar, O_2, and F_2 in all cases gave a doublet in the region of ν_3 (see Table 1).

A more likely explanation lies with the interactions between the molecule and the immediately surrounding matrix.[25] This is in many ways analogous to a solvation effect. Ritzhaupt *et al.* and Devlin and Consani[26] have looked at the solvation of $LiNO_3$ in argon matrices by doping-in various ligands. For example, they suggest that co-ordination of one ligand molecule such as tetrahydrofuran causes the frequency separation between the two components of the *e* mode (split due to bidentate co-ordination of the nitrate ion to the lithium cation) to decrease by 29 cm^{-1} compared to the separation in pure argon. More recently Jacox[27] has carried out a survey of the ground-state fundamentals of diatomics in the gas phase and in various matrices. Here it is noted that matrix shifts from the gas-phase value tend to increase in the order Ne < Ar < Kr < Xe < N_2.

We therefore decided to attempt to calibrate our matrix gases with respect to their 'donor ability' using $CsClO_4$ as a reference compound. The reason for the choice of $CsClO_4$ is outlined below.

The stretching modes of C_{2v} (edge or bidentate) $CsClO_4$ are shown below. The b_1 mode is essentially the antisymmetric

$$\begin{array}{ll} T_d & C_{2v} \\ a_1 \longrightarrow a_1 & \\ t_2 \longrightarrow a_1 + b_1 + b_2 & \end{array}$$



stretch of the bridge, while the b_2 is the corresponding terminal stretch. Thus the splitting of the triply degenerate ν_3 (t_2) mode of the initially regular tetrahedron will lead to a triplet with a higher frequency b_2 component (ν_t, terminal) and a lower frequency b_1 component (ν_b, bridge). (This has been confirmed by $^{16}O/^{18}O$ studies.[15]) The separation between these two may be taken as a measure of the interaction of the cation with the anion and hence of the degree of 'solvation.'

The $\Delta\nu_3 = \nu_t - \nu_b$ values for $CsClO_4$ in the various matrix gases fall in the order: Ne (163) > Ar (144) > O_2 (139) > Kr (136) > Xe (129) > CH_4 (126) > N_2 (117) > CO (113 cm^{-1}). Excellent spectra were obtained for nitrogen, krypton, and xenon; acceptable spectra for argon and methane. In the cases of neon, oxygen, and carbon monoxide the spectra were of poor quality. We therefore studied $KClO_4$ in these matrix gases and multiplied the observed $\Delta\nu_3$ value by 0.93 (a factor found from the ratio of the $\Delta\nu_3$ of $CsClO_4$ to that of $KClO_4$ in nitrogen[15] and xenon). The spectra of $KClO_4$ in these matrix gases were of good quality apart from some small multiplet splittings presumably due to site effects.

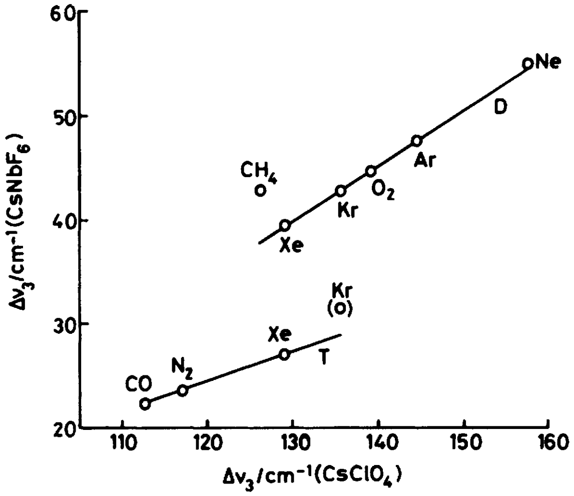


Figure 4. Plot of $\Delta\nu_3$ of $CsClO_4$ against $\Delta\nu_3$ of $CsNbF_6$ in various matrix gases; D = doublet, T = triplet, both referring to $CsNbF_6$

If we now plot $\Delta\nu_3$ for $CsClO_4$ in the various matrix gases against the corresponding doublet (D) separation or the separation between the highest and lowest frequency components of the triplet (T) for $CsNbF_6$, we obtain Figure 4.

This figure strongly suggests that our results can be interpreted in terms of the strength of the interaction between the $CsNbF_6$ molecule and the matrix gas. A 'solvating' matrix such as carbon monoxide or nitrogen leads to a triplet. Where there is little interaction as in neon or argon a doublet is observed.

