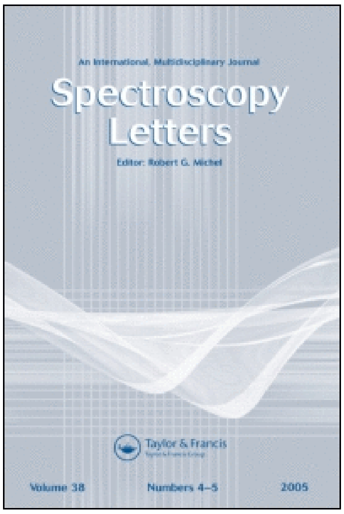

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Raman Spectra of $Zn(CD_3(CN)_2X_2$ (X=C1, Br and I)

Y. Hase[a]; C. Airoldi[a]; Y. Gushikem[a]; Y. Kawano[b]
[a] Instituto de Química, Universidade Estadual de Campinas, Campinas, SP [b] Instituto de Química, Universidade de São Paulo, São Paulo, SP, Brazil

To cite this Article Hase, Y. , Airoldi, C. , Gushikem, Y. and Kawano, Y.(1976) 'Raman Spectra of $Zn(CD_3(CN)_2X_2$ (X=C1, Br and I)', Spectroscopy Letters, 9: 3, 177 — 184

To link to this Article: DOI: 10.1080/00387017608067426

URL: http://dx.doi.org/10.1080/00387017608067426

SPECTROSCOPY LETTERS, 9(3), 177-184 (1976)

RAMAN SPECTRA OF Zn$(CD_3CN)_2X_2$ (X=Cl, Br AND I)

Key Words: Raman spectra, $Zn(CD_3CN)_2X_2$

Y. Hase, C. Airoldi and Y. Gushikem,

Instituto de Química, Universidade Estadual de Campinas,
C.P. 1170, Campinas, SP, Brazil

Y. Kawano,

Instituto de Química, Universidade de São Paulo,
C.P. 20780, São Paulo, SP, Brazil

ABSTRACT

The solid state Raman spectra of complexes of $Zn(CD_3CN)_2X_2$, where X is Cl, Br and I, are reported in the frequency region from 4000 to 27 cm^{-1}. The observed frequencies are assigned by comparison with those of $Zn(CH_3CN)_2X_2$. The isotopic effects on fundamental vibrations are discussed by applying the Teller-Redlich product rule.

INTRODUCTION

In the previous paper,[1] the Raman spectra of the zinc halide complexes with CH_3CN have been studied for the solid samples. The observed frequencies were assigned on the assumption that the molecular structure belongs to the C_{2v} point group and the localized symmetry of ligand CH_3CN is C_{3v}. The assignments of ligand vibrations have been easily carried out by comparison with those of uncomplexed CH_3CN. No band splitting caused by the ligand-ligand interactions has been observed. The skeletal vibrations were assigned on the basis of the frequency shifts by mass effect among Cl, Br and I, G matrix elements of $\nu(Zn-X)$, and Raman intensities observed.

The vibrational study of the complexes with CD_3CN is of interest to confirm the assignments of fundamental vibrations. The spectra of complexes containing CD_3CN have been measured by several authors,[2~7] however for the zinc halide complexes the spectra of $ZnCl_2$ with CD_3CN has been studied in aqueous solution only.[8]

In the present paper, the solid state Raman spectra of the complexes of $Zn(CD_3CN)_2Cl_2$, $Zn(CD_3CN)_2Br_2$ and $Zn(CD_3CN)_2I_2$ are studied and the observed frequencies are tentatively assigned. The fundamental frequencies are compared with those of $Zn(CH_3CN)_2X_2$, and the isotopic effects between $Zn(CH_3CN)_2X_2$ and $Zn(CD_3CN)_2X_2$ are discussed for each halogen atom by applying the Teller-Redlich product rule.

EXPERIMENTAL

The complexes, $Zn(CD_3CN)_2X_2$, were prepared by direct reaction between ZnX_2 and CD_3CN *in vacuo*, and the excess solvent CD_3CN was evaporated.

The solid state Raman spectra were measured in the frequency region from 4000 to 27 cm^{-1} for powder samples in capillary, on a Jarrell-Ash 25-300 spectrometer using an Ar$^+$ laser with excitation lines at 488.0 and 514.5 nm.

RESULTS AND DISCUSSION

The Raman frequencies observed are given in TABLE I, with the relative intensities and the tentative assignments. The molecular structure is assumed to belong to C_{2v}, and the localized structure of ligand to C_{3v} point group.[11] The fundamentals are classified into two groups, the ligand and skeletal vibrations.

