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FTIR studies of the CH_3CN-BF_3 complex in solid Ar, N_2 , and Xe: Matrix effects on vibrational spectra

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Abstract

FTIR spectra of the four isotopically substituted 1:1 complexes of acetonitrile and boron trifluoride were recorded in Ar, N₂ and Xe matrices. In Ar, previously unreported three vibrational modes of the complex were clearly observed. Several significant vibrational bands were also observed in N₂ and Xe. The observed frequency shifts on complexation, $\Delta \nu$, were qualitatively in good agreement with the computational results, which were calculated at the B3LYP/6-311 + +G(d,p) level using the optimized geometry of the $C_{3\nu}$ eclipsed conformation. The observed magnitudes of $\Delta \nu$ for most of the complex bands were larger than the calculated values. The BF₃ symmetric deformation mode is an exception. The observed frequency shits for this mode were smaller than the calculated values, especially in N₂. This suggests that even an inert matrix can significantly affect the vibrational spectrum of the complex. © 2005 Elsevier B.V. All rights reserved.

Keywords: Matrix isolation; Infrared spectroscopy; Matrix effects; Acetonitrile; Boron trifluoride

1. Introduction

Structures and bondings of the electron donor-acceptor (EDA) complexes containing boron trifluoride have been the subject of many experimental [1-11] and theoretical [12–15] studies. After the first preparation of the 1:1 adduct of boron trifluoride with acetonitrile [16], it has attracted attention for its significant difference of the B-N bond lengths between the crystalline and the gas phases [17–23]. X-ray crystallography showed that the B-N bond length and the FBN bond angle of CH₃CN-BF₃ in the crystalline solid were 1.630 Å and 105.6°, respectively [19]. On the other hand, Dvorak et al. investigated the microwave spectra of the complex in the gas phase [21]. They reported that the B–N bond length and the FBN bond angle in the gas phase were 2.011 Å and 95.6°, respectively, based on the analysis in which other structural parameters were constrained to the values of the component monomers. Theoretical studies on the structure of the complex including medium effects have also been published [24-29]. The MP2 calculation with

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a reasonable basis set [28] showed the B–N bond length of 1.8008 Å and the FBN bond angle of 101.20° , both of which are intermediate between the crystalline and the gas phase values.

Recently, Giesen et al. precisely studied the structure of the CH₃CN-BF₃ complex, especially the difference between the gas phase and the theoretical results, and the characteristics of the BN bond by the MP2 and B3LYP levels of calculations with larger basis sets [29]. According to their results, two local minima along with the B-N distance were obtained at the B3LYP level using sufficiently large basis sets. The longer B-N length of 2.315 Å was the global minimum for the largest aug-cc-pVQZ basis. However, the energy difference between the two minima is lower than 0.2 kcal/mol and the potential curve along with the B–N coordinate is extremely flat from 1.8 to 2.5 Å. They suggested that the difference between the B-N distance averaged over this flat potential and the equilibrium bond length is responsible for the discrepancy between the gas phase and the theoretical structures.

The vibrational spectra of the CH_3CN-BF_3 complex were also observed in the solid phase [18,20] and the Ar matrix [22,23]. The blue shift of the CN stretching mode on complexation and the characteristics of the BN bond have been the matters of interest. Comparisons of the calculated

and the experimental vibrational frequencies were also reported [28,29]. Roughly speaking, the vibrational frequencies of the complex in an Ar matrix are similar to the calculated values rather than the frequencies in the crystalline phase. This seems to indicate the structural similarity between the calculated and the matrix isolated complexes. Giesen et al. [29], however, suggested that the B-N bond length of the complex in an Ar matrix is somewhat shorter than that of the short minimum geometry (1.919 Å) optimized at the B3LYP/aug-cc-pVQZ level. They investigated the effect of Ar matrix environment on the equilibrium geometry of the complex using the SCRF CPCM model, and showed the significant shortening of the B–N bond length, which indicates that even a very low dielectric medium can dramatically change the shape of the B–N potential surface.

Vibrational spectroscopic studies of the CH_3CN-BF_3 complex in matrices other than Ar are expected to give more information about the matrix effects on the structure and vibrational frequencies of the complex. In this paper, we present the FTIR spectra of the CH_3CN-BF_3 complex including its isotopically substituted species in solid N₂ and Xe, together with some previously unreported vibrational modes in Ar. Matrix effects on the vibrational spectra, especially the frequency shift on complexation are also discussed.

2. Experimental and computational methods

BF₃ (99.99%) was purchased from Takachiho Chemical Industrial Co., Ltd ¹⁰BF₃ was prepared from ¹⁰B₂O₃ (Aldrich, 99%) and Na¹⁰BF₄ [30], which was prepared by mixing of HF (Morita Chemical Industries Co., Ltd.), $H_3^{10}BO_3$ (Aldrich, 99%) and Na₂CO₃ (Kanto Kagaku, 99.5%). CH₃CN (99.5%) and CD₃CN (99.8%) were purchased from Wako Pure Chemical Industries, Ltd. and Aldrich, respectively. All samples were purified by the trap-to-trap method in an all-glass vacuum line. Matrix gases, Ar (Nippon Sanso, 99.9995%), N2 (Nippon Sanso, 99.9995%) and Xe (Takachiho, 99.99%), were used without further purification. The mixtures of CH₃CN and BF₃ with excess matrix gases were prepared using standard manometric techniques. CH₃CN/M and BF₃/M (M=Ar, N_2) were co-deposited on a CsI plate maintained at 20 or 12 K. Subsequent annealing procedures were carried out at 33 K. For CH₃CN/Xe and BF₃/Xe, co-deposition and annealing temperatures were 30 and 60 K, respectively. The cryostat used was CTI Cryogenics LT-21, coupled with Tristan Technologies, Inc. LTC-20 temperature controller. Reagent/matrix ratios (R/M) were in the range of 1/200-1/400. All spectra were recorded on a Nicolet Magna 750 FTIR spectrometer, in the wavenumber range from 4000 to 400 cm⁻¹ at 1 cm⁻¹ resolution.

The MP2 and B3LYP calculations were carried out with several basis sets of valence triple-zeta level using

Gaussian03 program [31]. Geometry optimizations were performed using the 'opt=verytight' option. Harmonic vibrational frequencies were calculated numerically for MP2 and analytically for B3LYP.

3. Results and discussion

3.1. Optimized geometry and harmonic frequencies of the CH_3CN -BF₃ complex

Several computational studies on the structure and the vibrational frequencies of the CH₃CN-BF₃ complex have been published previously [24-29]. However, we had to know the calculated harmonic frequencies of some isotopically substituted species, which can be used for the vibrational assignment of all the observed frequencies. Therefore, we also calculated the optimized geometry and the harmonic frequencies of the complex at the MP2 and B3LYP levels with some standard basis sets. According to the previous studies [28,29], the eclipsed conformation with $C_{3\nu}$ symmetry was assumed during the geometry optimization. The important geometrical parameters of the 1:1 CH₃CN–BF₃ complex are presented in Fig. 1. The optimized values of these parameters and the harmonic frequencies for the $CH_3CN^{-11}BF_3$ species are compared with previously reported results in Tables 1 and 2. Note that the mode numbering scheme in Table 2 is that from Cho et al. [28].

Table 1 shows that the B–N bond length and the FBN bond angle have somewhat large dependence on the level of calculation. A significant shortening of the B-N bond length on introducing the diffuse functions [29] was also found for our basis sets. For B3LYP, most of the geometrical parameters calculated with the 6-311 + +G(d,p) and 6-311G(d,p) basis sets are similar to those calculated with the larger aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively. However, the B-N bond length at the B3LYP/6-311 + +G(d,p) level is somewhat shorter than that at the B3LYP/aug-cc-pVTZ, and closer to the value at the MP2/6-31+G(2d,p) level. The B-N, CN and CC bond lengths at the B3LYP level are slightly shorter than those at the MP2 level with the same basis set. The CN and CC bond lengths of the CH₃CN monomer in the gas phase are 1.1572 and 1.4596 Å, respectively [32]. Since the shortenings of these bonds are expected on complexation, the B3LYP



Fig. 1. Optimized geometry of the 1:1 CH₃CN–BF₃ complex. Determined values of geometrical parameters are listed in Table 1.

