

The Vibrational Spectra of the Cyanide Ligand Revisited. Bridging Cyanides

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The $\nu(\text{CN})$ vibrational spectra of cyanide groups bridging two metal atoms present a confused picture. Factors relevant to the interpretation of the available data are reviewed. Some mechanisms for frequency change, relative to the corresponding terminal species, are made more quantitative than previously described, and others are highlighted for the first time. The kinematic effect is much less important than previously assumed. It seems that an effect responsible for the major part of the frequency increase upon bridging commonly observed is the cation electric field, together with concomitant relaxation (the IVSE model). However, a contribution may well come from the change in the σ bonding in the CN unit.

Introduction

Species containing cyanide bridges between two metal atoms are currently of extensive interest, mostly because of their occurrence in extended systems, which may be one, two or three dimensional.¹ These extended systems, of which Prussian blue is the prototype, exhibit remarkable magnetic, electrical, and optical properties.² The fundamental building block of such systems is the M–CN–M' bridge, and simple molecules containing these bridges are also the subject of contemporary study.³

Although the vibrational spectra of the CN groups in these compounds have commonly been reported, it cannot be said

that their contemporary interpretation gives rise to a coherent picture, a statement which is as true of simple compounds containing CN⁻ bridges as of those with extended networks. In this paper we are concerned with an improved understanding of the vibrational spectra of transition metal cyanide complexes containing such bridging CN groups. Because of the continuing interest in species containing bridging cyanide groups, there are considerable data available. Unfortunately, historically, these have afforded few insights, and now vibrational spectra may not be mentioned in reports on new materials. In this situation, it seems sensible to draw together the factors which may influence the spectra of bridging cyanide groups, and this is our current objective. We exclude from the present discussion bridging cyanides which form part of extended networks; although they are very important, there are additional factors to be considered for these, and they will be discussed separately. For species containing a single M–CN–M' bridge, it is a common observation that the vibrational frequency associated with the stretching mode

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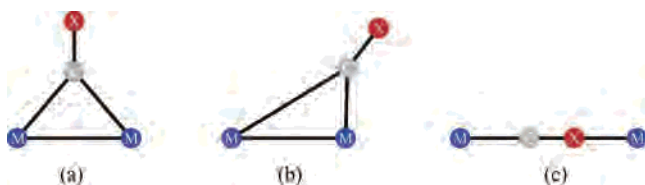


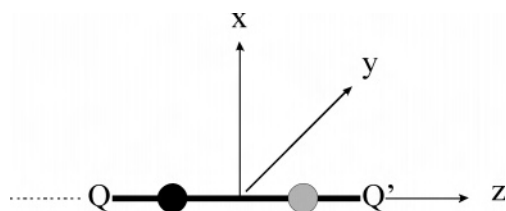
Figure 1. Schematic drawing of bridging CX ($X = O, N$) coordination, showing two limiting (a and c) forms and one intermediate (b). Form a is that predominantly adopted by CO, while form c is that commonly found for CN^- .

of the bridge cyanide is above that of the corresponding terminal cyanide,^{1b} although cases in which the frequency shift is in the opposite direction are well documented.⁴ Not surprisingly, there has been considerable discussion of these observations; while several explanations have been offered, they are largely post hoc and seem to have little predictive power of the direction of frequency shift and certainly not of its magnitude.⁵

The blue shift of $\nu(CN)$ is in contrast to that of carbonyl complexes (CO and CN^- are isoelectronic), where bridging is associated with a decrease of vibrational frequency. This is the more surprising in that the range of basic bridging structures adopted by the two ligands is very similar (Figure 1), consisting of two limiting (a and c) forms and one intermediate (b). Form a is that predominantly adopted by CO, while form c is that commonly found for CN^- .

However, for CO, the bridge frequency is always lower than the corresponding terminal frequency.⁷ The same statement is true for CN^- if the few compounds with bridge structures a⁸ or b⁹ are considered. It is the majority of CN^- compounds, with the bridge structure c, which are exceptional.¹⁰ Why are CN^- species with bridge structure c structure different? The clarification of this point would represent an important contribution toward the understanding of the cyanide ligand because the c form is present in many cyanide complexes and it represents the building block of those

Scheme 1



cyanide species which contain an extended metal–CN network. The object of the present work is to determine those factors which lead to frequency increases for structure c. With these established, it might, in the future, prove possible to develop a predictive model.

Experimental Section

All the calculations were performed with the Gaussian 03 package¹¹ The vibrational, geometrical, and charge data were obtained from the optimized structure which was obtained with the density functional method using Becke's three-parameter hybrid functional, the Lee–Yang–Parr correlation functional, and a 6-31+G(d,p) basis set. The geometry of the systems $Q-CX-Q'$ ($Q = H^+$, point charge, or noble gas atom; $X = C$ or O) were optimized in a standard orientation (see Scheme 1) with $C_{\infty v}$ geometry.

In the systems with $Q = H$, all the distances are optimized; in the systems with $Q =$ charge or noble gas, the $Q-C$ and $Q-X$ distances were maintained fixed (1.5 and 2.0 Å for point charges and 2.0 Å for noble gas atoms), and only the $C-X$ length was optimized. The MOs were examined by a Mulliken population analysis; the charges were calculated by NBO analysis.