Unfortunately in our experiments $KClO_4$ reacted with fluorine as a matrix gas and we were not able to obtain any useful results. However experiments on $CsUF_6$ isolated in N_2,[11] F_2, and O_2 (see Table 1) suggested that (in terms of the sequences found for $CsClO_4$ and $CsNbF_6$) fluorine would be approximately equivalent to oxygen. We also recall that in all these cases a characteristic doublet splitting was observed on ν_3. This would then lead to the sequence: Ne > Ar > $O_2 \approx F_2$ > Kr > Xe > N_2 > CO. Methane is anomalous in that for $CsClO_4$ it lies between Xe and N_2, while for $CsNbF_6$ it is equivalent to Kr.

Clearly the ordering found here is dependent on a variety of factors including both steric (packing) and electronic effects. It is interesting that a recent paper on gas-phase basicities gave the order:[28] N_2 < Xe < CH_4 < CO towards the proton.

(c) *Mixed-matrix Gases.*—It occurred to us that, as xenon showed *both* triplet (T) *and* doublet (D) splittings of ν_3, we might be able to mimic this behaviour by a suitable mixture of two matrix gases. Surprisingly many binary mixtures of the gases examined in this paper exhibit immiscibility in the phase diagram at temperatures appropriate to a matrix-isolation experiment. This applies to argon and carbon monoxide below 20 K. Even at 50 K only *ca.* 10 mole % of CO is soluble in argon.[29] Perhaps more unexpected is that below 23 K N_2 and O_2 are effectively immiscible.[30] Clearly the rapid cooling that occurs in most matrix-isolation experiments could lead to metastable conditions that would nonetheless be stable for the duration of an experiment. Fortuitously the phase diagram of the Ar–N_2 system[31] shows miscibility, with the presence of three distinct phases below 35 K: face-centred cubic for *ca.* 0—50 mole % N_2, hexagonal close-packed (β-N_2) for *ca.* 50—80% N_2, and α-N_2 above 80 mole % N_2. There is evidence of a temperature hysteresis in the argon-rich phase, while this is not true of the $\beta \longrightarrow \alpha$ transition which is reported to occur in less

Table 2. Values of Lennard-Jones parameters (ε/k and σ), dipole (μ), quadrupole (Q), and octapole (Ω) moments, and polarisabilities (α) for various matrix gases[a]

Matrix	ε/k (K)	σ/nm	$10^{18}\mu$/e.s.u.[b]	10^{26} Q/e.s.u.	10^{34} Ω/e.s.u.	10^{24} α/cm^3
Ne	47	2.72	0	0	0	0.396
Ar	141.2	3.336	0	0	0	1.642
O_2	128.8	3.362	0	-0.4	0	1.6
F_2			0	0.45 to 0.88	0	1.3
Kr	191.4	3.575	0	0	0	2.484
CH_4	159.7	3.706	0	0	*ca.* 2.4	2.6
Xe	257.4	3.924	0	0	0	4.06
N_2	103.0	3.613	0	*ca.* -1.4	0	1.7
CO			0.112	-2.0 to -2.5	0	1.97

[a] See, for example, G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, 'Intermolecular Forces,' Clarendon, Oxford, 1981; C. G. Gray and K. E. Gubbins, 'Theory of Molecular Fluids,' Clarendon, Oxford, 1984. [b] 1 e.s.u. = 3.38×10^{-12} C m.

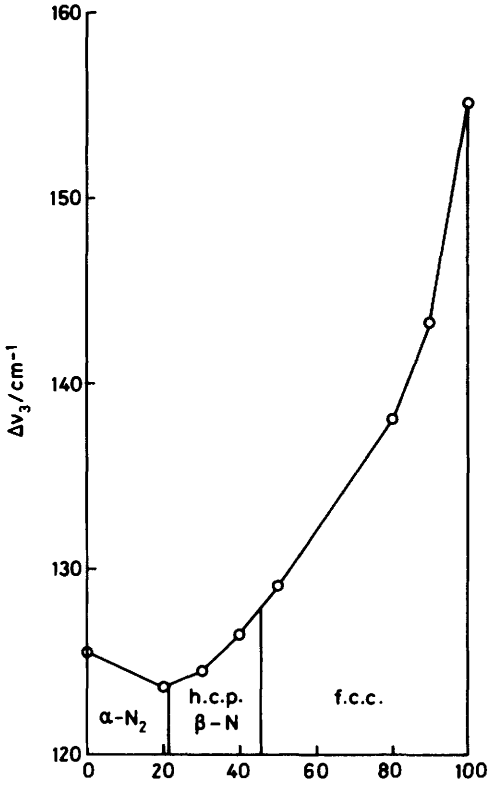


Figure 5. Plot of $\Delta\nu_3$ of $KClO_4$ isolated in the mixed-matrix gases argon-nitrogen for various mole ratios. h.c.p. = hexagonal close-packed, f.c.c. = face-centred cubic

than five seconds near to 35 K. It is also interesting to note that small amounts of nitrogen dissolved in argon have been reported[32] to result in a close-packed hexagonal phase near to the 'melting point.'