Table 1
Geometrical parameters of the 1:1 CH ₃ CN-BF ₃ complex optimized at various levels of calculation

Parameter	B3LYP/6-311++G(d,p)	B3LYP/6- 311G(d,p)	$\frac{MP2/6-311++}{G(d,p)^{a}}$	MP2/6- 311G(d,p)	$MP2/6-31 + G(2d,p)^{b}$	B3LYP/aug-cc- pVTZ ^c	B3LYP/aug-cc- pVQZ ^c
Bond length [Å]							
R(cc)	1.450	1.454	1.458	1.461	1.459	1.449	1.452
R(CH)	1.092	1.092	1.091	1.091	1.089	1.089	1.089
R(CN)	1.144	1.149	1.164	1.170	1.164	1.142	1.145
R(BN)	1.796	2.327	1.804	2.381	1.801	1.868	2.315
R(BF)	1.359	1.326	1.356	1.324	1.356	1.349	1.323
Bond angle [°]							
θ (HCC)	109.7	110.0	109.4	109.7	109.5	109.7	110.0
θ (FBN)	101.8	94.7	101.4	93.9	101.2	100.8	95.1

^a One imaginary frequency associated with torsional mode was obtained.

^b Ref. [28].

^c Ref. [29].

results for the complex seem to be more reliable. The MP2/ 6-311++G(d,p) level of calculation for the $C_{3\nu}$ eclipsed conformation gave one imaginary frequency corresponding to the torsional mode. Similar imaginary frequencies were also obtained for the $C_{3\nu}$ staggered and C_3 conformations. These results suggest that the torsional motion of the complex is almost free rotation.

The harmonic frequencies calculated at the B3LYP/ 6-311 + +G(d,p) level in Table 2 are qualitatively corresponding to those at the MP2/6-31 + G(2d,p) and those at the short minimum (R(BN) = 1.919 Å) of the B3LYP/aug-ccpVQZ, especially in terms of the frequency shift on complexation, $\Delta \nu$. On the other hand, $\Delta \nu$ of the CN stretching and BF₃ degenerate stretching calculated at the B3LYP/6-311 + +G(d,p) are obviously different from those at the long minimum (R(BN) = 2.315 Å, the global minimum) of the B3LYP/aug-cc-pVQZ. Giesen et al. predicted that the B–N bond length of the complex in an Ar matrix is shorter than 1.919 Å [29]. Therefore, the harmonic frequencies calculated at the optimized geometry of the B3LYP/6-311++G(d,p) level (R(BN) = 1.796 Å) are expected to be sufficiently useful for the vibrational assignment of the complexes observed in low temperature matrices.

Table 2

Comparison of calculated harmonic frequencies (cm⁻¹) of CH₃CN–¹¹BF₃ complex

Mode ^a		B3LYP/6	-311 + + 6	i(d,p)	MP2/6-3	I + G(2d,p)	b	B3LYP/a	ug-cc-pVQ)Z ^c			Approximate
		R(BN) = 1	.796 Å		R(BN) =	1.801 Å		R(BN) =	1.919 Å		R(BN) = 2	2.315 Å	description ^d
		$\nu_{\rm monomer}$	$\nu_{\rm complex}$	$\Delta \nu^{\rm e}$	$\nu_{ m monomer}$	$v_{\rm complex}$	$\Delta \nu^{\rm e}$	$\nu_{ m monomer}$	$v_{\rm complex}$	$\Delta \nu^{\mathrm{e}}$	$v_{\rm complex}$	$\Delta \nu^{\rm e}$	_
a_1	ν_1	3046.2	3050.6	+4.4	3125.2	3128.1	+2.9	3047	3051	+4	3050	+3	CH ₃ sym str
	ν_2	2362.6	2435.6	+73.0	2206.4	2301.8	+95.4	2363	2421	+58	2391	+28	CN str
	ν_3	1411.5	1409.3	-2.2	1437.6	1435.2	-2.4	1415	1413	-2	1414	-1	CH ₃ sym def
	ν_4	929.8	958.7	+28.9	926.1	958.0	+31.9	928	951	+23	938	+10	CC str
	ν_5	-	174.1	_	_	178.9	_	_	47	-	63	_	¹¹ BN str
	ν_6	869.0	809.8	-59.2	868.0	812.5	-55.5	884	830	-54	859	-25	¹¹ BF ₃ sym str
	ν_7	682.0	578.9	-103.1	721.4	573.8	-147.6	684	564	-120	587	-97	¹¹ BF ₃ sym def
a_2	ν_8	_	14.7	_	_	11.0	_	_	22	-	20	_	Torsion
e	ν_9	3116.1	3126.5	+10.4	3222.6	3230.6	+8.0	3116	3125	+9	3121	+5	CH ₃ deg str
	ν_{10}	1474.9	1464.8	-10.1	1513.2	1503.8	-9.4	1475	1468	-7	1472	-3	CH ₃ deg def
	ν_{11}	1061.3	1059.7	-1.6	1074.2	1073.3	-0.9	1063	1062	-1	1063	0	CH ₃ rock
	ν_{12}	381.9	416.1	+34.2	360.1	404.5	+44.4	380	412	+32	396	+16	CCN
	.2												$bend + {}^{11}BF_3$
													deg def
	v_{13}	1417.1	1242.4	-174.7	1426.6	1260.4	-166.2	1441	1306	-135	1395	-46	¹¹ BF ₃ deg str
	v_{14}	465.8	494.2	+28.4	481.8	490.5	+8.7	475	487	+12	474	-1	$^{11}BF_3 \text{ deg def} +$
													CCN bend
	v_{15}	_	285.9	_	_	279.5	_	_	266	_	187	_	¹¹ BF ₃ rock
	v_{16}	_	70.1	-	-	69.3	_	-	59	_	42	-	¹¹ BNC bend

^a Mode-numbering scheme is taken from Cho et al. [28].

^b Cho et al. [28] calculated frequencies by GAMESS package. Listed values in the table were calculated by Gaussian 03.

^c Frequencies higher than 2000 cm⁻¹ in Ref. [29] were scaled by 0.96. Listed frequencies are converted unscaled values.

^d Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.

 $^{e} \Delta \nu = \nu_{\text{complex}} - \nu_{\text{monomer}}$

3.2. Observed vibrational frequencies in Ar, N₂ and Xe matrices

The FTIR spectra of CH₃CN and BF₃ co-deposited in low temperature Ar, N2 and Xe matrices are shown in Figs. 2-4. The absorptions that can be assigned to the CH₃CN-BF₃ complex, which were absent in the spectra of free monomers, are indicated with arrows. In addition to the previously reported three major absorptions [23], several new features were observed near the CH₃CN monomer bands in the Ar matrix spectra. Fewer vibrational modes of the complexes were observed in N_2 and Xe than in Ar. Some significant frequency differences among the matrices are observed in these bands. The vibrational assignment of the complex bands was carried out using the calculated harmonic frequencies at the B3LYP/6-311 + + G(d,p) level. The fundamental frequencies of the CH₃CN-BF₃ complexes including isotopically substituted species together with the calculated values are summarized in Tables 3-6. Detailed descriptions on the absorptions assigned to the complexes in each characteristic frequency region are presented in the following sections. In reference to the component monomers, the vibrational frequencies of CD₃CN in N₂, CH₃CN, CD₃CN and BF₃ in Xe have not been previously reported. Therefore, the assignments of these monomer absorptions, which were made by comparison with the reported frequencies in the gas phase and in other matrices [11,33-39], are also described.



Fig. 2. FTIR spectra of acetonitrile and boron trifluoride co-deposited in low temperature matrices, in the 3050–2900 and 2400–2200 cm⁻¹ regions. (a) CH₃CN/BF₃/Ar=1/1/400, 20 K; (b) CH₃CN/BF₃/N₂=1/1/400, 20 K; (c) CH₃CN/BF₃/Xe=1/1/400, 30 K. The bands assigned to the CH₃CN–BF₃ complex are indicated with arrows.



Fig. 3. FTIR spectra of acetonitrile and boron trifluoride codeposited in low temperature matrices, in the $1600-1100 \text{ cm}^{-1}$ region. (a) CH₃CN/BF₃/Ar=1/1/400, 20 K; (b) CH₃CN/BF₃/N₂=1/1/400, 20 K; (c) CH₃CN/BF₃/Xe=1/1/400, 30 K. The bands assigned to the CH₃CN–BF₃ complex are indicated with arrows.