The normal coordinate analyses were performed using the CLIMAX program.¹²

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- (5) Sometimes vibrational data are reported on species that contain both terminal and bridge CN groups, but separate CN absorptions are not reported in the infrared. In such cases, it is the terminal CN groups which appear to lack a signature. It seems that this has recently been explained by the finding that the infrared activity of $M-N-C$ groups is much higher than that of $M-C-N$.⁶ Bridge CNs contain the former, while terminal CNs have the latter. The occasional observation of no terminal CN signature could thus be explained because, in comparison with the bridge, they are weak and easy to overlook.
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Results and Discussion

(1) Is the Shift Really Blue? A phrase that is commonly found in the literature when CN bridging frequencies are discussed is “it is a general trend that there is a shift to higher frequency when a terminal CN group becomes bridging”. When such frequency differences are computed, it is important that the quantities involved are properly comparable. A systematic error in one of a pair may well invalidate the subsequent discussion. We believe that, unfortunately, such errors are not uncommon, and in the next sections, we detail our reasons.

(a) Frequency Center-of-Gravity Effect. When a molecule contains symmetry-related cyanide groups, it is the degeneracy-weighted mean frequency that should be used in a frequency difference calculation. When there is a unique CN group, as may be the case in a bridged species, then the frequency observed in the infrared *is* the correct frequency. On the other hand, where there is high symmetry, and octahedral $M(CN)_6$ anions are the obvious example, the frequency observed in the infrared *is not* the correct frequency. The degeneracy-weighted mean frequency, the “center-of-gravity frequency” should be used.¹³ For such octahedral anions, the frequency of the E_g Raman-active mode may be appropriate in that it seems to approximate the center-of-gravity frequency, and its use obviates possible problems resulting from combining infrared and Raman data. Unfortunately, Raman spectra and, therefore, the E_g mode frequency are commonly not available. The error introduced by use of the infrared active T_{1u} mode for the unbridged characteristic is significant; for the well-characterized anions $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_6]^{4-}$, for example, it is 6, 10, and 14 cm^{-1} , respectively.¹³ If an uncorrected infrared frequency is used as the “before bridging” value and a single bridge is formed, then “blue shift” is increased by such an additional amount (Figure 2a). Although outside the major scope of the present paper, another example concerns complexes with two trans CN groups, which give rise to a linear double-bridged species;¹⁴ an additional correction will be needed to give the correct center-of-gravity frequency change. (Figure 2b). So, in this example, both the two terminal groups and the two bridges give rise to two $\nu(CN)$ modes, the ν_{asym} (infrared-active only, if the systems are centrosymmetric) and the ν_{sym} (possibly Raman-active only). For each species, the center-of-gravity frequency ($1/2(\nu_{sym} + \nu_{asym})$) may differ significantly from the IR mode frequency ν_{asym} . When center-of-gravity data are to be obtained, Raman spectra will be needed if the symmetry is

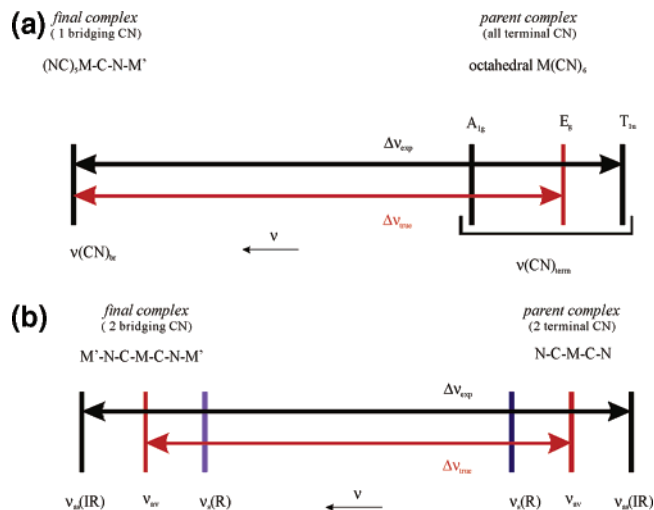


Figure 2. Schemes indicating how the use of the infrared data only can give rise to an incorrect value of the bridged/unbridged $\nu(CN)$ shift. Panel a refers to the octahedral $M(CN)_6$ model (the center-of-gravity of the frequencies is nearly co-incident with the E_g frequency); panel b refers to the linear double CN coordination model. In Figure 2b, for the bridged species, we have taken the symmetric mode to lie at a lower frequency than the asymmetric mode. While for bridging carbonyls such a pattern was never found, it seems to occur for some cyanides. See text for details.

centrosymmetric. However, infrared data are sufficient for low-symmetry cases.¹⁵

(b) Media Effect. $\nu(CN)$ frequencies recorded for dissolved species are both counterion and solvent sensitive.¹⁷ The data for reference molecules should therefore be obtained using the same conditions that were used for the target, although, even then, one makes the assumption that the target and reference molecules behave similarly under similar conditions. Although it would be possible to compile a list of “corrections”, this does not seem to be desirable. The fact that the same species can give rather different frequency data when in a crystalline form or in solution and when anhydrous crystals are compared with hydrated crystals is related.

