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Abstract

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On the Change in Vibrational Frequencies upon Coordination and Adsorption of Nitriles through the Nitrogen Atom

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Experience shows (1–17) that, when nitrile molecules RCN are coordinated through the nitrogen atom and the group $R—C \equiv N \rightarrow M$ is formed (M being an atom of the metal complex-former), an increase is always observed in the frequency in the region of ~ 2250 cm^{-1}, usually assigned to the stretching vibrations of the $C \equiv N$ bonds and hereinafter denoted by ν(CN) (as shown (18) for free acetonitrile, in a vibration with frequency ν(CN) the CC and CN bonds change substantially, judging from the form of the vibration; therefore the notation ν(CN) is conventional).

The experimentally observed increase in ν(CN) has until now had no satisfactory theoretical explanation. In principle, it can be explained either by an increase in the force constant k_{CN} (“strengthening”) of the $C \equiv N$ bond, caused by redistribution of the electron cloud upon coordination, or by a change in other parameters affecting ν(CN), with k_{CN} remaining practically unchanged or even somewhat decreasing. Both explanations have their supporters (7,9,14,19). Of course, the simultaneous influence of both causes is also possible.

We attempted to clarify the reasons for the increase in ν(CN) by an approximate analysis of the influence of the most important factors on ν(CN). The increase in ν(CN) is always observed, independently of the nature of the nitrile; therefore, for the analysis the simplest linear model, $CH_3—C—N—M$, was chosen. The influence of coordination on the vibrational frequencies was determined at unchanged values of the force constants of the nitrile, taken equal to those of free acetonitrile, i.e., the force constants (strengths) of the $C—C$ and $C \equiv N$ bonds were assumed to remain unchanged from the outset. If the growth of ν(CN) were caused mainly by an increase in k_{CN}, then, with unchanged force constants of acetonitrile, the frequency ν(CN) would not increase, or would increase not as strongly as is observed experimentally (several tens of cm^{-1}). Otherwise, ν(CN) will increase even with an unchanged value of k_{CN}.

For simplicity, the CH_3 group was taken as a single vibrating mass. For free acetonitrile, taking according to (20) the interaction coefficient $k_{\mathrm{CC,CN}} = 0.8$ mdyn/Å, it is not difficult to calculate, from the frequencies $\nu(\mathrm{CN}) = 2267$ and $\nu(\mathrm{CC}) = 920$ cm^{-1} of gaseous acetonitrile (20), the remaining two force constants: $k_{\mathrm{CC}} = 4.96$ and $k_{\mathrm{CN}} = 18.85$ mdyn/Å. The approximate forms of the vi-

Fig. 1

Figure 1: Fig. 1

brations (Table 2), calculated for the adopted model of free CH_3CN, show that in the vibration with frequency 2267 cm^{-1} the CN and CC bonds change substantially; in the vibration with frequency 920 cm^{-1}, however, the CC bond changes mainly, while the CN bond is deformed almost eight times less. Taking the foregoing into account, the force constants of the model CH_3—C—N—M were taken to be (in mdyn/Å): $k_{CC} = 4.96$, $k_{CN} = 18.85$, $k_{CN,CC} = 0.8$, $k_{MN,CC} = 0$, k_{MN} was varied from 0.5 to 4.0, and $k_{MN,CN}$ was varied from 0 to 0.2 (here k_{MN} is the force constant of the MN bond, while $k_{MN,CC}$ and $k_{MN,CN}$ are interaction coefficients). The mass m of atom M was varied from 50 to 200. In its symmetry properties, the accepted linear model belongs to the point group $C_{\infty v}$ and has three frequencies $\nu_1(A)$, $\nu_2(A)$, and $\nu_3(A)$ of linear vibrations, which were calculated. The calculated frequencies are given in Table 1; the approximate forms of the vibrations, calculated for several cases, are presented in Table 2. Figure 1 gives the changes in the frequencies as a function of k_{MN}. The data obtained show: 1) a change in the mass m of the metal complex-former has practically no effect on the frequencies $\nu_1(A) = \nu(CN)$ and $\nu_2(A) = \nu(CC)$;

the frequency $\nu_3(A) = \nu(MN)$ decreases with increasing m. 2) A change in the coefficient $k_{MN,CN}$ from 0 to 0.2 mdyne/Å has little effect on $\nu_1(A)$ (within $\sim$ 10 cm^{-1}) and almost no effect on $\nu_2(A)$ and $\nu_3(A)$. 3) Coordination of a nitrile through the nitrogen atom leads to an increase in $\nu_1(A) = \nu(CN)$ and $\nu_2(A) = \nu(CC)$ even when the force constants of the nitrile are unchanged. In this case $\nu_1(A)$ and $\nu_2(A)$ increase almost linearly with increasing force constant (strength) of the MN bond, and the frequency values for the uncoordinated nitrile also fall on the straight line (Fig. 1). The frequency $\nu_3(A) = \nu(MN)$ increases with increasing k_{MN}, but not linearly. 4) In a vibration with frequency $\nu_1(A)$, all three bonds CC, CN, and MN change substantially.

