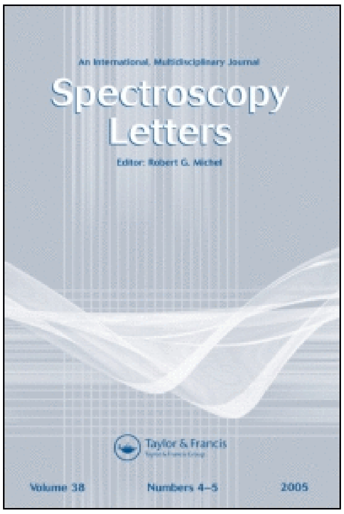

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Kristiansson, O.(1999) 'FT-IR Investigation of Acetonitrile-D_3-Cation Interactions', Spectroscopy Letters, 32: 5, 783 — 792

To link to this Article: DOI: 10.1080/00387019909350026

URL: http://dx.doi.org/10.1080/00387019909350026

SPECTROSCOPY LETTERS, 32(5), 783–792 (1999)

FT-IR INVESTIGATION OF ACETONITRILE-D_3-CATION INTERACTIONS

Keywords: FT-IR spectroscopy, CD_3CN, CN stretching vibration, cations

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ABSTRACT

The adduct formation between CD_3CN and the Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, Cu^+, Cu^{2+}, Zn^{2+}, Au^+, Ag^+, Cd^{2+}, Hg^{2+} and Tl^{3+} cations has been investigated by FTIR spectroscopy. The ν_2 vibrational mode, mainly consisting of the CN stretching vibration, was studied. Upon adduct formation with a Lewis acid this band shifted to higher frequencies relative to that of pure CD_3CN. In spite of the widely varying electronic configurations of the cations studied, this frequency shift was found to be approximately proportional to the polarizing power of the cation, measured as the charge to squared radius ratio, suggesting that the cation-acetonitrile interaction is of mainly electrostatic nature. No evidence of π back-donation was detected.

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INTRODUCTION

An interesting feature of the solvent properties of acetonitrile is its apparent special affinity for the univalent coinage metals. For example, the equilibrium constants for the disproportionation reaction 2 $Cu^+ = Cu^{2+} + Cu^0$ in the solvents water [1], dimethyl sulfoxide [2] and acetonitrile [3] are 10^6, 2 and 10^{-21} M^{-1}, respectively. Transfer thermodynamic measurements from water to acetonitrile for the Ag^+ and Cu^+ ions show particularly low ΔH_{tr}^0 values, indicating a notably strong solvation of these soft cations in acetonitrile.[4] It is also noteworthy that the N-Cu^+ and N-Cu^{2+} distances are identical (1.99 Å) in acetonitrile as determined by EXAFS spectroscopy.[5] It might be suggested that the strong solvation of soft metal ions such as Cu^+ and Ag^+ is an effect of $d\pi$ - $p\pi$ bonds formed by a back-donation of electron density from the T_{2g} level of the cation to the π^* orbitals of the CN group.

Acetonitrile has an intense vibrational absorption band centered at 2253 cm^{-1}. This vibrational mode consists mainly of the CN stretching vibration but also contain other contributions, in particular the C-C stretching vibration. This band provides a convenient probe for solute-solvent interactions. Upon adduct formation with a Lewis acid this band shifted to higher wavenumbers. This increase in frequency has by normal coordinate analysis been shown to result from an increase of the force constant of the CN bond.[6] The coupling of the adduct bond with the CN bond causes only a minor increase of the CN stretching frequency. The effect of several cations upon this mode has been investigated. An increased stretching frequency is always observed.[7-10] The interpretation of the spectra is however somewhat complicated by a combination band at 2293 cm^{-1} with an enhanced intensity due to Fermi resonance. For CD_3CN this band is absent which makes the deuterated analog preferable for detailed studies.[11]

The aim of the present paper is to present CN stretching frequencies of adducts between CD_3CN and a number of cations with widely different electronic configurations, ranging from typically soft, such as Au^+, to typically hard cations with low polarizabilities. Possibly, this will enable us to separate various bonding contributions in the adducts. The trifluoromethanesulfonate (TFMS) anion has been chosen as counterion due to its low tendency to form contact ion pairs.