(c) Zeroth-Order Frequency Effect. There is a further uncertainty connected with the interpretation of frequency data for bridging cyanide groups, even when a single terminal CN becomes a bridge CN: for example, $M-CN$ becomes $M-CN-M'$. What should be used as the frequency of the terminal CN? $\nu(MC-N)$ and $\nu(C-NM')$ are equally valid. The fact that the former is more experimentally accessible does not invalidate the claim of the latter to be included. The simplest solution would be to use $1/2[\nu(MC-N) + \nu(C-NM')]$; unfortunately, there are little relevant experimental data on $\nu(C-NM')$ frequencies. Those available are

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(15) Several examples of linear $MCN'M'NCM$ complexes show a single infrared band, easily assigned to the ν_{asym} .¹⁶ When the complexes are slightly bent, an additional weak band appears at lower frequency, which is undoubtedly ascribed to the ν_{sym} . So the center-of-gravity frequency is lower than the ν_{asym} , and the claimed blue shift should be accordingly reduced. Interestingly, these examples show that a point made in ref 13, which states that a totally symmetric mode may not be at the highest frequency, is also applicable to bridging cyanides.
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for species in which M' is a rather electropositive metal, such as Li, and these can scarcely be expected to be representative. Recent work has shed some light on this situation. A theoretical study of the species $MC-N$ and $MN-C$ ($M = Cu, Ag, Au$) found, for each, that the $MN-C$ has a frequency approximately 100 cm^{-1} below that of $MC-N$ (97, 96, and 111 cm^{-1} for $M = Cu, Ag, Au$, respectively).⁶ However, it is not known if these data are representative of other metals or how they vary with oxidation state or with the presence of other ligands. We shall return to this point below; our calculations suggest that these results may have some generality.

Although the sum $\frac{1}{2}[\nu(MC-N) + \nu(C-NM')]$ contains a variable about which little is known, this does not mean that it is without application. For two complexes between related M_aC-N and M_bC-N species and a common M' , the unknown variable can be eliminated to give

$$\frac{1}{2}[\nu(M_aC-N) - \nu(M_bC-N)]$$

as the expected frequency difference observed for the two final species, if they both behave in the same way (details of these and related calculations are reported in the Supporting Information). This equation focuses attention on the *differences* between two similar complexes, in contrast to the common approach which is concerned with the difference between $\nu(MC-N)$ and $\nu(MC-NM')$. Comparisons of complexes which differ only in whether they contain a C-N or N-C ligand as bridges are relevant but difficult to use in the present general discussion. For instance, it has been found that in a series of Fe- bonded to Cr, Mn or W complexes, the effect of CN isomerization can be up to 65 cm^{-1} .¹⁸ For some Cr-(CN)-Hg species there is evidence that the isomers have a frequency difference of ca. 100 cm^{-1} .¹⁹

(2) How is the Blue Shift to be Explained? In the previous sections, we have argued for caution before the acceptance of literature reports which claim a blue shift on a cyanide frequency. Some are red shifts. Nonetheless, there are many examples of bridging complexes where the CN frequency has undoubtedly moved to higher energy. In the following sections, we comment on the commonly invoked explanations.

(a) Kinematic Effect. Many years ago it was pointed out that the restraint associated with attachment of both bridging atoms to metals would cause an increase in frequency, and this suggestion was confirmed with an outline of normal coordinate calculations.²⁰ The phenomenon was termed the kinematic effect. Since that time it has become part of the accepted wisdom as the origin of the frequency increase commonly observed. In view of its importance, it is perhaps surprising that there seems to have been no systematic study