Figure 5 shows a plot of $\Delta\nu_3$ for $KClO_4$ isolated in a mixed Ar-N_2 matrix for various mole ratios. The behaviour is broadly a regular change between the extremes of pure argon and pure nitrogen. On an elementary 'solvation' approach we might regard a mixture of argon and nitrogen as approximating to xenon. Figure 6 compares the spectrum of $CsNbF_6$ in a 1:1 mole ratio of argon-nitrogen with that of the same compound in xenon. The two spectra are strikingly similar. (Note the 5-cm^{-1} scale shift between the two spectra.)

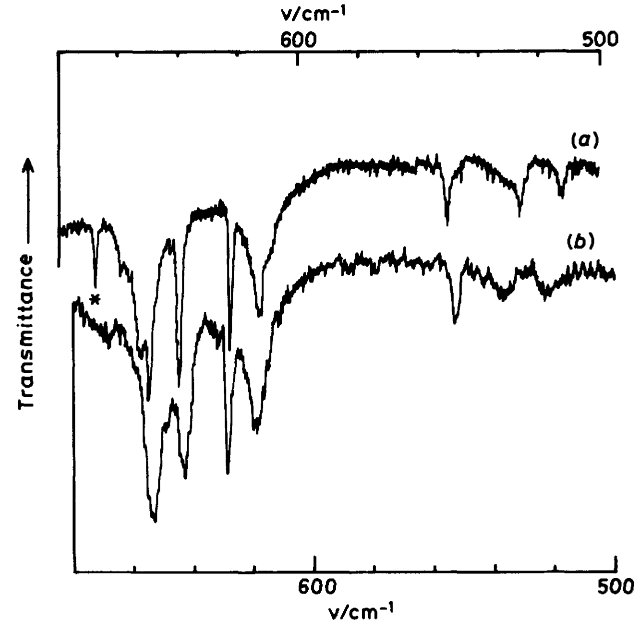


Figure 6. The i.r. spectrum of $CsNbF_6$ (500—680 cm^{-1}) isolated in (*a*) xenon, (*b*) a 1:1 mole ratio of argon-nitrogen. * Matrix-isolated CO_2

Cluster formation has been suggested to occur for dilute solutions of Ne, O_2, and CO in argon[33] for example. The only evidence for this behaviour from our experiments was the relative insensitivity of the frequencies of the triplet (T) and doublet (D) bands with respect to matrix gas composition in the argon-nitrogen system.

Conclusions

For all the matrix gases studied here the primary interaction will be between the alkali-metal cation and the anion, leading to a molecule with a substantial dipole moment. In Table 2 we give * values for ε/k and σ representing the energy and length parameters for an assumed Lennard-Jones potential.[34] This can explain the sequence Ne < Ar < Kr < Xe in terms of the interaction of the host with the guest. However the positions of nitrogen and carbon monoxide are quite anomalous. Carbon monoxide is the only species with a dipole, but this is small and we neglect dipole-dipole interactions. On the other hand there

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* We are indebted to Dr. Dominic Tildesley for the inclusion of this Table and the related discussion.

are likely to be substantial quadrupole (Q)–dipole interactions and we note the importance of these for both nitrogen and carbon monoxide. The values for oxygen and fluorine are considerably smaller but could still influence their positions in the sequence of matrix gases.

Apart from dispersion and permanent electrostatic interactions, induced effects may be important. Large central dipoles can induce dipoles in neighbouring molecules, the magnitude of these being dependent on the polarisability of these neighbours. Table 2 gives values of the scalar polarisabilities for matrix molecules. As with the Lennard–Jones approach there is a good correlation for the inert gases, which may be appropriately modified for nitrogen and carbon monoxide (and to a lesser extent fluorine and oxygen) by quadrupole–dipole interactions.

The remaining anomaly is that of methane. This polyatomic molecule has an octapole, but it also can hydrogen bond to the anions.