Fig. 1. Change in vibrational frequencies as a function of the change in the force constant of the MN bond: *a*—change in $\nu_1(A) = \nu(CN)$ for the case $m = 200$ (for 1-4 the coefficient $k_{MN,CN} = 0$; 0.05; 0.1 and 0.2, respectively); *b*—change in $\nu_2(A) = \nu(CC)$ for the case $m = 200$; *c*—change in $\nu_3(A) = \nu(MN)$

In a vibration with frequency $\nu_2(A)$, mainly the CC and MN bonds are deformed; the CN bond changes less. In a vibration with frequency $\nu_3(A)$, predominantly the MN bond changes; as k_{MN} increases, the other two bonds also take an increasingly substantial part in the vibration with this frequency. Thus, none of the vibrations is localized on any one bond, so that the designations $\nu(CN)$, $\nu(CC)$, and $\nu(MN)$ are conventional and indicate the coordinate that changes most strongly. A change in the mass m has little effect on the forms of the vibrations.

On the basis of the results obtained, one may conclude that the observed increase in ν(CN) may also not be connected with an increase in the force constant (strength) of the CN bond. Moreover, if the observed increase in ν(CN) is small, then a decrease in k_{CN} is not excluded, as apparently occurs in complexes of divalent nickel with benzonitrile. It is further significant that the frequency ν(CC) also increases upon coordination.

Since the actual values of the force constants in nitrile complexes are unknown, and their calculation from experimentally found frequencies is inevitably connected with arbitrariness in the choice of some of the parameters, the following indirect method may be used for an approximate estimate of the force constant of the MN bond, at least for acetonitrile complexes. Obviously, if k_{CC} and k_{CN} remained unchanged upon coordination, then the change in ν(CC) and ν(CN) would approximately obey the regularities presented in Fig. 1; therefore, the values of k_{MN} estimated from the graphs in Fig. 1 from the experimentally found

Table 1

Calculated vibrational frequencies, cm^{-1}

m	k_{MN}	$k_{\mathrm{MN,CN}}$	ν_1 (A)	ν_2 (A)	ν_3 (A)	m	k_{MN}	$k_{\mathrm{MN,CN}}$	ν_1 (A)	ν_2 (A)	ν_3 (A)
50	0.5	0	2273.2	928.3	191.8	150	2.0	0.05	2287.3	955.7	309.8
100	0.5	0	2273.2	928.2	168.8	200	2.0	0.05	2287.3	955.5	301.3
150	0.5	0	2273.1	928.2	160.5	50	2.0	0.1	2285.0	957.3	370.0
200	0.5	0	2273.0	928.2	156.1	100	2.0	0.1	2284.8	955.8	326.2
50	1.0	0	2278.7	937.6	267.9	150	2.0	0.1	2284.8	955.3	310.3
100	1.0	0	2278.7	937.3	235.9	200	2.0	0.1	2284.8	955.1	301.8
150	1.0	0	2278.7	937.2	224.3	50	2.0	0.2	2279.8	956.5	371.0
200	1.0	0	2278.6	937.1	218.1	100	2.0	0.2	2279.7	955.0	327.1
50	2.0	0	2290.0	958.1	368.1	150	2.0	0.2	2279.7	954.5	311.1
100	2.0	0	2289.9	956.6	325.2	200	2.0	0.2	2279.7	954.3	302.6
150	2.0	0	2289.9	956.1	309.4	50	3.0	0.05	2299.3	980.6	439.7
200	2.0	0	2289.9	955.8	300.9	100	3.0	0.05	2299.0	977.0	388.5
50	3.0	0	2301.9	980.9	439.1	150	3.0	0.05	2298.9	975.9	369.8
100	3.0	0	2301.6	977.3	387.9	200	3.0	0.05	2298.8	975.3	359.7
150	3.0	0	2301.5	976.2	369.2	50	3.0	0.1	2296.7	980.2	440.3
200	3.0	0	2301.4	975.6	359.2	100	3.0	0.1	2296.4	976.6	389.0
50	4.0	0	2314.2	1005.8	491.8	150	3.0	0.1	2296.3	975.5	370.3
100	4.0	0	2313.6	999.3	435.8	200	3.0	0.1	2296.6	975.0	360.2
150	4.0	0	2313.4	997.3	415.2	50	3.0	0.2	2291.5	979.5	441.5
200	4.0	0	2313.3	996.3	404.1	100	3.0	0.2	2291.2	975.9	390.1
50	2.0	0.05	2287.5	957.7	369.5	150	3.0	0.2	2291.2	974.8	371.3
100	2.0	0.05	2287.4	956.2	325.7	200	3.0	0.2	2291.1	974.3	361.2