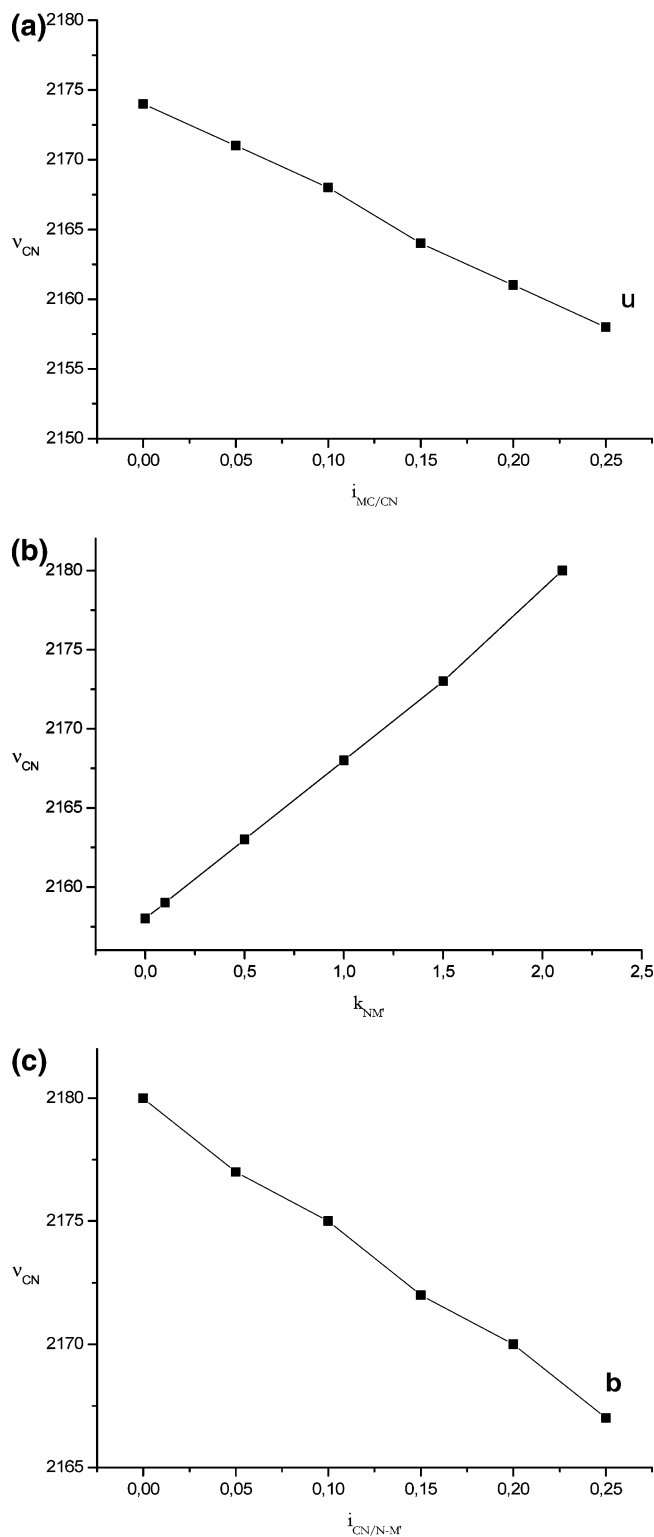


Figure 3. (a) Plot of $\nu(\text{CN})$ vs MC/CN coupling constant values in the $M-C-N$ model, when the $C-N$ force constant and the $M-C$ force constant have fixed values of 17.4 and $2.1\text{ mdynes \AA}^{-1}$, respectively. The frequency of 2158 cm^{-1} (**u**) is taken as the idealized value of the unbridged $C-N$ unit. (b) Plot of $\nu(\text{CN})$ vs the NM stretching force constant values in the $M-C-N-M'$ model, starting from point **u** in Figure 3a. (c) Plot of the $\nu(\text{CN})$ vs CN/NM' coupling constant values in the $M-C-N-M'$ model, starting from the final point in Figure 3b. The frequency value of 2167 cm^{-1} (**b**) is taken as the idealized value of the bridged $C-N$ unit.

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of the magnitude of the consequences of this effect. We are aware of only one study that considered the effect of the

variation of the M–C–N bond angle on the predicted frequency shifts (for a change to 160°, there was a drop of 5 cm⁻¹).²¹

The paper that suggests the existence of the kinematic effect also reported experimental data;⁶ the infrared shifts to higher frequency reported on going from MCN to MCNM were M = Au (98 cm⁻¹), Ag (24 cm⁻¹), Cu (47 cm⁻¹), Pd (73 cm⁻¹), Ni (48 cm⁻¹), and Hg (48 cm⁻¹). When numerical values were inserted into the detailed model, shifts of 20 and 40 cm⁻¹ were obtained, in reasonable agreement with some of the data but not with all of it.

In this situation, we decided to investigate the kinematic model further. Specifically, we carried out a series of normal coordinate calculations to assess the effect of changes in the various parameters involved. Because we are not attempting to fit spectra, we are not constrained by the requirement that the number of variables be fewer than the number of observables. We can therefore introduce variables one at a time and determine their relative significance. Because the system we studied is, apart from minor variants, a linear MCNM' one, there is no bond length dependence of our results. It turns out that there is also rather little (± 1 cm⁻¹) dependence of $\nu(\text{CN})$ on the mass of either metal atom (however, $\nu(\text{MC})$ and $\nu(\text{M}'\text{N})$ are very dependent on the values chosen). Discussions which attribute significant $\nu(\text{CN})$ frequency changes to metal atom mass differences are therefore not in accord with our findings. That which follows, then, relates simply to the variation of the kinematic effect with the variation of choice of force and interaction constants. Of these, two force constants were fixed throughout our calculations, $k(\text{CN})$ and $k(\text{MC})$. These were given values reported in the literature for the [Co(CN)₆]³⁻ ion,²² specifically, $k(\text{CN}) = 17.4$ and $k(\text{MC}) = 2.1$ (both in mdyne Å⁻¹). An interaction constant between the $\nu(\text{CN})$ and $\nu(\text{MC})$ was introduced and, following the literature, given a value of 0.25 Å mdyne⁻¹.²² Its effect (Figure 3a) was to lower $\nu(\text{CN})$: the value of 2158 cm⁻¹ (**u**) can be considered to be the frequency of the idealized unbridged M(CN) model.

Next, variations in two other constants were studied, the $k(\text{NM}')$, initially set equal to zero, was increased to, ultimately, the same value as $k(\text{MC})$; the variation of $\nu(\text{CN})$ with $k(\text{NM}')$ is shown in Figure 3b.

Finally, an interaction constant between $\nu(\text{CN})$ and $\nu(\text{NM}')$ was introduced and varied from zero to 0.25 Å mdyne⁻¹. The effect (Figure 3c) was to lower all values of $\nu(\text{CN})$, giving a limiting value of 2167 cm⁻¹ (**b**), which can be considered the value of the idealized bridged M–CN–M' model.

The resulting, calculated kinematic effect is the frequency difference between the points **b** and **u** and corresponds to an increase in frequency of 9 cm⁻¹. It is possible to increase this value by increasing the force constant and reducing the interaction constant associated with the N–M' bond. However, it is difficult to envision realistic combinations of force

and interaction constants which give a value for the kinematic effect which differs by more than a few wavenumbers from 9 cm⁻¹; the most probable changes would decrease it.

