The Complexes between CH_3OH and CF_4. Infrared Matrix Isolation and Theoretical Studies

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The complex formed between methanol and tetrafluoromethane has been identified in argon and neon matrixes by help of FTIR spectroscopy. Three fundamentals (ν(OH), ν(FCF), and ν(CO)) were observed for the complex isolated in the two matrixes, and the OH stretch was red shifted in a neon matrix and blue shifted in an argon matrix with respect to the corresponding vibration of the methanol monomer. The theoretical studies of the structure and spectral characteristics of the complexes formed between CH_3OH and CF_4 were carried out at the MP2 level of theory with the 6-311+G(2df,2pd) basis set. The calculations resulted in three stationary points from which two (I-1, I-2) corresponded to structures involving the O−H···F hydrogen bond and the third one (I-3) to the non-hydrogen-bonded structure. The topological analysis of the distribution of the charge density (AIM theory) confirmed the existence of the hydrogen bond in I-1, I-2 complexes and indicated weak interaction between the oxygen atom of CH_3OH and three fluorine atoms of CF_4 in the I-3 complex. The comparison of the experimental and theoretical data suggests that in the matrixes only the non-hydrogen-bonded complex I-3 is trapped. The blue/red shift of the complex OH stretching vibration with respect to the corresponding vibration of CH_3OH in argon/neon matrixes is explained by the different sensitivity of the complex and monomer vibrations to matrix material. The ab initio calculations performed for the ternary CH_3OH-CF_4-Ar systems indicated a negligible effect of an argon atom on the binary complex frequencies.

Introduction

Tetrafluoromethane CF_4 (also known as Freon-14) is a molecule of wide-ranging industrial and environmental interest. It is utilized widely as an insulator and extinguisher gas in high-voltage application and as an etching gas in the semiconductor industry.[1] The ionization dynamics of the $CF_4\cdots H_2O$ complexes have been recently investigated to shed light on the mechanism of plasma dry etching of silicon surface by CF_4.[2] The formation of $CF_4\cdots O_2$ adducts was considered as a model system for the use of liquid perfluorochemicals in artificial blood.[3]

Recently, Alabugin et al.[4] have suggested that the hydrogen-bonded complexes of tetrafluoromethane with various alcohols $ROH\cdots CF_4$ (R=Me, CH_2OH, *t*-Bu, NH_2CH_2) should display the characteristic features of improper, blue-shifting H-bonding. The blue-shifting hydrogen bonding has been recently in the center of interest of many researchers.[4−7] A characteristic feature of the improper hydrogen bond is the X−H bond shortening with a concomitant blue shift of the X−H IR stretching frequency after X−H···Y bond formation. This behavior is opposite of that expected for a conventional X−H···Y hydrogen bond. Experimental evidence for the blue shifts was obtained mainly for the C−H···Y hydrogen bonds.[7] From its discovery, blue-shifting H-bonding received much attention from theoreticians who suggested several explanations for this phenomena.[5,6,8] Recent theoretical studies suggest that improper hydrogen bonding is more general and can be observed for the hydrogen bonds in which Si−H, P−H, N−H,[4,6,9,10] and even OH[4] are proton donors. A blue shift of the OH stretching frequency has been reported recently for the O−H···Ar hydrogen bond in the hydroquinone−argon complex.[11] Alabugin et al.[4] reported that tetrafluoromethane complexes with methanol should display all characteristic features of improper H-bonding and are strong enough to be observed experimentally.

In this paper, we present the detailed infrared matrix isolation and theoretical studies of the tetrafluoromethane complexes with methanol. To minimize the effect of surrounding on the complex, we studied the complexes in argon and neon matrixes. For comparison, the results obtained for the CH_3F complexes with methanol are also presented.

Experimental Section

Infrared Matrix Isolation Studies. The methanol and tetrafluoromethane (CF_4) or fluoromethane (CH_3F) were premixed with argon or neon in a stainless steel vacuum line. The concentration of MeOH/CF_4/Ar(Ne) varied in a range between 1/*n*/2000 ($n = 2, 5$) and *m*/*n*/1000 ($m = 1, 2, 5$; $n = 1, 2, 4, 6$). The gas mixtures were condensed onto a gold plated copper block kept at 18 K (Ar matrix) or 4.7 K (Ne matrix). The temperature was maintained by means of a closed-cycle helium cryogenerator (Air Products, Displex 202A or Cryomech PT-405). Infrared spectra were recorded at 11 K (Ar matrix) or 4.7 K (Ar and Ne matrixes) with a resolution of 0.5 or 0.12 cm^{-1} by means of a Bruker 113v FTIR or Bruker IFS/66S spectrometer equipped with a liquid N_2 cooled MCT detector.