3.2.1. $CH(D)_3$ degenerate stretching (v_9) and $CH(D)_3$ symmetric stretching (v_1)

In the spectrum of CH₃CN/BF₃/Ar, the CH₃ degenerate stretching (ν_9) absorptions assigned to the complex were observed as a slightly split band at 3022.0/3021.0 cm⁻¹ and a shoulder at 3018.8 cm⁻¹, which are in the higher frequency region of the CH₃CN monomer absorption at 3007.2 cm⁻¹. The corresponding absorptions for



Fig. 4. FTIR spectra of acetonitrile and boron trifluoride co-deposited in low temperature matrices, in the 900–450 cm⁻¹ region. (a) CH₃CN/BF₃/ Ar=1/1/400, 20 K; (b) CH₃CN/BF₃/N₂=1/1/400, 20 K; (c) CH₃CN/BF₃/ Xe=1/1/400, 30 K. The bands assigned to the CH₃CN–BF₃ complex are indicated with arrows.

Table 3 Calculated and experimental fundamental frequencies (cm⁻¹) of CH₃CN-¹¹BF₃ complex

Mode ^a		Calculat	ed		Experim	ental								Approximate description ^b
		B3LYP/	6-311++	G(d,p)	in Ar			in N ₂			in Xe			-
		<i>v</i> _{complex}	₽ _{monom-} er	$\Delta \nu$	$v_{\rm complex}$	₽ _{monom-} er	$\Delta \nu$	$v_{\rm complex}$	v _{monom-} er	$\Delta \nu$	$v_{\rm complex}$	$ u_{ m monom-} $ er	$\Delta \nu$	
a_1	ν_1	3050.6	3046.2	+4.4	2953.6	2950.4	+3.2	_	2949.6	_	_	2939.4	_	CH ₃ sym str
	ν_2	2435.6	2362.6	+73.0	2365.6	2258.3	+107.3	2367.0	2257.2	+109.8	2357.6	2262.3	+95.3	CN str
	ν_3	1409.3	1411.5	-2.2	1374.3 ^c	1375.7	-1.4	1377.4 ^c	1378.6	-1.2	1368.2	1371.6	-3.4	CH ₃ sym def
	ν_4	958.7	929.8	+28.9	-	916.5	-	-	917.5	-	-	927.1	-	CC str
	ν_5	174.1	-	-	-	-	-	-	-	-	-	-	-	¹¹ BN str
	v_6	809.8	869.0	- 59.2	811.7 ^c	876.0	-64.3	835.8 ^c	879.9	-44.1	809.0 ^c	880.6	-71.6	¹¹ BF ₃ sym str
	ν_7	578.9	682.0	-103.1	601.2	675.9	-74.7	625.3	657.6	-32.3	601.7	675.4	-73.7	¹¹ BF ₃ sym def
					631.8 ^d		-44.1	617.1 ^d		-40.5	631.1 ^d		-44.3	
a_2	ν_8	14.7	-	-	-	-	-	-	-	-	-	-	-	Torsion
	ν_9	3126.5	3116.1	+10.4	3022.0	3007.2	+14.8	-	3009.7	-	-	2997.5	-	CH ₃ deg str
	v_{10}	1464.8	1474.9	-10.1	-	1445.4	-	-	1446.5	-	-	1437.7	-	CH ₃ deg def
	v_{11}	1059.7	1061.3	-1.6	1036.8 ^c	1038.2	-1.4	-	1041.0	-	1033.2	1036.1	-2.9	CH ₃ rock
	v_{12}	416.1	381.9	+34.2	-	-	-	-	-	-	-	-	-	CCN bend + ¹¹ BF ₃ deg def
	v_{13}	1242.4	1417.1	-174.7	1248.7	1447.2	-198.5	1235.0	1443.2	-208.2	1239.0	1440.1	-201.1	¹¹ BF ₃ deg str
	ν_{14}	494.2	465.8	+28.4	502.9	479.7	+23.2	-	479.2	-	502.5	477.8	+24.7	¹¹ BF ₃ deg def + CCN bend
	v_{15}	285.9	_	_	_	_	_	_	-	_	-	-	_	¹¹ BF ₃ rock
	v_{16}	70.1	-	-	-	-	-	-	-	-	_	-	-	¹¹ BNC bend

^a Mode-numbering scheme is taken from Cho et al. [28].
 ^b Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.
 ^c Tentative assignment.

^d Minor site.

Table 4
Calculated and experimental fundamental frequencies (cm ⁻¹) of CH ₃ CN- ¹⁰ BF ₃ complex

Mode ^a		Calculate	ed		Experime	ental								Approximate description ^b
		B3LYP/6	5-311++ 0	G(d,p)	in Ar			in N ₂			in Xe			
		$\nu_{\rm complex}$	$\nu_{ m monom}$ er	$\Delta \nu$	v _{complex}	$\nu_{ m monom-}$ er	$\Delta \nu$	$\nu_{\rm complex}$	$ u_{\rm monom-} $ er	$\Delta \nu$	$\nu_{\rm complex}$	$ u_{ m monom-} $ er	$\Delta \nu$	
a_1	ν_1	3050.6	3046.2	+4.4	2953.4	2950.4	+3.0	-	2949.6	-	-	2939.4	-	CH ₃ sym str
	ν_2	2435.6	2362.6	+73.0	2365.7	2258.3	+107.4	2367.0	2257.2	+109.8	2357.6	2262.3	+95.3	CN str
	ν_3	1409.3	1411.5	-2.2	1374.3 ^c	1375.7	-1.4	1377.4 ^c	1378.6	-1.2	1368.3	1371.6	-3.3	CH ₃ sym def
	ν_4	958.9	929.8	+29.1	-	916.5	-	-	917.5	-	-	927.1	-	CC str
	ν_5	175.6	-	-	-	-	-	-	-	-	-	-	-	¹⁰ BN str
	ν_6	814.5	869.0	-54.5	813.5 ^c	876.0	-62.5	843.5 ^c	879.9	-36.4	810.8 ^c	880.6	-69.8	¹⁰ BF ₃ sym str
	ν_7	595.6	709.9	-114.3	618.0	703.1	-85.1	640.6	683.6	-43.0	616.9	702.4	-85.5	¹⁰ BF ₃ sym def
					646.3 ^d		-56.8	633.0 ^d		-50.6	645.6 ^d		-56.8	
a_2	ν_8	14.7	-	-	-	-	-	-	-	-	-	-	-	Torsion
е	ν_9	3126.5	3116.1	+10.4	3022.2	3007.2	+15.0	-	3009.7	-	-	2997.5	-	CH ₃ deg str
	ν_{10}	1464.8	1474.9	-10.1	-	1445.4	-	-	1446.5	-	-	1437.7	-	CH ₃ deg def
	ν_{11}	1059.7	1061.3	-1.6	1036.9 ^c	1038.2	-1.3	-	1041.0	-	1033.2	1036.1	-2.9	CH ₃ rock
	ν_{12}	416.5	381.9	+34.6	-	-	-	-	-	-	-	-	-	CCN bend $+ {}^{10}\text{BF}_3$ deg def
	v_{13}	1288.8	1469.1	-180.3	1293.3	1498.4	-205.1	1277.8	1494.5	-216.7	1284.8	1491.2	-206.4	¹⁰ BF ₃ deg str
	ν_{14}	495.8	467.7	+28.1	504.5	481.2	+23.3	-	481.1	-	503.5	479.7	+23.8	¹⁰ BF ₃ deg def + CCN bend
	v_{15}	286.0	-	-	-	-	-	-	_	—	-	-	-	¹⁰ BF ₃ rock
	ν_{16}	70.1	-	-	-	-	-	-	-	-	-	-	-	¹⁰ BNC bend

а

Mode-numbering scheme is taken from Cho et al. [28]. Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation. b с

Tentative assignment.

^d Minor site.