EXPERIMENTAL

CD_3CN (99%) was purchased from Merck and used with no further purification. For all cations, the trifluoromethanesulfonate (TFMS) counterion was used. The TFMS salts were prepared by adding anhydrous trifluoromethanesulfonic acid to the metal oxides, hydroxides or carbonates. The salts were then dried under reduced pressure at 120 °C for prolonged periods. The Cu(TFMS) salt was prepared by refluxing $Cu(TFMS)_2$ and excess Cu(s) in CD_3CN at 120 °C. The Ag(TFMS) salt was purchased from Fluka Chemie AG. The salt concentrations were 0.1 mol dm^{-3} if solubility permitted, otherwise saturated solutions were used.

Spectra were recorded on a Perkin-Elmer 1760 X FT-IR spectrometer. A resolution of 4 cm^{-1} was chosen. The solutions were contained in a cell with CaF_2-windows and a Teflon spacer. The path length was 0.0504 mm as determined interferometrically. The cell was thermostatically controlled by circulating water through the mounting plates of the cell. The temperature used in the experiments was 20.0 °C. Spectra evaluation was done with SpectraCalc™.

RESULTS AND DISCUSSION

Pure CD_3CN possesses a high intensity absorption band centered at 2261 cm^{-1}. The main contribution to this normal mode is the CN stretching vibration. When electrolytes are dissolved in the liquid this band splits into two components. One band remains at the same position as the band in pure acetonitrile while the other is shifted to higher frequencies. The frequency of this band is independent of the nature of the anion and is a result of the CD_3CN - cation interaction only. A number of cations with widely varying electronic configurations has been investigated. Band maxima and widths of the cation-induced bands are given in *Table 1*. The band profiles are well described with a mixed Gaussian/Lorenzian band shape. The band widths and frequency shifts are apparently uncorrelated.

The frequency shifts of the cation - CD_3CN adducts relative that of pure CD_3CN, $\Delta\nu$, are plotted versus the polarizing power of the cation, expressed as the charge to squared radius ratio, Z/r^2 , in *Figure 1*. The selection of an adequate set of internally consistent cation radii is not without difficulties. Cation-acetonitrile solution distances would be ideally suited but, unfortunately, diffraction studies are relatively scarce on these systems and only few distances are determined. [5,12-14] The cation radii used in Figure 1 are taken from Shannon [15] and Dean [16]. The frequency shifts are seen to be approximately proportional to Z/r^2. In particular, no apparent division between the cations is observed between so called "hard" cations with low polarizabilities and "soft" where $d\pi$ - $p\pi$ bonding could be envisaged. Only small effects, or none, on the CN stretching vibration by the Ag^+, Cu^+ and Au^+ ions is observed. The influence of π interactions is not detectable, a conclusion also reached by Bertrán and Ruís. [10] It thus appears that the cation-acetonitrile interaction is of predominantly electrostatic nature.

Spectra were for comparison also recorded for some cations (K^+, Na^+, Li^+, Mg^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+}) using CH_3CN as solvent (*Table 1*).

TABLE 1

The frequency of band maxima for adducts of various cations with CD_3CN and CH_3CN (cm^{-1}). $\Delta\nu$ is the frequency difference between the cation induced bands and that of pure CD_3CN and $\Delta\nu_{½}$ is the full width at half height (cm^{-1}).