Computational Details. All calculations were performed using the Gaussian 03 program.[12] The structures of the CF_4, CH_3F, and CH_3OH monomers and CF_4-CH_3OH, CF_4-CH_3OH-

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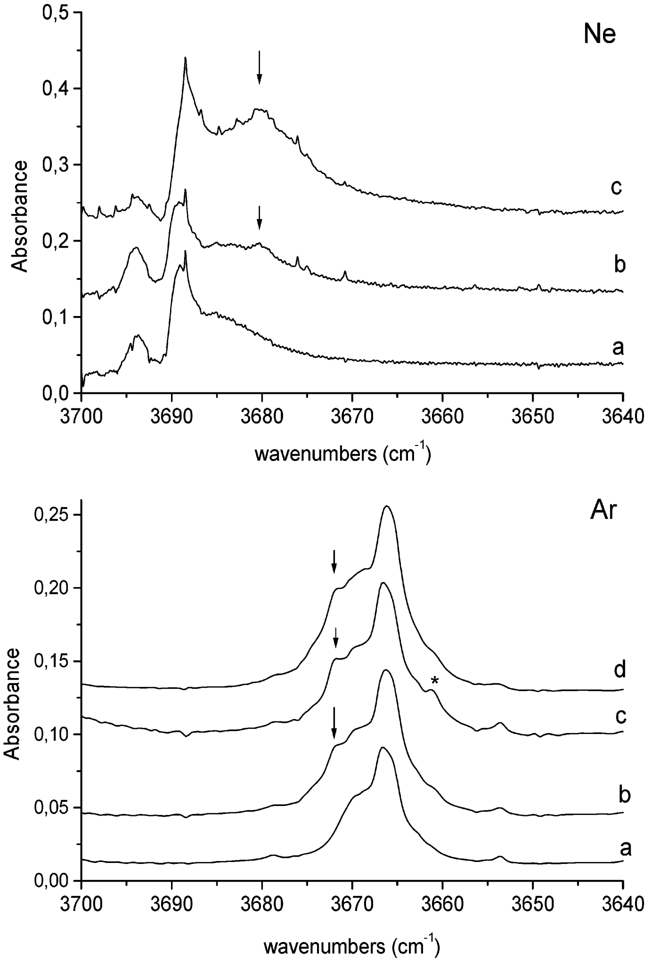

Figure 1. The spectra of the CH$_3$OH/CF$_4$/Ne(Ar) matrixes in the OH stretching region. Ne: (a) the spectrum of the CH$_3$OH/Ne = 1/1000 matrix; (b,c) the spectra of the CH$_3$OH/CF$_4$/Ne = 1/5/1000, 1/2/500, respectively. Ar: (a) the spectrum of the CH$_3$OH/Ar = 1/1000 matrix; (b,d) the spectra of the CH$_3$OH/CF$_4$/Ar = 1/4/1000, 1/6/1000, respectively; (c) the spectrum of matrix (b) after annealing to 32 K for 15 min. The bands due to CF$_4$$\cdots$CH$_3$OH complexes are indicated by arrows; the band due to the water−methanol complex is indicated by an asterisk.

Ar, and CH$_3$F−CH$_3$OH complexes were optimized at the MP2 level with the 6-311+G(2df,2pd) basis set.[13,14] Vibrational frequencies and intensities for the monomers and for the binary complexes were obtained at the same level of theory.

The interaction energies of the clusters were corrected by the Boys−Bernardi full counterpoise correction (CP).[15] The interaction energy of the ternary complex has been obtained by subtracting the energies of the isolated monomers from the energy of the complex. Here, the geometries of the monomers correspond to those in the complex and are deformed from their equilibrium values. The two-body interaction energy ΔE^2 in the ternary complex was evaluated as a sum of the two-body interaction terms. The difference between the total interaction energy ΔE_{tot} of trimers and the pairwise interaction energies ΔE^2 represents the cooperative effect in trimer: $\Delta E^3 = \Delta E_{\mathrm{tot}} - \Delta E^2$.