Table 5	
Calculated and experimental fundamental frequencies (cm ⁻¹) of CD ₃ CN- ¹¹ BF ₃ comple	х

Mode ^a		Calculate	ed		Experim	ental								Approximate description ^b
		B3LYP/	6-311++C	G(d,p)	in Ar			in N ₂			in Xe			-
		$\nu_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	$\nu_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	$\nu_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	$\nu_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	
a_1	ν_1	2189.9	2187.2	+2.7	2124.0	2121.9	+2.1	2129.0 ^c	2127.1	+1.9	-	2115.4	_	CD3 sym str
	ν_2	2435.3	2362.3	+73.0	2362.0	2267.0	+95.0	2365.3	2266.4	+98.9	2356.1	2269.9	+86.2	CN str
	ν_3	1130.9	1128.4	+2.5	-	1104.4	_	-	1105.9	-	-	1103.8	-	CD ₃ sym def
	ν_4	874.5	839.9	+34.6	875.6	828.9	+46.7	875.5 ^c	830.2	+45.3	-	835.4	-	CC str $+^{11}$ BF ₃
	ν_5	169.8	_	_	_	_	_	_	_	_	_	_	_	sym str ¹¹ BN str
	ν_6	802.2	869.0	-66.8	808.1 ^c	876.0	-67.9	-	879.9	-	-	880.6	-	¹¹ BF ₃ sym str+CC str
	ν_7	578.3	682.0	-103.7	601.5	675.9	-74.4	623.7	657.6	-33.9	599.7	675.4	-75.7	¹¹ BF ₃ sym def
					629.5 ^d		-46.4	616.0 ^d		-41.6	628.6 ^d		-46.8	
a_2	ν_8	10.6	-	-	-	-	_	-	-	-	-	-	-	Torsion
е	ν_9	2315.9	2307.8	+8.1	2257.8 ^c	2253.5	+4.3	-	2255.8	-	-	2247.0	-	CD ₃ deg str
	ν_{10}	1051.3	1059.3	-8.0	1031.2	1040.0	-8.8	-	1041.4	-	-	1034.7	_	CD ₃ deg def
	ν_{11}	865.7	862.8	+2.9	-	845.5	_	-	850.9	-	-	845.0	_	CD3 rock
	v_{12}	397.7	350.6	+47.1	-	-	-	-	-	-	-	-	-	CCN bend $+$ ¹¹ BF ₃ deg def
	v_{13}	1242.4	1417.1	-174.7	1250.2	1447.2	-197.0	1233.2	1443.2	-210.0	1241.3	1440.1	-198.8	¹¹ BF ₃ deg str
	ν_{14}	489.8	465.8	+24.0	498.0	479.7	+18.3	-	479.2	-	497.6 ^c	477.8	+19.8	$^{11}\mathrm{BF}_3 \mathrm{deg}$ def + CCN bend
	v_{15}	274.6	-	_	-	-	_	-	_	_	-	-	_	¹¹ BF ₃ rock
	v_{16}	67.1	_	-	_	-	-	-	-	-	-	_	-	¹¹ BNC bend

^a Mode-numbering scheme is taken from Cho et al. [28]
 ^b Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.
 ^c Tentative assignment.
 ^d Minor site.

Table 6
Calculated and experimental fundamental frequencies (cm ⁻¹) of CD ₃ CN- ¹⁰ BF ₃ complex

Mode ^a		Calculate	ed		Experime	ental								Approximate description ^b
		B3LYP/6	6-311++C	i(d,p)	in Ar			in N ₂			in Xe			-
		<i>v</i> _{complex}	$\nu_{\rm monomer}$	$\Delta \nu$	$\nu_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	$v_{\rm complex}$	$v_{\rm monomer}$	$\Delta \nu$	$v_{\rm complex}$	$\nu_{\rm monomer}$	$\Delta \nu$	Approximate description ^b CD ₃ sym str CN str CD ₃ sym def CC str + ¹⁰ BF ₃ sym str ¹⁰ BF ₃ sym str + CC str ¹⁰ BF ₃ sym def Torsion CD ₃ deg str CD ₃ deg def CD ₃ rock CCN bend + ¹⁰ BF ₃ deg str ¹⁰ BF ₃ deg str
a_1	ν_1	2189.9	2187.2	+2.7	2124.1	2121.9	+2.2	2129.0 ^c	2127.1	+1.9	-	2115.4	-	CD3 sym str
	ν_2	2435.3	2362.3	+73.0	2361.9	2267.0	+94.9	2365.2	2266.4	+98.8	2355.4	2269.9	+85.5	CN str
	ν_3	1131.0	1128.4	+2.6	-	1104.4	-	-	1105.9	-	-	1103.8	-	CD3 sym def
	ν_4	875.6	839.9	+35.7	878.5	828.9	+49.6	877.3°	830.2	+47.1	-	835.4	-	CC str $+$ ¹⁰ BF ₃ sym str
	ν_5	171.3	-	-	-	-	-	-	-	-	-	-	-	¹⁰ BN str
	ν_6	806.0	869.0	-63.0	814.9 ^c	876.0	-61.1	-	879.9	-	-	880.6	-	¹⁰ BF ₃ sym str+ CC str
	ν_7	595.1	709.9	-114.8	621.4	703.1	-81.7	639.1	683.6	-44.5	614.5	702.4	-87.9	¹⁰ BF ₃ sym def
					644.1 ^d		-59.0	631.9 ^d		-51.7	643.1 ^d		-59.3	
a_2	ν_8	10.6	-	-	-	-	-	-	-	-	-	-	-	Torsion
е	ν_9	2315.9	2307.8	+8.1	2257.8 ^c	2253.5	+4.3	-	2255.8	-	-	2247.0	-	CD3 deg str
	ν_{10}	1051.3	1059.3	-8.0	1031.2	1040.0	-8.8	-	1041.4	-	-	1034.7	-	CD3 deg def
	ν_{11}	865.7	862.8	+2.9	-	845.5	-	-	850.9	-	-	845.0	-	CD3 rock
	ν_{12}	398.0	350.6	+47.4	-	-	-	-	-	-	-	-	-	CCN bend+ ¹⁰ BF ₃
	ν_{13}	1288.7	1469.1	-180.4	1291.5	1498.4	-206.9	1278.8	1494.5	-215.7	1282.7	1491.2	-208.5	deg def ${}^{10}\text{BF}_3$ deg str
	v_{14}	491.6	467.7	+23.9	500.1	481.2	+18.9	-	481.1	-	-	479.7	-	¹⁰ BF ₃ deg def + CCN bend
	ν_{15}	274.7	-	-	-	-	-	-	-	-	-	-	-	¹⁰ BF ₃ rock

^a Mode-numbering scheme is taken from Cho et al. [28].
 ^b Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.
 ^c Tentative assignment.
 ^d Minor site.

CH₃CN/¹⁰BF₃/Ar were observed at almost the same frequencies of 3022.2/3021.0 and 3019.0 cm⁻¹. The bands at the highest frequencies among these absorptions would be corresponding to a major matrix site. For CD₃CN/BF₃/Ar, a very weak absorption was observed at 2257.8 cm⁻¹ in the higher frequency region of the CD₃ degenerate stretching absorption of the CD₃CN monomer, which appeared at 2253.5/2251.5 cm⁻¹ as a site-split band. The corresponding absorption was observed at the same frequency for CD₃CN/¹⁰BF₃/Ar. Therefore, the band at 2257.8 cm⁻¹ was tentatively assigned to the CD₃ degenerate stretching (ν_9) of the complex.

In the spectrum of CH₃CN/BF₃/Ar, the CH₃ symmetric stretching (ν_1) absorptions of the complex were observed at 2956.5 cm⁻¹ as a shoulder and at 2953.6 cm⁻¹ as a weak but distinct peak. The corresponding absorptions were observed at 2956.0 and 2953.4 cm⁻¹ for CH₃CN/¹⁰BF₃/Ar. This mode was observed at 2950.4 cm⁻¹ for the CH₃CN monomer in Ar. The CD₃ symmetric stretching (ν_1) absorption of the complex was observed at 2124.0 cm⁻¹ for CD₃CN/BF₃/Ar, which is slightly higher in frequency than the CD₃CN monomer band at 2121.9 cm⁻¹. The corresponding absorption appeared at 2124.1 cm⁻¹ for CD₃CN/¹⁰BF₃/Ar.

In the spectra of CH₃CN/BF₃/N₂ and CH₃CN/¹⁰BF₃/ N₂, no new absorptions that can be assigned to the ν_9 and v_1 of the complex were observed partly because of the poor isolation quality of matrices. Similarly, no new absorptions were observed for both CD₃CN/BF₃/N₂ and $CD_3CN/^{10}BF_3/N_2$ in the ν_9 region besides the slightly broadened band at 2255.8 cm⁻¹ of the CD₃CN monomer. However, a very weak absorption, which was not observed for free CD₃CN, was observed as a shoulder at 2129.0 cm⁻¹ in the v_1 region of the CD₃CN/BF₃/N₂ spectrum. The corresponding absorption was observed at the same frequency for $CD_3CN/^{10}BF_3/N_2$. We tentatively assigned this absorption to the v_1 of the complex. Three absorptions were observed at 2127.1, 2124.2 and 2120.9 cm^{-1} in the CD₃ symmetric stretching region of the spectrum of the CD₃CN monomer. We assigned the sharp band at the highest frequency of 2127.1 cm^{-1} to the CD₃CN monomer.