Table 2

Calculated forms of vibrations of acetonitrile and of the system CH_3 –C–N–M in natural coordinates q_{CC}, q_{CN}, and q_{NM} of changes in the lengths of the CC, CN, and NM bonds, respectively

	Frequency, cm^{-1}	q_{CC}	q_{CN}	q_{NM}
Acetonitrile	2267	−0.618	1	–
Acetonitrile	920	1	0.123	–
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 50,$	2290.0	−0.601	1	−0.452
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 50,$	958.1	1	0.094	−0.511
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 50,$	368.9	0.168	0.069	1
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 200,$	2289.9	−0.602	1	−0.447
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 200,$	955.8	1	0.095	−0.481
$k_{\mathrm{MN}} = 2.0, k_{\mathrm{MN,CN}} = 0, m = 200,$	300.9	0.157	0.067	1
$k_{\mathrm{MN}} = 4, k_{\mathrm{MN,CN}} = 0, m = 50,$	2314.2	−0.586	1	−0.471
$k_{\mathrm{MN}} = 4, k_{\mathrm{MN,CN}} = 0, m = 50,$	1005.8	1	0.056	−0.574
$k_{\mathrm{MN}} = 4, k_{\mathrm{MN,CN}} = 0, m = 50,$	491.8	0.404	0.149	1
$k_{\mathrm{MN}} = 4, k_{\mathrm{MN,CN}} = 0, m = 200,$	2313.3	−0.586	1	−0.461

	Frequency, cm^{-1}	q_{CC}	q_{CN}	q_{NM}
$k_{MN} = 4, k_{MN,CN} = 0, m = 200,$	996.3	1	0.063	−0.511
$k_{MN} = 4, k_{MN,CN} = 0, m = 200,$	404.1	0.352	0.141	1

the frequencies ν(CN) and ν(CC) must in this case be approximately the same. Complete agreement, of course, cannot be expected because of the approximate nature of the calculations on the basis of which the graphs in Fig. 1 were constructed. If the values of k_{MN} actually estimated from ν(CN) and ν(CC) prove not too···

Table 3

Force constants of the Pt–N bond, estimated from the frequencies ν(CN) and ν(CC)

Complex	ν(CN), cm^{-1} (^{11})	ν(CC), cm^{-1} (^{11})	k_{PtN}, mdyn/Å, from ν(CN)	k_{PtN}, mdyn/Å, from ν(CC)
cis-$[Pt(CH_3CN)_2Cl_2]$	2307*	957	~ 3.5	~ 2.05
cis-$[Pt(CH_3CN)_2Br_2]$	2314	953	~ 4.1	~ 1.85
trans-$[Pt(CH_3CN)_2Cl_2]$	2307	958	~ 3.5	~ 2.1

* Average of 2300 and 2314 cm^{-1}.

If they are different, then for k_{MN} one may approximately take the mean value. If, however, the estimated values of k_{MN} differ substantially, this means that upon coordination some change in k_{CN} and k_{CC} may have occurred, the greater the larger the difference between the estimated values of k_{MN}.

Let us illustrate what has been said using the example of acetonitrile complexes of divalent platinum. Using the experimentally found frequency values (^{11}), we estimate k_{PtN} from the curves of Fig. 1. We obtain different values (Table 3), with the values estimated from ν(CN) turning out to be higher than those estimated from ν(CC). The actual value of k_{PtN} evidently lies somewhere in between and, apparently, slightly exceeds 2 mdyn/Å.

The foregoing is evidently also valid for the case of adsorption of nitriles on any surfaces. If some of the atoms (ions) of the surfaces possess electron-acceptor properties (for example, have suitable "vacant" d-orbitals), then nitrile molecules can form bonds with these atoms through the nitrogen atom. Formally such a bond does not differ from the coordination bond considered above, and therefore the change in vibrational frequencies will be the same as upon coordination. Depending on the strength of binding of the nitrile on the surface, the increase in ν(CN) will be different: the larger the rise in ν(CN), the larger, other conditions being equal, the force constant (strength) of the nitrogen—surface-atom bond. For the particular case of acetonitrile, from the values of ν(CN) and ν(CC) one can, with the aid of the curves in Fig. 1, *a* and *b*, approximately estimate this force constant and the character of the change in the force field of the nitrile. If, however, upon adsorption of nitriles (at least aliphatic ones) ν(CN) does not increase, then with high probability one may conclude that the bond of the nitriles with the surface atoms is effected not through the nitrogen atom, but in some other way.

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