The topological analysis of the electron density has been performed at the MP2/6-311+G(2df,2pd) level of theory with the AIMPAC set of programs.[16]

Results

Experimental Spectra. Infrared spectra of CH$_3$OH in argon and nitrogen matrixes have been extensively studied;[17−20] the spectra of CF$_4$ in argon and neon matrixes have been also recently studied.[21] In the spectra of argon and neon matrixes doped with methanol and tetrafluoromethane or fluoromethane, new absorptions appeared as compared to the spectra of parent molecules: CH$_3$OH, CF$_4$, and CH$_3$F. The new absorptions are assigned to the complexes formed between methanol and CF$_4$ or CH$_3$F and will be discussed below.

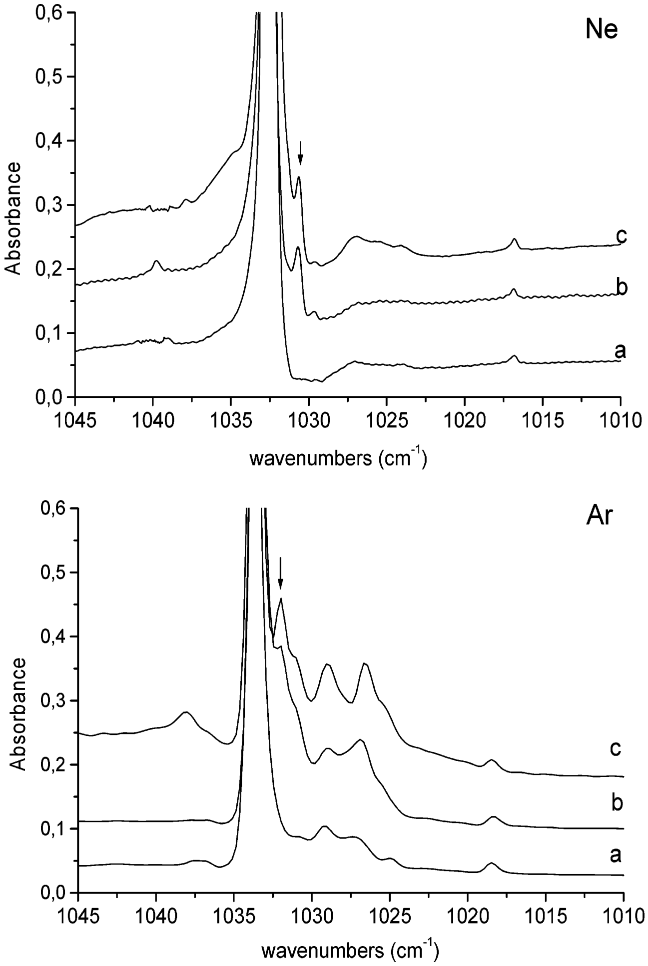

Figure 2. The spectra of the same matrixes as presented in Figure 1 in the C−O stretching region.

Methanol−Tetrafluoromethane Complex. Figures 1−3 present the spectra of the CH$_3$OH/CF$_4$/Ar and CH$_3$OH/CF$_4$/Ne matrixes in the regions of the O−H and C−O stretching vibrations of methanol and in the region of the asymmetric FCF stretching vibrations of CF$_4$. In the spectra of argon matrixes doped with both CH$_3$OH and CF$_4$, a shoulder appears at 3671.7 cm^{-1} on the high-frequency side of the ν(OH) stretching band of CH$_3$OH monomer (Figure 1). The 3671.7 cm^{-1} shoulder is accompanied by a 1032.0 cm^{-1} band occurring on the low-frequency side of the C−O stretching absorption of CH$_3$OH (Figure 2) and by a 1248.4 cm^{-1}, 1246.9 cm^{-1} doublet in the region of the asymmetric FCF stretching vibrations (ν_3) of CF$_4$ (Figure 3). A shoulder at 1282.0 cm^{-1} observed in the region of the ν_3, CF$_4$ vibration on the 1281.0 cm^{-1} absorption is also tentatively assigned to the CH$_3$OH$\cdots$CF$_4$ complex. In addition, very weak bands at 2050.9 cm^{-1} and at 1472.2 cm^{-1}, which appear close to 2ν(CO) overtone and to δ_{as}(CH$_3$) absorptions of CH$_3$OH monomer, respectively, are also assigned to the CH$_3$OH$\cdots$CF$_4$ complex. All of the above product bands are observed in the spectra of matrixes with very low CH$_3$OH concentration (in which mostly CH$_3$OH monomers are present). The relative intensities of all bands are constant within the range