In the spectra of CH₃CN/BF₃/Xe and CH₃CN/¹⁰BF₃/ Xe, no absorptions attributable to the complex were observed in the ν_9 and ν_1 regions. Two absorptions observed at 2997.5 and 2939.4 cm⁻¹ were assigned to the CH₃ degenerate and symmetric stretchings of the CH₃CN monomer in Xe, respectively. No new absorptions were observed in the CD₃ stretching region of the CD₃CN/BF₃/Xe and CD₃ CN/¹⁰BF₃/Xe spectra. The CD₃ degenerate and symmetric stretching absorptions of the CD₃CN monomer were observed at 2247.0 and 2115.4 cm⁻¹, respectively.

For the CH_3 and CD_3 stretching modes described above, the observed and the calculated frequency shifts

listed in Tables 3–6 are, at least qualitatively, in good agreement.

3.2.2. CN stretching (ν_2)

In the spectrum of CH₃CN/BF₃/Ar, the CN stretching (ν_2) absorption of the complex was observed at 2365.6/2364.6 cm⁻¹ as a slightly split band. The additional broad absorptions observed at 2373.8 and 2371.8 cm⁻¹ could not be assigned to the 1:1 complex because of their dependence on R/M ratios. The corresponding absorption for CH₃CN/¹⁰BF₃/Ar was observed at essentially the same frequency of 2365.7/2364.4 cm⁻¹. We adopted the higher frequency bands of the matrix-split absorptions for a major site. In the spectra of CD₃CN/BF₃/Ar and CD₃CN/¹⁰BF₃/Ar, the ν_2 absorptions of the complexes were observed at 2363.6/2362.0 and 2363.7/2361.9 cm⁻¹, respectively. In these cases, we adopted the lower frequency bands for a major site because of their stronger intensities in contrast to the cases of CH₃CN.

In the spectra of both CH₃CN/BF₃/N₂ and CH₃CN/¹⁰BF₃/N₂, the ν_2 absorption of the complex was observed at 2367.0 cm⁻¹. The corresponding frequencies for CD₃CN/BF₃/N₂ and CD₃CN/¹⁰BF₃/N₂ were 2365.3 and 2365.2 cm⁻¹, respectively. The absorptions observed at 2266.4, 2275.6 and 2264.0 cm⁻¹ in the spectrum of free CD₃CN in N₂ were assigned to the major site monomer, the minor site monomer and the dimer, respectively.

For CH₃CN/BF₃/Xe and CH₃CN/¹⁰BF₃/Xe, the ν_2 absorption of the complex was observed at 2357.6 cm⁻¹. In the spectrum of free CH₃CN in Xe, the absorptions of the CH₃CN monomer at 2262.3 cm⁻¹, those of the dimer or polymer at 2258.5 and 2253.8 cm⁻¹ were observed. The combination bands ($\nu_3 + \nu_7$) of the monomer, dimer and polymer, which are enhanced by Fermi resonance, were observed at 2299.9, 2298.3, 2293.0 cm⁻¹, respectively. For CD₃CN/BF₃/Xe, the sharp absorption due to the ν_2 of the complex was observed at 2356.1 cm⁻¹. The corresponding absorption for CD₃CN/¹⁰BF₃/Xe appeared at 2355.4 cm⁻¹, though its frequency is less reliable because of its low intensity. The CN stretching of the CD₃CN monomer was observed at 2269.9 cm⁻¹ in Xe.

The CN stretching frequencies predicted by the B3LYP/6-311++G(d,p) calculations for all isotopically substituted species reveal blue shifts of 73.0 cm^{-1} on complexation. The experimental large blue shifts observed in all matrices qualitatively agree with the predictions. The frequency shifts in Xe are somewhat smaller than those in Ar and N₂ because of the higher frequencies of the acetonitrile monomers as well as the lower frequencies of the complexes.

3.2.3. $CH(D)_3$ degenerate deformation (v_{10})

In the spectra of CH₃CN/BF₃/Ar and CH₃CN/¹⁰BF₃/Ar, no absorptions attributable to the complex were observed in this region partly because of the overlap with the strong and complicated absorptions of the BF₃ degenerate stretchings

of the BF₃ polymers. The CH₃ degenerate deformation of the CH₃CN monomer in Ar, which was not precisely described in the literature [34], was probably observed at 1445.4 cm⁻¹. For both CD₃CN/BF₃/Ar and CD₃CN/¹⁰BF₃/Ar, the CD₃ degenerate deformation (ν_{10}) absorptions of the complexes were observed at 1031.2 cm⁻¹. The calculated red shifts on complexation, which are less than 10 cm⁻¹, correspond to the experimental results.

In all co-deposited spectra of N₂ and Xe matrices, no absorptions attributable to ν_{10} of the complexes were observed. The absorptions of the CH₃CN and CD₃CN monomers were observed at 1446.5 and 1041.4 cm⁻¹ in N₂, respectively. The corresponding bands were observed at 1437.7 and 1034.7 cm⁻¹ in Xe, respectively.

3.2.4. BF₃ degenerate stretching (ν_{13})

In the spectrum of CH₃CN/BF₃/Ar, as reported in the literature [23], several new absorptions appeared at considerably lower frequencies from the BF₃ degenerate stretching region of the free species. The two characteristic features, which had the intensity ratio of 1:4 and similar shape, were observed at 1293.3 and 1248.7 cm^{-1} . These bands have been assigned to the BF₃ degenerate stretchings (v_{13}) of CH₃CN-¹⁰BF₃ and CH₃CN-¹¹BF₃, respectively [23]. The additional weaker absorptions were observed at 1307.9 and 1265.1 cm⁻¹, which were tentatively assigned to ν_{13} of CH₃CN-¹⁰BF₃ and CH₃CN-¹¹BF₃ in a minor site, respectively. For CH₃CN/¹⁰BF₃/Ar, ν_{13} of CH₃CN-¹⁰BF₃ in minor and major sites was observed at 1307.9 and 1293.3 cm^{-1} , respectively. In the spectrum of CD₃CN/ BF₃/Ar, ν_{13} of CD₃CN-¹⁰BF₃ and CD₃CN-¹¹BF₃ were observed at 1291.4 and 1250.2 cm⁻¹, respectively. The absorptions attributable to a minor site could not be clearly observed. For CD₃CN/¹⁰BF₃/Ar, the only absorption at 1291.5 cm^{-1} was observed.

In the spectrum of CH₃CN/BF₃/N₂, several weak absorptions were newly observed at considerably lower frequencies from the BF₃ degenerate stretching region of the free species. The significant features appeared at 1280.8, 1277.9, 1269.9, 1235.0, 1227.6 and 1220.7 cm⁻¹. For CH₃CN/ 10 BF₃/N₂, similar new absorptions were observed at 1280.9, 1277.8 and 1270.3 cm^{-1} . Since the BF₃ degenerate stretchings of the free species reveal matrix-split features in N_2 [11,37], we assigned the bands at 1280.9, 1277.8 and 1270.3 cm⁻¹ to ν_{13} of $CH_3CN^{-10}BF_3$ as well as the bands at 1235.0, 1227.6 and 1220.7 cm^{-1} to that of CH₃CN-¹¹BF₃. It is reasonable to associate the bands at 1277.8 and 1235.0 cm^{-1} to major site. Several new absorptions were also observed in the spectrum of CD₃CN/BF₃/N₂. The significant features were at 1278.7, 1271.8, 1266.3, 1236.1, 1233.2, 1227.7 and 1218.0 cm⁻¹. For CD₃CN/¹⁰BF₃/N₂, new absorptions were observed at 1278.8, 1272.1 and 1266.3 cm⁻¹. We assigned the bands at 1278.8, 1272.1 and 1266.3 cm⁻¹ to ν_{13} of CD₃CN-¹⁰BF₃ as well as the bands at 1236.1, 1233.2, 1227.7 and 1218.0 cm^{-1} to that of CD₃CN-¹¹BF₃ for the same reason mentioned

above. The bands at 1278.8 and 1233.2 cm^{-1} would correspond to a major site.