	CD_3CN			CH_3CN	
Cation	ν_2	$\Delta\nu$	$\Delta\nu_{½}$	ν_2	$\nu_3+\nu_4$
Li^+	2285	24	12	2275	2305
Na^+	2275	14	11	2264	2298
K^+	2261	0	-	2253	2293
Mg^{2+}	2302	41	14	2287	2315
Ca^{2+}	2286	25	12	-	-
Sr^{2+}	2280	19	13	-	-
Ba^{2+}	2274	13	12	-	-
Mn^{2+}	2294	33	14	2283	2310
Fe^{2+}	2298	37	15	2292	2312
Co^{2+}	2304	43	14	2291	2316
Ni^{2+}	2310	49	15	2294	2321
Cu^+	2282	21	14	-	-
Cu^{2+}	2322	61	14	-	-
Zn^{2+}	2303	42	18	-	-
Ag^+	2279	18	16	-	-
Cd^{2+}	2292	31	17	-	-
Au^+	2261	0	-	-	-
Tl^{3+}	2304	43	20	-	-
Pb^{2+}	2270	9	20	-	-
Pure liquid	2261	-	-	2253	2293

The ν_2 CN stretching band of pure CH_3CN is found at 2253 cm^{-1}. At 2293 cm^{-1} a combination band (ν_3 + ν_4) is found, originating from the CH_3 bending and CC stretching vibrations with an enhanced intensity due to Fermi resonance. When ions are dissolved in the liquid, both these bands are shifted to higher wave-numbers. The wave-number shifts of the ν_2 and ν_3 + ν_4 bands of CH_3CN are in *Figure 2* plotted as a function of the

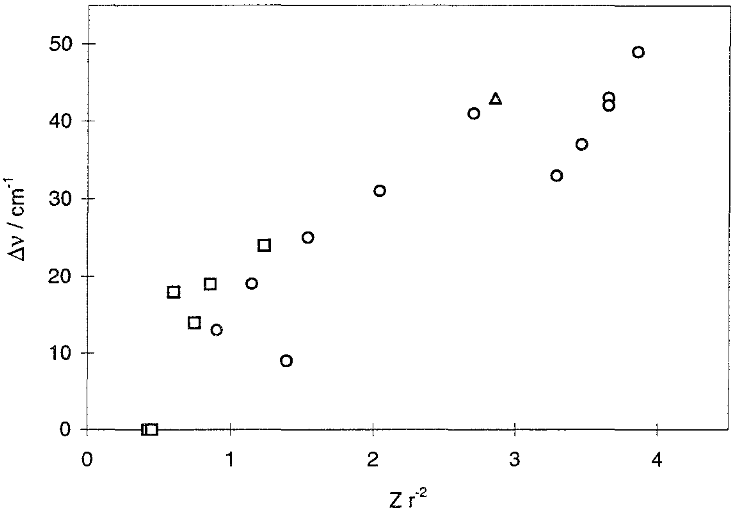

Fig. 1. The frequency shift of the CN stretching vibration band of cation-CD_3CN adducts relative to the frequency of pure CD_3CN ($\Delta\nu$) as a function of the cation charge to squared radius ratio ($Z\ r^{-2}$).
□ = monovalent, ○ = divalent and Δ = trivalent cations.

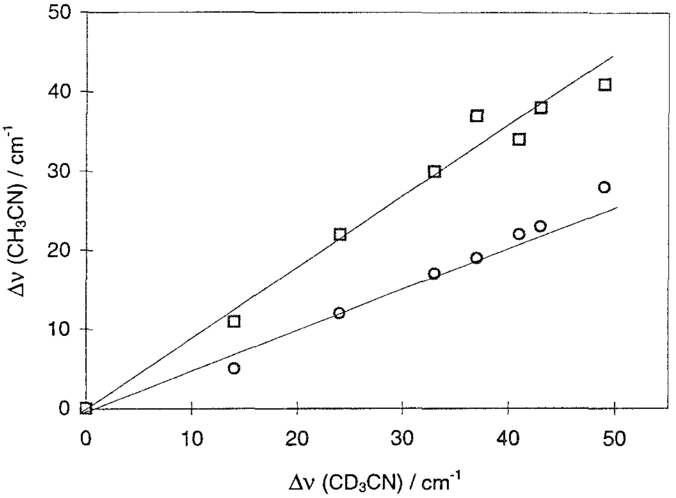

Fig. 2. The frequency shifts of the ν_2 (○) and $\nu_3 + \nu_4$ (□) bands of CH_3CN as a function of the frequency shift of the ν_2 band of CD_3CN.