We have also studied the effects of a small displacement of the CN⁻ from the M–M' axis, of a symmetric twist of the group about this axis, and of a combined symmetric twist and displacement. A displacement and a symmetric twist each lowered $\nu(\text{CN})$ by rather little, about 2 cm⁻¹ for a 10° twist and for a 0.15 Å displacement. (All the data are collected in the Supporting Information.) In this study, we considered the case of a symmetric twist of the CN group; the case of an asymmetric twist has already been reported (a 20° twist gave a 5 cm⁻¹ frequency change).²¹

We conclude that the magnitude of the kinematic effect has been overestimated in the past and that it does not provide an explanation for more than a small part of the $\nu(\text{CN})$ frequency increase associated with some bridging cyanides. The fact that MCOM' invariably shows a decrease in frequency, not an increase, compared to MCO is also strong evidence that the kinematic effect is not dominant, since it should in no way be confined to CN complexes.

(b) Bonding Effects. Because there are changes in the electron-density distribution associated with bridge formation, it is to be expected that there will be consequent bond-strength and bond stretch frequency changes. Indeed, such effects have been widely invoked to explain the data reported. Frequency decreases have been associated with decreases in σ bonding and increases in π antibonding density and frequency increases with the opposite. The models have been reviewed.²³

Unfortunately, the discussions in the literature tend to focus on the examples in a particular report and so are lacking in generality, and even for those that appear to be general, later reports may not be in conformity. Further, some of the largest frequency changes reported are not in agreement with a bonding explanation. So, the large frequency increases on bridge formation to d¹⁰ cations do not agree well with the fact that they might be expected to lead to an enhanced population of CN antibonding π orbitals, with a resulting frequency decrease. In most systems, one can easily find sufficient number of π/σ bonding/antibonding orbitals to support almost any discussion. The key question is that of whether some general picture has emerged from the totality of such discussions. The clear answer is in the negative. In the present paper, we suggest that bonding effects make a contribution to the observed frequency increases, but we attribute the effect to σ bonding, not π . It is interesting that, despite the general attitude that π effects are dominant for the cyanide ligand, detailed calculations do not seem to support this view.²⁴

(c) Vibronic Effects. A mechanism that has been suggested for a *reduction* in frequency of a bridging CN group relative to the parent terminal involves vibronic coupling of the electronic ground state with a low-lying charge transfer

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(24) Hummel, P.; Winkler, J. R.; Gray, H. B. *J. Chem. Soc., Dalton Trans.* **2006**, 168.

state (which flattens the ground state potential energy surface and thereby reduces vibrational frequencies).²⁵

This is an ingenious suggestion, one which is potentially applicable to bridges between terminal metal atoms which can be in a facile charge-transfer relationship. However, as was recognized, there are species to which it does not seem applicable even within series to which it provides a rationalization. One possible explanation is that as the mechanism becomes less applicable, its effect may become that of reducing the magnitude of a blue shift rather than producing a red one. This model is still being explored. It seems well worth a more general study, but for this, near-ultraviolet spectra need to be routinely reported.

(d) Charge Effect, Revisited. In principle, a charge effect may arise from one or both of two factors: a change in the center-of-gravity of the frequencies (see above) dependent on (i) a change in charge on the metal atoms resulting from bridge formation and (ii) because the spread of $\nu(\text{CN})$ frequencies increases with charge. These points are well documented and may be illustrated by reference to the $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ anions, whose frequency centers-of-gravity are some 70 cm^{-1} apart.¹³ The relevant point is that usually an increase of positive charge (or decrease of negative charge) on a species increases the frequency. From a parent terminal to a product bridging complex, a charge redistribution has to be expected. Part of this redistribution arises from the fact that in a CN bridge the charge on the anion is shared by two metal atoms (point i). So, the effective charge on the metal may change and a charge effect-induced frequency shift on the center-of-gravity will result. A second charge-induced effect arises if infrared and not center-of-gravity frequency data are used as reference frequencies (point ii). This effect concerns the overall spread of the spectral bands. For $[\text{Fe}(\text{CN})_6]^{3-}$, the experimental spread is 18 cm^{-1} , but for $[\text{Fe}(\text{CN})_6]^{4-}$, it is 51 cm^{-1} . Because of the consequences of degeneracy, the effects of these frequency changes on the spectra are most evident for the A_{1g} mode, but the effects on the T_{1u} are real. So, if the infrared active T_{1u} mode was taken as reference point, there is an additional shift in reference of 4 cm^{-1} moving from $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ because of the different spectral spreads. Although not a large quantity itself, if combined with a center-of-gravity shift, a significant frequency displacement in either direction could result.