In the spectrum of CH₃CN/BF₃/Xe, two significant absorptions were observed at 1284.8 and 1239.0 cm⁻¹. These bands should be assigned to v_{13} of CH₃CN-¹⁰BF₃ and $CH_3CN^{-11}BF_3$, respectively, though their intensity ratio was slightly different from 1:4. The corresponding absorption was observed at 1284.8 cm⁻¹ for CH₃CN/¹⁰BF₃/Xe. Three new absorptions were observed at 1282.9, 1241.3 and 1235.2 cm^{-1} for CD₃CN/BF₃/Xe. The highest frequency band was assigned to ν_{13} of CD₃CN-¹⁰BF₃ with no problem. The lower two bands were interpreted as ν_{13} of $CD_3 CN^{-11}BF_3$ with site splitting. Although there is no clear explanation for this specific site splitting, we adopted the slightly stronger absorption at 1241.3 cm⁻¹ for a major site. The corresponding absorption was observed at 1282.7 cm^{-1} for CD₃CN/¹⁰BF₃/Xe. The BF₃ degenerate stretching absorptions of the ¹⁰BF₃ and ¹¹BF₃ monomers in Xe were observed at 1491.2 and 1440.1 cm⁻¹, respectively.

3.2.5. $CH(D)_3$ symmetric deformation (v_3)

No distinctive peak attributable to the complex was observed in this region for CH₃CN/BF₃/Ar. However, a weak absorption was observed at 1374.3 cm⁻¹ as the lower frequency shoulder of the CH₃ symmetric deformation absorption of the CH₃CN monomer at 1375.7 cm⁻¹. Since the calculated frequency for this mode reveals a small red shift on complexation, we tentatively assigned this absorption to the CH₃ symmetric deformation (ν_3) of the CH₃CN–BF₃ complex. The corresponding shoulder was observed at the same frequency for CH₃CN/¹⁰BF₃/Ar. In the spectra of CD₃CN/BF₃/Ar and CD₃CN/¹⁰BF₃/Ar, no new absorptions attributable to the complexes were observed around the CD₃ symmetric deformation of the CD₃CN monomer at 1104.4 cm⁻¹.

In the spectra of CH₃CN/BF₃/N₂ and CH₃CN/¹⁰BF₃/N₂, no new distinctive peaks were observed around the CH₃CN monomer absorption at 1378.6 cm⁻¹. However, a weak shoulder at 1377.4 cm⁻¹ was found in both spectra. We tentatively assigned this absorption to ν_3 of the complex. For CD₃CN/BF₃/N₂ and CD₃CN-¹⁰BF₃/N₂, no absorptions attributable to the complex were observed around the CD₃CN monomer absorption at 1105.9 cm⁻¹.

In the spectrum of CH₃CN/BF₃/Xe, ν_3 of the complex was observed at 1368.2 cm⁻¹ as well as the CH₃CN monomer absorption at 1371.6 cm⁻¹. The corresponding absorption was observed at 1368.3 cm⁻¹ for CH₃CN/¹⁰BF₃/Xe. For both CD₃CN/BF₃/Xe and CD₃CN/¹⁰BF₃/Xe, no new absorptions were observed around the CD₃ symmetric deformation absorption of the CD₃CN monomer at 1103.8 cm⁻¹.

3.2.6. $CH(D)_3$ rocking (v_{11})

In the spectra of $CH_3CN/BF_3/Ar$ and $CH_3CN/^{10}BF_3/Ar$, no distinctive peaks were observed around the CH_3 rocking absorption of the CH_3CN monomer at 1038.2 cm⁻¹. However, the intensities of the shoulders at 1036.8 cm⁻¹ for CH₃CN/BF₃/Ar and at 1036.9 cm⁻¹ for CH₃CN/¹⁰BF₃/Ar were obviously stronger than those of free CH₃CN. We tentatively assigned these weak shoulders to the CH₃ rocking (ν_{11}) of the complexes based on the agreement with the calculated small red shift. No absorptions attributable to the complexes were observed around the CD₃ rocking of the CD₃CN monomer at 845.5 cm⁻¹ in the spectra of CD₃CN/BF₃/Ar and CD₃CN/¹⁰BF₃/Ar.

The ν_{11} absorptions for all isotopically substituted complexes could not be observed in N₂ matrices. The absorptions of the CH₃CN and CD₃CN monomers were observed at 1041.0 and 850.9 cm⁻¹, respectively.

In the spectra of CH₃CN/BF₃/Xe and CH₃CN/¹⁰BF₃/Xe, the absorptions assigned to ν_{11} of the complexes were observed at 1033.2 cm⁻¹. Two partly overlapping absorptions were observed at 1038.1 and 1036.1 cm⁻¹ with comparable intensities in the spectrum of free CH₃CN in Xe. We assigned the latter band to the CH₃ rocking of the CH₃CN monomer based on the results with different R/M ratios. The former band was tentatively assigned to the dimer. For CD₃CN/BF₃/Xe and CD₃CN/¹⁰BF₃/Xe, no absorptions attributable to the complexes were observed around the CD₃ rocking of the CD₃CN monomer at 845.0 cm⁻¹.

3.2.7. CC stretching (v_4)

In the spectra of CH₃CN/BF₃/Ar and CH₃CN/¹⁰BF₃/Ar, no new absorptions attributable to the CC stretchings (ν_4) of the complexes were observed. Although the calculated frequency for this mode reveals a distinguishable blue shift of about 30 cm^{-1} on complexation, the extremely weak infrared intensity prevents the observation of this mode. Two absorptions attributable to the complex were observed at 878.6 and 875.6 cm⁻¹ in the spectrum of CD₃CN/BF₃/ Ar. The lower frequency band was stronger though their intensity ratio was rather different from 1:4. For CD₃CN/¹⁰BF₃/Ar, only the higher frequency absorption was observed at 878.5 cm^{-1} . According to the B3LYP calculations, the CC stretching (ν_4) and the BF₃ symmetric stretching (ν_6) absorptions are expected in this region. The predicted v_6 bands reveal considerable red shifts on complexation, whereas the observed frequencies are higher than that of the BF₃ monomer described in the next section. Therefore, we assigned the absorptions at 878.5 and 875.6 cm⁻¹ to ν_4 of $CD_3CN^{-10}BF_3$ and $CD_3CN^{-11}BF_3$, respectively.

No absorptions that can be assigned to ν_4 of the complexes were observed in the spectra of CH₃CN/BF₃/N₂ and CH₃CN/¹⁰BF₃/N₂. In the spectrum of CD₃CN/BF₃/N₂, new absorptions were observed at 877.2 and 875.5 cm⁻¹. Their intensities are, however, rather weak compared to the corresponding bands in Ar. Although the exact comparison of the band intensities was difficult because of their weak intensities, the higher frequency band was a little stronger. However, only the absorption corresponding to the above stronger band was observed at 877.3 cm⁻¹ in the spectrum of CD₃CN/¹⁰BF₃/N₂.

Therefore, we only tentatively assigned the absorptions at 877.3 and 875.5 cm⁻¹ to ν_4 of CD₃CN-¹⁰BF₃ and CD₃CN-¹¹BF₃, respectively. The CC stretching absorption of the CD₃CN monomer in N₂ was observed at 830.2 cm⁻¹ for a major site and at 836.4 cm⁻¹ for a minor site.

For CH₃CN/BF₃/Xe and CH₃CN/¹⁰BF₃/Xe, no new absorptions were observed in the v_4 region. The CC stretching absorptions of the CH₃CN monomer and the polymer were observed at 927.1 and 917.7 cm⁻¹, respectively. Two new absorptions were observed at 875.5 and 872.0 cm⁻¹ in the spectrum of CD₃CN/BF₃/Xe. However, these bands had similar intensities, i.e. their intensity ratio was far from 1:4. Thus, we could not conclude whether the above two absorptions should be assigned to the complexes. No absorption was observed in this region of the spectrum of CD₃CN/¹⁰BF₃/Xe because of its poor spectral quality. The CC stretching absorption of the CD₃CN monomer in Xe was observed at 835.4 cm⁻¹.