The asymmetric C-D stretching vibrations are assigned to two weak bands in the 2240 and 2200 cm^{-1} regions. This band separation may be explained by mechanical coupling between ν_a(C-D) and ν(C≡N), therefore the separation of $Zn(CD_3CN)_2X_2$, *ca*. 40 cm^{-1}, is larger than that of $Zn(CH_3CN)_2X_2$, *ca*. 10 cm^{-1},[1] because the frequencies coupled are more close. The lower bands at about 2200 cm^{-1} are, accordingly, assigned to a_1 and b_1 species which are the same species for ν(C≡N). On the other hand, the higher bands at about 2240 cm^{-1} are assigned to a_2 and b_2 species. The symmetric

TABLE I

Raman frequencies (in cm^{-1}) of $Zn(CD_3CN)_2X_2$

X=Cl		X=Br		X=I		assignments	species
2311	vs	2310	vs	2310	vs	ν (C≡N)	a_1,b_1
2247	w	2242	w	2239	w	ν_a(C-D)	a_2,b_2
2210	w	2204	w	2200	w	ν_a(C-D)	a_1,b_1
2105	vs	2102	vs	2101	vs	ν_s(C-D)	a_1,b_1
1097	w	1095	w	1094	w	$\delta_s(CD_3)$	a_1,b_1
1032	vw	1023	vw	1020	vw	$\delta_a(CD_3)$	a_1,a_2,b_1,b_2
856	m	854	m	850	m**	ν (C-C)	a_1,b_1
850	vw	850	vw	850	m**	ρ (CD_3)	a_1,a_2,b_1,b_2
720	vw	718	vw	712	vw	combination	a_1,a_2,b_1,b_2
363	s	363	s	361	s	δ (CCN)	a_1,a_2,b_1,b_2
336	vw					ν_a(Zn-Cl)	b_2
311	vs					ν_s(Zn-Cl)	a_1
		256	vw			ν_a(Zn-Br)	b_2
246	vw*	243	vw*	241	vw*	ν_s(Zn-N)+δ (NZnN)	a_1
				216	vw	ν_a(Zn-I)	b_2
		208	vs			ν_s(Zn-Br)	a_1
165	m*	162	m*	172	m*	δ (NZnN)+ν_s(Zn-N)	a_1
				152	vs	ν_s(Zn-I)	a_1
133	w	122	w	115	w	δ (NZnX)	b_1,b_2
93	m					δ (ClZnCl)	a_1
77	w	77	w	75	w	δ (NZnX)	a_2
		71	m			δ (BrZnBr)	a_1
67	w	65	w	62	vw	δ (ZnNC)	a_2
58	m	55	m	54	vs**	δ (ZnNC)	b_2
				54	vs**	δ (IZnI)	a_1
45	w	39	w	31	vs**	δ (ZnNC)	b_1
37	vs	35	vs	31	vs**	δ (ZnNC)	a_1

* Mechanical coupling between ν_s(Zn-N) and δ(NZnN), see text.

** Accidental degeneracy at 850, 54 and 31 cm^{-1}.

C-D stretching and C≡N stretching vibrations are assigned to the intense bands in the 2100 and 2310 cm^{-1} regions, respectively. By comparison with the fundamentals of CD_3CN,[9] the asymmetric and symmetric CD_3 bending, C-C stretching, CD_3 rocking and CCN linear bending vibrations are assigned to bands at about 1025, 1095, 855, 850 and 360 cm^{-1}. A weak band in the 710 cm^{-1} region is an overtone of δ(CCN).

The skeletal vibrations can be assigned easily by reference to the assignments of $Zn(CH_3CN)_2X_2$,[1] because the frequency shifts between the complexes with CH_3CN and CD_3CN are not expected to be large. Accordingly, the Zn-X stretching vibrations are assigned to the bands at 336 and 311 cm^{-1} of $Zn(CD_3CN)_2Cl_2$, at 256 and 208 cm^{-1} of $Zn(CD_3CN)_2Br_2$, and at 216 and 152 cm^{-1} of $Zn(CD_3CN)_2I_2$. A slight frequency shift by isotopic effect is observed for the Zn-N stretching and NZnN bending vibrations of the ZnX_2 complexes with pyridine and pyridine-d_5, where X is Cl, Br and I,[10] therefore the bands at about 240 and 170 cm^{-1} of $Zn(CD_3CN)_2X_2$ are assigned to the mechanical coupled vibrations of ν_s(Zn-N) and δ(NZnN) of a_1 species, as already mentioned for $Zn(CH_3CN)_2X_2$. The asymmetric Zn-N stretching vibrations could not be observed in Raman spectra. The skeletal bending vibrations are assigned rather tentatively as due to $Zn(CH_3CN)_2X_2$.

The fundamental frequencies of $Zn(CH_3CN)_2X_2$ and $Zn(CD_3CN)_2X_2$ are listed in TABLE II. For ν(C≡N) of $Zn(CH_3CN)_2X_2$, the Fermi resonance corrected values are given. The frequencies of ν_a(Zn-N) are assumed to be the same values as those of $Zn(CH_3CN)_2X_2$, though

TABLE II

Fundamental Raman frequencies (in cm^{-1}) of $Zn(CY_3CN)_2X_2$.