There is another charge effect. We have recently suggested that the $\nu(\text{CN})$ frequency of a terminal CN group is largely determined by the effective charge on the metal atom to which it is attached and the subsequent electron relaxation (the internal vibrational Stark effect (IVSE) model).¹³ Is the IVSE model applicable to bridging CN groups? To answer this question, we have carried out several sets of calculations which are an extension of those used to support the IVSE model for simple cyanides. In Table 1, we detail the results of the first set: frequency calculations for the systems CO, CN, and CN^- as free species, protonated at either end, and

Table 1. Calculated Frequency Changes on Protonation of CN^- , CN, and CO, along with Calculated Atomic Charges

species	qC	qX	qH	$\nu(\text{CX})$	shift	CX distance
$[\text{CN}]^-$	-0.228	-0.722		2124		1.184
HCN	0.073	-0.314	0.241	2203	+52	1.158
CNH	0.295	-0.759	0.464	2102	-22	1.176
$[\text{HCNH}]^+$	0.512	-0.387	H(C) 0.332 H(N) 0.542	2249	+125	1.140
CN	0.414	-0.414		2151		1.174
$[\text{HCN}]^+$	0.514	0.152	0.335	1917	-234	1.217
$[\text{CNH}]^+$	0.978	-0.530	0.552	2318	+167	1.141
$[\text{HCNH}]^{2+}$	0.872	0.022	H(C) 0.457 H(N) 0.650	1870	-281	1.215
CO	0.514	-0.514		2202		1.137
$[\text{HCO}]^+$	0.814	-0.154	0.340	2261	+59	1.113
$[\text{COH}]^+$	0.954	-0.651	0.698	1961	-241	1.165
$[\text{HCOH}]^{2+}$	1.130	-0.391	H(C) 0.466 H(O) 0.794	2076	-126	1.124

doubly protonated. Protonation is the simplest way of introducing a charge at either end of the CN unit in a way which mimics the charge effect of a transition metal.

Although the data in Table 1 show errors in the frequencies calculated for known species of up to $\sim 100\text{ cm}^{-1}$; however, the data given in the shift column should be more accurate. Relevant to the present work is the striking difference between HCNH^+ ($+125\text{ cm}^{-1}$ relative to CN^-) and HCOH^{2+} (-126 cm^{-1} relative to CO). This pattern mimics the qualitatively different behavior of CN^- and CO when two metal atoms are linearly bridged (vide supra); bridging causes the CN frequency to increase and the CO frequency to decrease. Further, the frequency changes calculated for CN^- are much greater than those that result from any other effect which has been suggested. Indeed, they potentially enable an understanding of the very largest frequency increases observed on bridge formation.²⁶ We note that the frequency changes upon formation of linear CO bridge systems are typically larger than those given in Table 1; however, Table 1 is limited to an initial charge on H of +1, the metals may have larger values, and as we will see, there are other relevant effects.

In the calculations just described, there are two inseparable effects. The effect of the proton charge and the effect on CX ($X = \text{O}, \text{N}^-$) of σ bonding between the hydrogens and the adjacent atom. To explore in more detail the applicability of the IVSE model to the vibrational spectra of cyanides, we have carried out a second set of calculations in which the hydrogen atoms in the above calculations were replaced by (variable) positive charges, which were placed at a fixed distances from the C and N atoms of CN^- and similarly from the C and O atoms of CO. It is, of course, impossible for us to cover the whole range of metal–ligand bond length patterns in the literature. We have therefore limited ourselves to those cases in which $\text{M}-\text{C}$ and $\text{M}'-\text{X}$ are equal and have values of either 1.5 or 2 \AA . These values were chosen because the latter is a typical experimental interatomic separation,

(26) The data for CN are very different from those for CN^- (the species HCNH^{2+} shows a frequency decrease compared with that of CN), so it is to be expected that if coordination to a metal introduces significant unpaired electron density into the C–N bonding, rather different $\nu(\text{CN})$ frequency patterns from those discussed in the text may well result.

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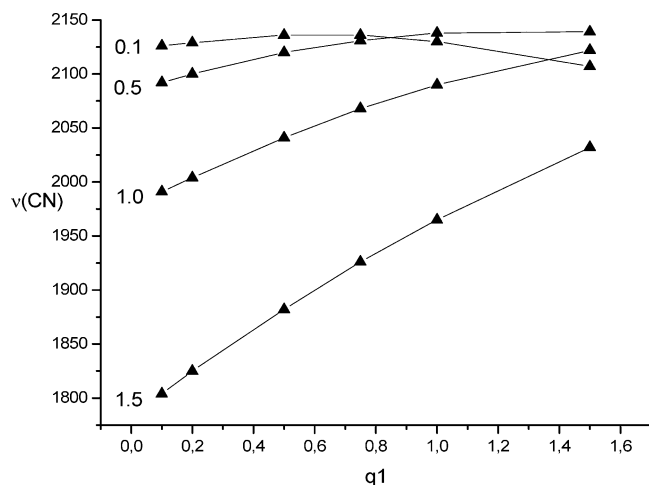


Figure 4. Plot of calculated $\nu(\text{CN})$ values vs the q_1 charge values in the system $q_2\text{-C-N-}q_1$ at a $q_i\text{-X}$ fixed distance of 2.0 Å. The fixed values of the q_2 charge are indicated at the left of each curve.