3.2.8. BF₃ symmetric stretching (ν_6)

In the spectrum of CH₃CN/BF₃/Ar, several new absorptions were observed in this region, together with the bands of the BF₃ monomer and the polymers. The significant bands were located at 856.7, 841.4 and 811.7 cm^{-1} , which would correspond to the three features previously reported by Wells et al. [23]. They tentatively assigned the highest frequency band to the BF₃ symmetric stretching (ν_6) activated by complexation. For CH₃CN/¹⁰BF₃/Ar, new absorptions were observed at 876.0, 870.8 842.3, 827.7 and 813.5 cm^{-1} . The band at 870.8 cm^{-1} seems to be corresponding to that at 856.7 cm⁻¹ in the CH₃CN/BF₃/Ar spectrum in view of the similarity between their band shapes. However, the pair of absorptions at 813.5 and 811.7 cm^{-1} would be the alternative candidate. A very weak absorption was observed at 876.0 cm^{-1} in the spectrum of free BF₃ in Ar, which can be assigned to the BF₃ symmetric stretching absorption of the BF₃ monomer activated in a matrix environment. The calculated frequencies for the BF3 symmetric stretchings reveal red shifts of larger than 50 cm⁻¹ and ¹⁰B/¹¹B splittings of about 5 cm⁻¹ on complexation. Therefore, we tentatively adopted the absorptions at 813.5 and 811.7 cm^{-1} as the first candidates for ν_6 of CH₃CN–¹⁰BF₃ and CH₃CN–¹¹BF₃, respectively. In the spectrum of CD₃CN/BF₃/Ar, a new absorption was observed at 808.1 cm⁻¹, together with several bands due to free BF₃ and CD₃CN. The corresponding absorption was observed at 814.9 cm^{-1} for $CD_3CN/^{10}BF_3/Ar$. Although the intensity of the band in CD₃CN/BF₃/Ar was rather weak, we tentatively assigned the bands at 814.9 and 808.1 cm⁻¹ to ν_6 of CD₃CN⁻¹⁰BF₃ and CD₃CN⁻¹¹BF₃, respectively.

Two new absorptions were observed at 843.5 and 835.8 cm⁻¹ in the spectrum of CH₃CN/BF₃/N₂. For CH₃CN/¹⁰BF₃/N₂, only the band at 843.5 cm⁻¹ was observed. The matrix-activated BF₃ symmetric stretching absorption [8] was observed at 879.9 cm⁻¹ in the spectrum

of free BF₃. Thus, we assigned the absorptions at 843.5 and 835.8 cm⁻¹ to ν_6 of CH₃CN–¹⁰BF₃ and CH₃CN–¹¹BF₃, respectively, though the observed red shifts were smaller than the predicted values. No absorptions attributable to the complexes were observed in the spectra of CD₃CN/BF₃/N₂ and CD₃CN/¹⁰BF₃/N₂.

In the spectrum of CH₃CN/BF₃/Xe, several new absorptions were observed at 873.3, 858.2, 838.4 and 809.0 cm⁻¹. For CH₃CN/¹⁰BF₃/Xe, the observed absorptions were located at 873.1, 827.2 and 810.8 cm⁻¹. Two pairs of absorptions, 873.1/858.2 cm⁻¹ and 810.8/809.0 cm⁻¹, are considered to be candidates for ν_6 of the complexes. We tentatively adopted the latter pair according to the same reason explained for the results in Ar. A very weak absorption observed at 880.6 cm⁻¹ in the spectrum of free BF₃ in Xe was assigned to the matrix-activated BF₃ symmetric stretching of the BF₃ monomer. In the spectra of CD₃CN/BF₃/Xe and CD₃CN/¹⁰BF₃/Xe, no new absorptions attributable to the complexes were observed.

3.2.9. BF₃ symmetric deformation (ν_7)

Several new absorptions were observed at considerably lower frequencies from the BF₃ symmetric deformation region of free BF₃ in the spectrum of CH₃CN/BF₃/Ar. The significant features appeared at 646.4, 631.8, 617.1 and 601.2 cm^{-1} . The intensity ratio between the former two bands, as well as that between the latter two, were about 1:4. The corresponding absorptions were observed at 646.3 and 618.0 cm^{-1} for CH₃CN/¹⁰BF₃/Ar. As previously reported, the absorptions at 618.0 and 601.2 cm^{-1} are the BF₃ symmetric deformations (ν_7) of CH₃CN-¹⁰BF₃ and CH₃CN-¹¹BF₃, respectively. The other two absorptions at 646.3 and 631.8 cm⁻¹ were assigned to the corresponding species in a minor site. Somewhat large site splittings of about 30 cm^{-1} suggest that this vibrational mode is sensitive to a microscopic environment around the complex. In the spectrum of CD₃CN/BF₃/Ar, the absorptions at 629.5 and 601.5 cm^{-1} were distinguished from a number of absorptions of the BF₃ polymers. The corresponding absorptions were observed at 644.1 and 621.4 cm^{-1} for $CD_3CN/^{10}BF_3/$ Ar. The bands at 621.4 and 601.5 cm⁻¹ were assigned to ν_7 of CD₃CN-¹⁰BF₃ and CD₃CN-¹¹BF₃, respectively. The other two bands at 644.1 and 629.5 cm^{-1} were assigned to the corresponding species in a minor site.

In the spectrum of CH₃CN/BF₃/N₂, several new absorptions were observed at somewhat lower frequencies from the BF₃ symmetric deformation region of free BF₃. The significant features appeared at 640.5, 632.8, 625.3 and 617.1 cm⁻¹. The intensity ratio between the bands at 632.8 and 617.1 cm⁻¹ was about 1:4. However, the ratio between the bands at 640.5 and 625.3 cm⁻¹ was slightly different from 1:4 probably because of the overlapping with other absorptions. The only two corresponding absorptions were observed at 640.6 and 633.0 cm⁻¹ for CH₃CN/¹⁰BF₃/N₂. Therefore, we assigned the absorptions at 640.6 and 625.3 cm⁻¹ to ν_7 of CH₃CN/⁻¹⁰BF₃ and CH₃CN/⁻¹¹BF₃ in

N₂, respectively. The other two bands at 633.0 and 617.1 cm^{-1} were assigned to the corresponding species in a minor site. The intensities of these bands of the complexes in N₂ are rather weak compared to those in Ar. Furthermore, the magnitudes of the frequency shifts on complexation for major and minor sites are altered. In the spectrum of CD₃CN/BF₃/N₂, several absorptions were observed at 639.0, 632.0, 623.7 and 616.0 cm^{-1} with a spectral pattern similar to CH₃CN/BF₃/N₂. The only two corresponding absorptions were observed at 639.1 and 631.9 cm⁻¹ for CD₃CN/¹⁰BF₃/N₂. Thus, the absorptions at 639.1 and 623.7 cm⁻¹ were assigned to ν_7 of CD₃CN-¹⁰BF₃ and $CD_3CN-^{11}BF_3$, respectively. The other two bands at 631.9 and 616.0 cm^{-1} were assigned to the corresponding species in a minor site. The BF₃ symmetric deformations of the $^{10}BF_3$ and $^{11}BF_3$ monomers were observed at 683.6 and 657.6 cm⁻¹, respectively, which are about 20 cm⁻¹ lower than those in Ar.

In the spectrum of CH₃CN/BF₃/Xe, new absorptions were observed at considerably lower frequencies from the BF₃ symmetric deformation region of free BF₃. The significant features appeared at 645.7, 631.1, 616.9 and 601.7 cm⁻¹. The intensity ratio between the bands at 645.7 and 631.1 cm^{-1} as well as the ratio between the bands at 616.9 and 601.7 cm^{-1} were about 1:4. The only two absorptions were observed at 645.6 and 616.9 cm⁻¹ for CH₃CN/¹⁰BF₃/ Xe. Thus, we assigned the absorptions at 616.9 and 601.7 cm⁻¹ to ν_7 of CH₃CN-¹⁰BF₃ and CH₃CN-¹¹BF₃ in Xe, respectively. The other two absorptions at 645.6 and 631.1 cm^{-1} were assigned to the corresponding species in a minor site. Relative intensities of the minor site absorptions in Xe were much weaker than those in Ar. The BF₃ symmetric deformations of the ¹⁰BF₃ and ¹¹BF₃ monomers in Xe were observed at 702.4 and 675.4 cm^{-1} , respectively. The associated weak absorptions observed at 697.4 and 670.2 cm^{-1} were assigned to BF₃ dimers. A lot of new absorptions were observed in this region of the CD₃CN/BF₃/Xe spectrum. We assigned the absorptions observed at 614.5 and 599.7 cm⁻¹ to ν_7 of CD₃CN-¹⁰BF₃ and CD₃CN-¹¹BF₃, respectively. The corresponding bands for a minor site were observed at 643.1 and 628.6 cm^{-1} .