shift of the ν_2 band of CD_3CN. It is seen that in addition to the ν_2 band also the shift of $\nu_3 + \nu_4$ band of CH_3CN correlates well with the ν_2 band of CD_3CN. This is essentially accounted for by the observation that also the frequency of the CC stretching vibration, found at 919 cm^{-1} for pure CH_3CN, increase upon complexation with cations.[7]

The enthalpy of transfer from water to acetonitrile of the ions Na^+ and Ag^+ are -13.1 and -41.4 kJ mol^{-1}, respectively.[17] The ion radii of Na^+ and Ag^+ are similar (1.03 resp. 1.05 Å). As observed by the change of the CN stretching frequency upon complexation with these ions, Na^+ and Ag^+ behave similarly with only a small induced strengthening of the CN bond. An increased strength of the CN σ-bond is, obviously, accompanied with an increased CN force constant. A pπ - dπ bond would, either as $\pi \rightarrow d$ or $\pi^* \leftarrow d$ electron redistributions, decrease the bond order. As only a minor change is observed in the CN force constant upon Ag^+ coordination, this ion is either quite weakly coordinated by acetonitrile or the σ and pπ-dπ contributions are of equal magnitude but of opposite signs. The first possibility implies that the large negative transfer enthalpy of Ag^+ from water to acetonitrile is not due to a particularly strong solvation in acetonitrile but rather to a weak hydration in aqueous solution.

It is interesting to compare acetonitrile with the related cyanide ion. This ion occupies a very high position in the spectrochemical series and produces a strong trans effect for ligand displacement reactions for square complexes.[18] The cyanide ion has the ability to stabilize metal ions in low formal oxidation states, and does this by accepting d electron density into its π* orbitals. Spectroscopically, we observe here a large difference between for example the Na^+ and Au^+ ions. The CN stretching vibration for NaCN(s) and AuCN(s) are found at 2080 and 2239 cm^{-1}, respectively, suggesting a large difference in bonding.[19]

The strenghtening of the C≡N bond upon cation coordination, as observed by the increase of the CN stretching vibration, might appear somewhat surprising. One model of rationalization consists of the assumption that the cation attracts a major part of the nitrogen lone pair electron density, which has a partly antibonding character, and results in an increased force constant of the CN bond. This view is supported by early semi-empirical calculations on cation-acetonitrile adducts. [20,21] Present calculations indicate that great caution must be exercised when describing the bond in the acetonitrile-cation adduct in terms of the molecular orbitals of the free acetonitrile molecule. [23] Ab initio calculations at the 6-31G** level of acetonitrile and for the complexes with Li^+, Na^+ [22], Mg^{2+} and Al^{3+} [23] shows frequency downshifts of 10, 11, 94 and 332 cm^{-1}, respectively. The discrepancy between exeperimental values and those calculated arises partly from that in calulations 1:1 adducts between acetonitrile and cations were considered, whereas in solution higher coordination numbers are prevalent. Electron correlation effects are certainly also quite important within these systems. To reproduce the experimental data, calculations must probably be done on the entire metal-acetonitrile complex, with six acetonitrile molecules in most cases at, at least the MP2 level of theory. These calculations are time consuming but under progress. [23]

ACKNOWLEDGEMENTS

We are grateful to Professor Ingmar Persson who provided the necessary facilities for this work.

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Date Received: August 25, 1998
Date Accepted: June 15, 1999