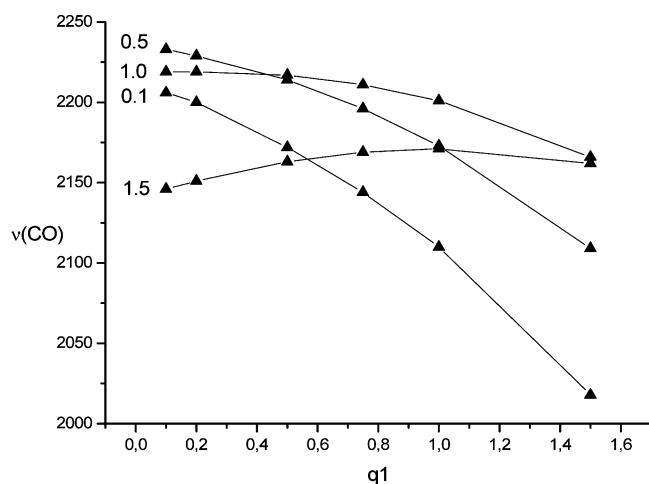


Figure 5. Plot of calculated $\nu(\text{CO})$ values vs the q_1 charge values in the system $q_2\text{-C-O-}q_1$ at a $q_i\text{-X}$ fixed distance of 2.0 Å. The fixed values of the q_2 charge are indicated at the left of each curve.

while the former is below any value observed experimentally and so, by interpolation, enables almost any observed interatomic distance to be covered by our work. In contrast to those described in the preceding paragraph, the charges in the present calculations do not change the basis set and so allow the electrostatic and orbital effects to be separated. The results of the calculations are shown in Figures 4 and 5, for CN^- and CO , respectively, when the M-C and M'-X distances are 2 Å (see Figures 1 and 2 in the Supporting Information for 1.5 Å distances). The two species behave very differently. For CO , a decrease in frequency is generally observed, while for CN^- , it is an increase. It seems clear that there is a charge effect and that the IVSE model is applicable to the systems.

(3) Blue Shift, An Overview. The above discussion points to two main contributors to the observed blue shifts: the effect of the cationic charges and metal–ligand σ bonding. Of these, the first is adequately covered by Figures 4 and 5. The second demands more detail, detail which will also give insights into the mechanism of the IVSE. For this, we consider the differences in orbital occupancies in C-N^- , H-C-N-H^+ , and $+ \cdots \text{C-N}^- \cdots +$. All of these differences

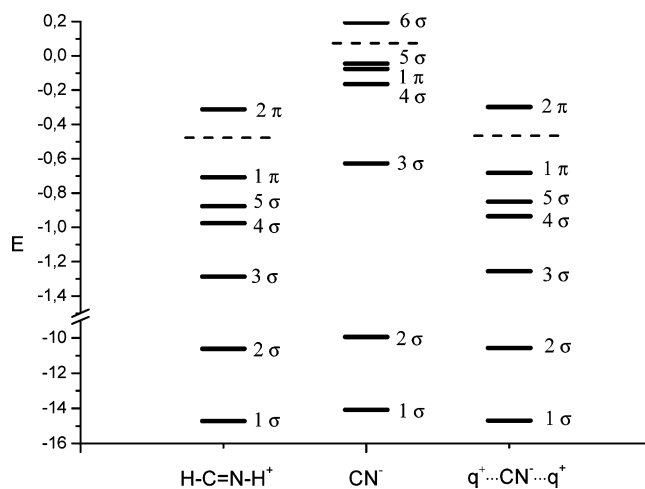


Figure 6. Energy (hartrees) plot of the molecular orbitals of H-C=N-H^+ , CN^- , and $q^+ \cdots \text{CN}^- \cdots q^+$.

concern the σ orbitals; for $+ \cdots \text{C-N}^- \cdots +$, we consider $+ \cdots \text{X}$ separations of 1 Å, akin to the H-X bond lengths in H-C-N-H^+ . There are five occupied σ orbitals in C-N^- . The two lowest of these are the 1s orbitals on C and N (that on N being lower). Then, a C-N σ bonding orbital and, finally and important for the present discussion, the two lone-pair orbitals, interestingly, separated in energy by the π bonding pair (Figure 6 and Table 3 Supporting Information). However, they are not quite localized lone-pair orbitals.

The lower energy is a, roughly, sp hybrid on N, pointing away from C, but with a considerable carbon s orbital component. That at higher energy is, roughly, a sp hybrid on C, pointing away from N, but with a significant nitrogen $2p_z$ component. In H-C=N-H^+ and $+ \cdots \text{C-N}^- \cdots +$, these two orbitals drop in energy by about the same amount in both species and now lie below the C-N π bonding orbitals. However, the origin of the changes are somewhat different. In H-C-N-H^+ , for just the C-N unit, the two atoms participate more equally in the interactions, and the orbitals are less localized. C-N bonding increases. In $+ \cdots \text{C-N}^- \cdots +$, in the lower orbital, electron density is moved onto the positive charges by involvement of $4s$ and $4p_z$, essentially, polarization functions. The inner functions have phases which assist this process, and so there is probably little contribution to C-N bonding. On the other hand, the upper orbital, which has little involvement with charge delocalization, has orbital phases which indicate significant C-N bonding (Figure 7).