The detailed nature of the interaction between the host and the guest, or between the alkali-metal ion and the cation is an open question. Clearly in the case of MF_6^- species it will be related to the charge on the fluorine and hence the nature of the M–F bond. There is some evidence that non-transition element species will be less ionic than related compounds of the transition elements. This could explain the smaller splittings observed for species such as PF_6^- and AsF_6^- compared with NbF_6^-.

A recent crystal structure on an iron(III) porphyrin complex[35] 'illustrates the most significant factor—a coordinated SbF_6^- ion.' A similar metal–fluorine interaction is found[36] for a tungsten nitrosyl cation. However a study[37] of the electron deformation density in Li_2BeF_4 offers 'no support for the proposed Li–F covalent bonding.'

In matrices for which the host–guest interaction is weak our experiments on $CsNbF_6$ can be interpreted in terms of a C_{3v} distortion of the NbF_6^- ion *via* a facial interaction with the cation. Where the host–guest interaction is stronger a C_{2v} (or lower) distortion of the NbF_6^- ion occurs *via* an edge interaction with the cation. In a rather elementary way this can be thought of as an increasing interaction with the matrix leading to a weakening of the cation–anion interaction.

Experimental

$CsPF_6$ was precipitated by mixing aqueous solutions of CsCl (BDH) and KPF_6 (Aldrich) in stoicheiometric ratio. $CsAsF_6$ was prepared by treatment of Cs_3AsO_4 with anhydrous HF (BOC) followed by removal of volatiles in a vacuum. The tacky solid obtained was recrystallised from water. The Cs_3AsO_4 was made by adding a slight excess of CsOH (Aldrich) to a filtered solution of 'arsenic pentoxide' (BDH) in water, and allowing crystals to form. $CsSbF_6$ was obtained from the reaction of BrF_3 (BDH) with Sb_2O_3 (BDH) and CsF (Aldrich).[38]

$CsVF_6$ was formed when VF_5 and CsF were allowed to react in a small quantity of anhydrous HF.[39] The VF_5 was produced by placing vanadium foil (Johnson-Matthey) in a prefluorinated monel autoclave, adding F_2 (4 atm) (Matheson) and heating to 250 °C for 4 h. $CsNbF_6$ and $CsTaF_6$ were obtained as crystals by mixing stoicheiometric amounts of solutions of CsF and Nb (BDH) or Ta (BDH) metal in HF (40% w/v) (BDH).[40]

$CsUF_6$ was prepared by the reaction between a 1 : 1 mixture of CsF and UF_5 dissolved in HF (60% w/v) as described previously.[11]

The samples were characterised by their i.r. spectra in dry Nujol (PF_6^-, VF_6^-,[41] AsF_6^-, SbF_6^-,[42] NbF_6^-,[43] TaF_6^-[44]) or X-ray powder data (for $CsUF_6$[45]).

Caesium perchlorate was prepared by adding a slight excess of 70% perchloric acid (BDH AnalaR) to a solution of CsOH in water. The liquid was heated to redissolve the $CsClO_4$ precipitate, filtered, and allowed to cool, when crystals were obtained.

Research-grade matrix gases (Ne, Ar, Ke, Xe, N_2, O_2, CO, and CH_4) were obtained from BOC and used as supplied. F_2 was obtained from Matheson and was passed through a metal U-tube surrounded by ethyl acetate slush (−84 °C, to condense any HF) into an evacuated, prefluorinated stainless steel container.

Matrix isolation studies were carried out using two independent Displex units, the first (Air Products CS202) operating at a temperature of ~12 K and the second (Air Products DE204SL) capable of isolating samples in neon (estimated tip temperature 8—9 K). The second instrument was constructed from a modified cryopump system. Other general features of the apparatus have been described elsewhere.[46]

Vaporisation of $CsMF_6$ samples was carried out routinely from a monel holder fitted with a thermocouple (Philips TCI 15/10/2) and heated inductively using an RF coil. Earthing the outer sheath of the thermocouple prevented coupling with the RF and allowed an accurate measurement of the vaporisation temperature to be obtained. Typically $CsMF_6$ samples were found to sublime in the range 300—400 °C and deposition times were of the order of 1 h. Occasionally the monel cell was lined with metal foils (Cu, Ni, Pt). I.r. spectra (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 225 i.r. spectrometer calibrated using the characteristic bands of the trace impurities CO_2 and H_2O, almost invariably present in the matrices.

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