3.2.10. BF₃ degenerate deformation (v_{14})

In the spectrum of CH₃CN/BF₃/Ar, a weak new absorption was observed at 502.9 cm⁻¹, which can be clearly distinguished from the complicated absorptions of the BF₃ polymers in a region of 510–520 cm⁻¹. The corresponding absorption was observed at 504.5 cm⁻¹ for CH₃CN/¹⁰BF₃/Ar. The calculated frequencies of the BF₃ degenerate deformations reveal medium blue shifts on complexation. Thus, we assigned the absorptions at 504.5 and 502.9 cm⁻¹ to the BF₃ degenerate deformations (ν_{14}) of CH₃CN-¹⁰BF₃ and CH₃CN-¹¹BF₃ in Ar, respectively. Similar new absorptions were observed at 498.0 cm⁻¹ for CD₃CN/BF₃/Ar and at 500.1 cm⁻¹ for CD₃CN-¹¹BF₃

and $CD_3CN-{}^{10}BF_3$, respectively. The BF₃ degenerate deformations of the ${}^{10}BF_3$ and ${}^{11}BF_3$ monomers in Ar were observed at 481.2 and 479.7 cm⁻¹, respectively.

No absorptions attributable to the complexes were observed in this region of the spectra for all isotopically substituted species in N₂. The BF₃ degenerate deformations of the ¹⁰BF₃ and ¹¹BF₃ monomers in N₂ were observed as matrix-split bands at 481.1/479.7 and 479.2/477.8 cm⁻¹, respectively.

In the spectrum of CH₃CN/BF₃/Xe, a new absorption was observed at 502.5 cm⁻¹. The corresponding absorption was observed at 503.5 cm⁻¹ for CH₃CN/¹⁰BF₃/Xe, though its intensity was quite weak. Thus, the absorptions at 503.5 and 502.5 cm⁻¹ were assigned to ν_{14} of CH₃CN–¹⁰BF₃ and CH₃CN–¹¹BF₃, respectively. The absorptions of the ¹⁰BF₃ and ¹¹BF₃ monomers in Xe were observed at 479.7 and 477.8 cm⁻¹, respectively. For CD₃CN/BF₃Xe, a less reliable broad absorption was observed at 497.6 cm⁻¹, which was tentatively assigned to ν_{14} of CD₃CN–¹¹BF₃ in Xe.

3.3. Matrix effects on vibrational spectra

The structures of the 1:1 complexes of acetonitrile and boron trifluoride trapped in Ar, N₂ and Xe matrices are thought to be essentially the same as the optimized geometry obtained at the B3LYP/6-311 + +G(d,p) level by considering the observed and the calculated vibrational frequencies, especially the frequency shifts on complexation $\Delta \nu$, described in the above sections. However, some matrix effects on the vibrational spectra of the complexes were also recognized. As can be seen in Figs. 2–4, the absorptions of the complexes in N_2 are weaker than those in Ar and Xe. Because of the stronger interaction of the lonepair electron in N_2 molecule with the boron atom in free BF₃, it is expected that N_2 and BF₃ form a weak van der Waals complex [14] during the co-deposition of N_2 matrices. Although the interaction of CH₃CN with BF₃ is stronger than that of N_2 , a great number of N_2 molecules would prevent the formation of the CH₃CN–BF₃ complex to a certain extent. As a result, the percentage of BF₃ that forms the complex with CH₃CN, therefore the infrared intensities of the complex, would have decreased in N_2 matrices.

The $\Delta \nu$ of the selected vibrations of the complexes in Ar, N₂ and Xe matrices are compared in Table 7. The $\Delta \nu$ of the BF₃ degenerate stretchings and symmetric deformations reveal comparable magnitudes in Ar and Xe matrices. However, the $\Delta \nu$ of the CN stretchings are somewhat smaller in Xe. The CN stretching frequency of the CH₃CN monomer is slightly different from that in Ar or N₂. This suggests that a particular vibrational mode is more affected by a matrix environment than others.

The magnitudes of the observed $\Delta \nu$ for most of the vibrational modes that reveal remarkable shifts are larger than the calculated values at the B3LYP/6-311 + +G(d,p) level. This seems to indicate that the interaction between acetonitrile and boron trifluoride in low temperature matrices is stronger than that predicted by calculation. However, the BF₃ symmetric deformation mode is an exception. The observed magnitudes of $\Delta \nu$ for this mode are obviously smaller than the calculated values. As one reason for this,

Table 7

Comparison of the frequency shift $\Delta \nu$ (cm⁻¹) of the acetonitrile-boron trifluoride complexes in different matrices

Species	Mode	Calculated	Experimental			Approximate
		B3LYP/6-311 + +G(d,p)	in Ar	in N ₂	in Xe	description ^a
CH ₃ CN- ¹¹ BF ₃						
	ν_2	+73.0	+107.3	+109.8	+95.3	CN str
	ν_7	-103.1	-74.7	-32.3	-73.7	¹¹ BF ₃ sym def
			-44.1	-40.5	-44.3	Minor site
	ν_{13}	-174.7	-198.5	-208.2	-201.1	¹¹ BF ₃ deg str
CH ₃ CN- ¹⁰ BF ₃						
	ν_2	+73.0	+107.4	+109.8	+95.3	CN str
	ν_7	-114.3	-85.1	-43.0	-85.5	¹⁰ BF ₃ sym def
			-56.8	-50.6	-56.8	Minor site
	v_{13}	-180.3	-205.1	-216.7	-206.4	¹⁰ BF ₃ deg str
CD ₃ CN- ¹¹ BF ₃						
	ν_2	+73.0	+95.0	+98.9	+86.2	CN str
	ν_7	-103.7	-74.4	-33.9	-75.7	¹¹ BF ₃ sym def
			-46.4	-41.6	-46.8	Minor site
	v_{13}	-174.7	-197.0	-210.0	-198.8	¹¹ BF ₃ deg str
CD ₃ CN- ¹⁰ BF ₃						
	ν_2	+73.0	+94.9	+98.8	+85.5	CN str
	ν_7	-114.8	-81.7	-44.5	-87.9	¹⁰ BF ₃ sym def
	-		-59.0	-51.7	-59.3	Minor site
	ν_{13}	-180.4	-206.9	-215.7	-208.5	¹⁰ BF ₃ deg str

^a Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.

coordination of the matrix atom or molecule to the BF₃ moiety of the complex from the opposite side of the CH₃CN moiety seems to be important. This weak interaction with a matrix environment would reduce the red shift of the BF₃ symmetric deformation of the complex. Particularly small magnitudes of $\Delta \nu$ in N₂ seem to support this explanation.

The frequency differences between the BF_3 symmetric deformations of the major and minor site species are remarkably large in Ar and Xe matrices. A large site splitting suggests that even a low dielectric matrix can affect the nature of the vibrations or bondings of the complex. Furthermore, this matrix effect is mode specific for the vibrational spectra. A similar consideration of the theoretical study on the B–N bond length of the complex was reported in the literature [29].

4. Conclusions

The FTIR spectra of CH₃CN-BF₃ including its isotopically substituted species were observed in Ar, N2 and Xe matrices, and matrix effects on the vibrational spectra of the complexes were investigated. Several previously unreported new absorptions were observed in Ar. The vibrational spectra in N₂ and Xe were recorded for the first time. The observed frequency shifts on complexation, $\Delta \nu$, were qualitatively in good agreement with the results calculated at the $C_{3\nu}$ eclipsed optimized geometry at the B3LYP/6-311 + + G(d,p) level. For most of the vibrational modes that reveal remarkable frequency shifts, the observed magnitudes of $\Delta \nu$ were larger than the calculated values. Therefore, the interaction that is responsible for the complex formation in low temperature matrices is considered to be stronger than that predicted by calculation. However, the observed frequency shits for the BF₃ symmetric deformations were smaller than the calculated values, especially in N₂. This suggests that even an inert matrix like rare gas or N₂ has a significant effect on a particular vibrational mode.

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