In this discussion, we have ignored the H-X bonding density, in which the hydrogen 1s orbitals play the role of the $4s$ and $4p_z$ orbitals in $+ \cdots \text{X}$. That is, the outputs of the two calculations have more in common than is immediately evident, although in H-C-N-H^+ , both of the orbitals are involved in $\text{H} \cdots \text{X}$ bonding. In particular, in both of them one can see an increase in C-N bonding with a resultant increase in $\nu(\text{CN})$. We conclude that each mechanism can make a contribution to the observed frequency rise when the cyanide ligand becomes bridging. It is to be noted that the effective charge on a transition metal atom may be greater than unity and variable, so that it is appropriate to separate

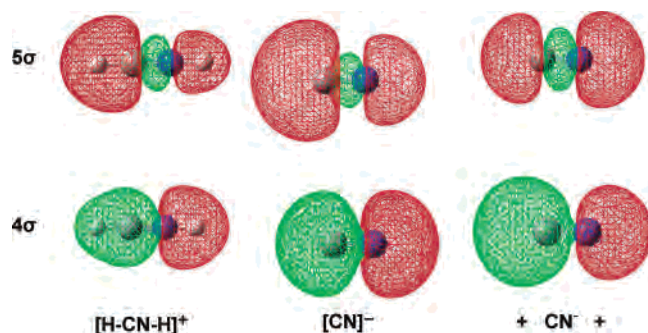


Figure 7. Shapes of the 4 σ and 5 σ molecular orbitals.

overlap effects from charge. Note that the effects that we have just discussed are electronic effects. As such, they are quite distinct from the purely mechanical effect which is the basis of the classical kinematic effect. The data which are the basis of the above discussion can be found in the orbital coefficients listed in Table 3, Supporting Information.

This may not complete the list of contributors to the observed blue shift. We have also carried out calculations in which noble gas atoms replaced the H atoms in $\text{H}-\text{C}-\text{N}-\text{H}^+$. These calculations are significant in that the atoms were given basis sets, although, obviously, bonding interactions are not of importance. Again, frequency changes were obtained; for CN^- and Ne, Ar, and Kr, there was an average increase of 31 cm^{-1} , with little difference between the three noble gases. For CO, the noble gases differed considerably. For Ne, there was a frequency increase of 12 cm^{-1} , while Ar and Kr showed *decreases* with that for Kr (104 cm^{-1}) being greater than that for Ar (43 cm^{-1}). All the data (Table 4 and Figure 3, SI) are reported in the Supporting Information. These results suggest that a contribution to the frequency changes observed in bridged complexes arises from differences in electron repulsion effects for CN^- and CO; the data obtained for Ar and Kr, both with complete d shells, mirror the experimental observations.

Conclusions

No clear picture has emerged in the literature which gives a general understanding of the vibrational spectra of bridging MCXM' groups, $\text{X} = \text{O}$ and N , even at the level of predicting whether there will be a frequency increase or decrease relative to the starting material. In this paper, we have attempted to draw together factors which we believe should be taken into consideration when one attempts to interpret $\nu(\text{CN})$ vibrational data of bridged complex species. That some of these seem not to have been previously highlighted may, in some part, account for the apparent lack of order in and the multiple explanations for the data available. The major conclusion, however, is that these earlier explanations point to relatively minor aspects of the problem. It seems clear that the frequency increases commonly observed upon CN bridge formation are more complicated phenomena than has been previously thought and are the result of several components. The contribution of the classical kinematic

effect is much less than is often assumed, although nonzero, and does not explain the different behavior of CN^- and CO. Two components which differ for these ligands are the effects of σ bonding and of the effects of the cation charge (the IVSE); their contributions seem to lead to frequency increases for the CN^- ligand but to decreases for the CO. Electron repulsion may make a contribution, but this is difficult to quantify with any certainty. It may be that π effects also exist, but we suspect that their role is relatively minor. Certainly, the contributions that we have listed, taken together, seem to give frequency changes which comfortably span the range of frequency increases observed. Although it is not the complete explanation, the IVSE appears to mirror the effects of other contributions and has the advantage of being applicable to both bridge and terminal CN ligands.

The way that data are presented may introduce artifacts; center-of-gravity data should be used when compiling frequency changes, for instance. The choice of $\nu(\text{MC}-\text{N})$ as the original frequency has limitations; there may be advantages in considering $\frac{1}{2}[\nu(\text{M}_a\text{C}-\text{N}) - \nu(\text{M}_b\text{C}-\text{N})]$. However, a problem is that much of the data in the literature are far from ideal for analysis, and this is a factor that must surely inhibit understanding. Spectroscopic data which have been obtained as part of a characterization process and which are reported as simple numbers are of limited value, particularly when it is not always clear whether a solution or a solid had been studied. Band profiles may indicate the existence of shoulders in addition to giving relative intensity data, and shoulders can be important. It is disturbing that the infrared signature of terminal CN groups can sometimes be missing from the data reported (the infrared intensity of bridging features being greater). What else is missing? Raman data are usually lacking, and unfortunately, the relevance of some of the items given above cannot fully be assessed without them. There is a clear need, then, for Raman spectral data to be obtained and reported wherever possible.

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Supporting Information Available: Calculation of the CN frequency consequent upon a uniform sideways displacement of the CN group (Table 1) or a symmetric twist of the CN group (Table 2), the energy of the molecular orbitals of the three species CN^- , HCNH , and $+\text{CN}-+$ (Table 3) and the coefficients of the atomic orbital components of the 4 σ and 5 σ molecular orbitals (Table 4), the values of the (CX) frequency in the system (noble gas)– $\text{C}-\text{X}$ –(noble gas) (Table 5 and Figure 3), the plot of calculated $\nu(\text{CN})$ or $\nu(\text{CO})$ values versus charge values in the system (charge)– $\text{C}-\text{N}$ –(charge) at a X –(charge) fixed distance of 1.5 \AA (Figures 1 and 2), and the calculation concerning the zeroth-order frequency effect (appendix).

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