	Y=H*			Y=D**		
	X=Cl	X=Br	X=I	X=Cl	X=Br	X=I
Ligand vibrations						
ν_a(C-Y)	3004 2994	2990 2982	2983 2968	2247 2210	2242 2204	2239 2200
ν_s(C-Y)	2932	2928	2923	2105	2102	2101
ν (C≡N)	2300[a)]	2301[a)]	2304[a)]	2311	2310	2310
$\delta_a(CY_3)$	1420	1417	1416	1032	1023	1020
$\delta_s(CY_3)$	1358	1357	1354	1097	1095	1094
ρ (CY_3)	1028	1028	1028	850	850	850
ν (C-C)	949	947	943	856	854	850
δ (CCN)	394	392	388	363	363	361
Skeletal vibrations						
ν_a(Zn-X)	338	258	216	336	256	216
ν_s(Zn-X)	314	212	155	311	208	152
ν_a(Zn-N)	210[b)]	212[b)]	219[b)]	210[c)]	212[c)]	219[c)]
ν_s(Zn-N)+δ (NZnN)	260 177	253 168	246 177	246 165	243 162	241 172
δ (XZnX)	97	71	54	93	71	54
δ (NZnX)	135 86	123 85	115 83	133 77	122 77	115 75
δ (ZnNC)	68 60 46 37	67 56 39 36	63 54 37 31	67 58 45 37	65 55 39 35	62 54 31 31

* Raman frequencies from Ref. 1.

** Raman frequencies of this work.

a) Values corrected by Fermi resonance.

b) Infrared frequencies from Ref. 11.

c) Values assumed to be the same frequencies of $Zn(CH_3CN)_2X_2$.

a slight shift is expected in the case of Zn$(CD_3CN)_2X_2$. In addition to the CH_3 and CD_3 group vibrations which are expected to show frequency shifts due to isotopic effect, the bands assigned to ν(C-C) and δ(CCN) also show shifts of about 90 and 30 cm^{-1}, respectively. It may be due the mechanical coupling. To confirm the isotopic effects between the fundamentals of Zn$(CH_3CN)_2X_2$ and Zn$(CD_3CN)_2X_2$, the Teller-Redlich product rule was applied for each halogen atom. The observed and calculated values are given in TABLE III. The Raman frequencies are used in calculations except for the infrared frequencies of ν_a(Zn-N). The torsional vibrations, τ(CCNZn), of a_2 and b_2 species are neglected for both observed and calculated values. On the whole the agreement between the values is good, and the differences are probably atributable

TABLE III

Application of Teller-Redlich product rule.

Zn$(CH_3CN)_2X_2$/Zn$(CD_3CN)_2X_2$.

		X=Cl	X=Br	X=I
a_1 species	Obs.	5.58	5.30	4.99
	Calc.	5.57	5.59	5.60
a_2 species	Obs.	2.73	2.74	2.69
	Calc.	2.68	2.72	2.74
b_1 species	Obs.	4.85	4.72	5.56
	Calc.	5.25	5.29	5.31
b_2 species	Obs.	2.54	2.49	2.39
	Calc.	2.70	2.73	2.74

to experimental error, molecular parameters assumed,[11] and neglect of torsional vibrations.

ACKNOWLEDGEMENTS

The authors thank Fundação de Amparo ã Pesquisa de Estado de São Paulo (FAPESP) for financial assistence.

REFERENCES

1. Y. Hase, C. Airoldi, Y. Gushikem and Y. Kawano, Spectroscopy Ltrs., to be published.
2. Y. Kawano, Y. Hase and O. Sala, J. Mol. Struct., accepted for publication.
3. B. Swanson and D. F. Schriver, Inorg. Chem., 9, 1406 (1970).
4. D. F. Schriver and B. Swanson, Inorg. Chem., 10, 1354 (1971).
5. G. A. Ozin and R. A. Walton, J. Chem. Soc. (A), 1970, 2236.
6. M. Webster and H. E. Blayden, J. Chem. Soc. (A), 1969, 2443.
7. D. M. Byler and D. F. Schriver, Inorg. Chem., 12, 1412 (1973).
8. J. C. Evans and G. Y.-S. Lo, Spectrochim. Acta, 21, 1033 (1965).
9. E. L. Pace and L. J. Noe, J. Chem. Phys., 49, 5317 (1968).
10. Y. Saito, M. Cordes and K. Nakamoto, Spectrochim. Acta, 28A, 1459 (1972).
11. T. Kamo and M. Kimura, Bull. Chem. Soc. Japan, 45, 3309 (1972).

Received: 10-29-75
Revised manuscript received: 11-29-75
Accepted: 1-6-76