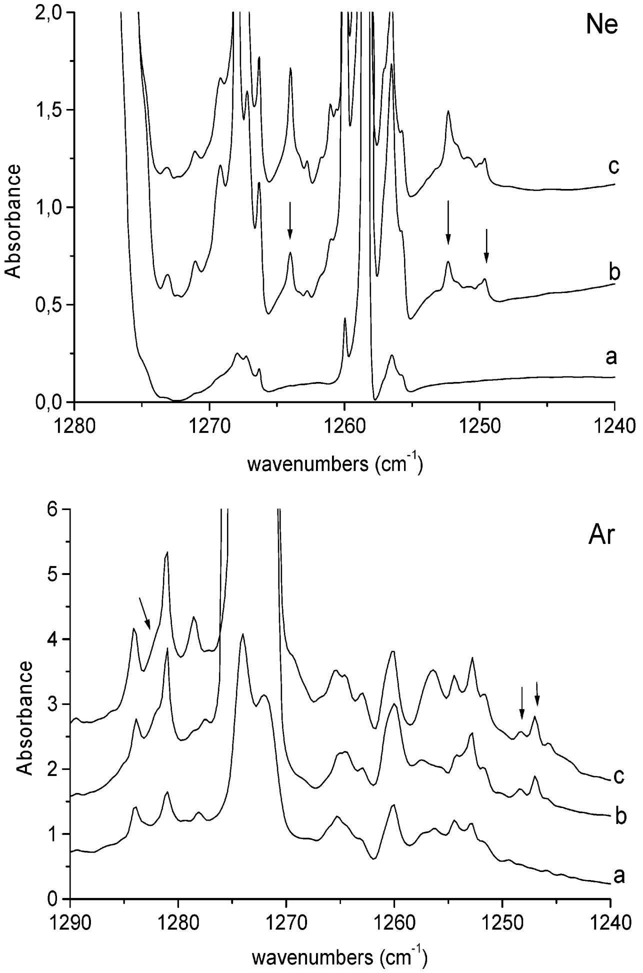

Figure 3. The spectra of the same matrixes as presented in Figure 1 in the $\nu_3(CF_4)$ stretching region.

TABLE 1: The Experimental Frequencies and Frequency Shifts (cm^{-1}) for the $CH_3OH\cdots CF_4$ Complexes Isolated in Neon and Argon Matrixes

Ne matrix			Ar matrix			
CH_3OH/CF_4	complex		CH_3OH/CF_4	complex		
ν	ν	$\Delta\nu$	ν	ν	$\Delta\nu$	assignment
3688.5	3680.0	−8.5	3666.4	3671.7sh	+5.3	ν(OH)
			2054.3	2050.9	−3.4	2ν(CO)
1277.6s	1252.3	−25.3	1274.2s	1246.9 s	−27.3	$\nu_{as}(CF_4)$
1278.4	1249.6	−28.8	1272.2	1248.4	−23.8	$\nu_{as}(CF_4)$
1032.6	1030.6	−2	1033.4	1032.0	−3.4	ν(CO)

of studied concentrations, indicating that they are due to the 1:1 $CH_3OH\cdots CF_4$ complex. The experimental frequencies of the $CH_3OH\cdots CF_4$ complex isolated in argon and neon matrixes are presented in Table 1.

The absorptions observed in the spectra of argon matrixes at 3671.7, 1032.0 cm^{-1} and the doublet at 1248.4, 1246.9 cm^{-1} have their counterparts in the spectra of neon matrixes at 3680.0, 1030.6 cm^{-1} and at 1252.3, 1249.6 cm^{-1}, respectively (see Figures 1−3). It is interesting to note that the OH stretching vibration of $CH_3OH\cdots CF_4$ is red shifted (−8.5 cm^{-1}) with respect to the OH stretch of methanol monomer when the complex is isolated in neon, whereas it is blue shifted (+5.3 cm^{-1}) for the complex isolated in argon. The other complex absorptions show similar perturbation in both argon and neon matrixes (see Table 1). In addition, a product band at 1264 cm^{-1} is also assigned to the $CH_3OH\cdots CF_4$ complex; no other bands were identified for the complex in neon matrixes.

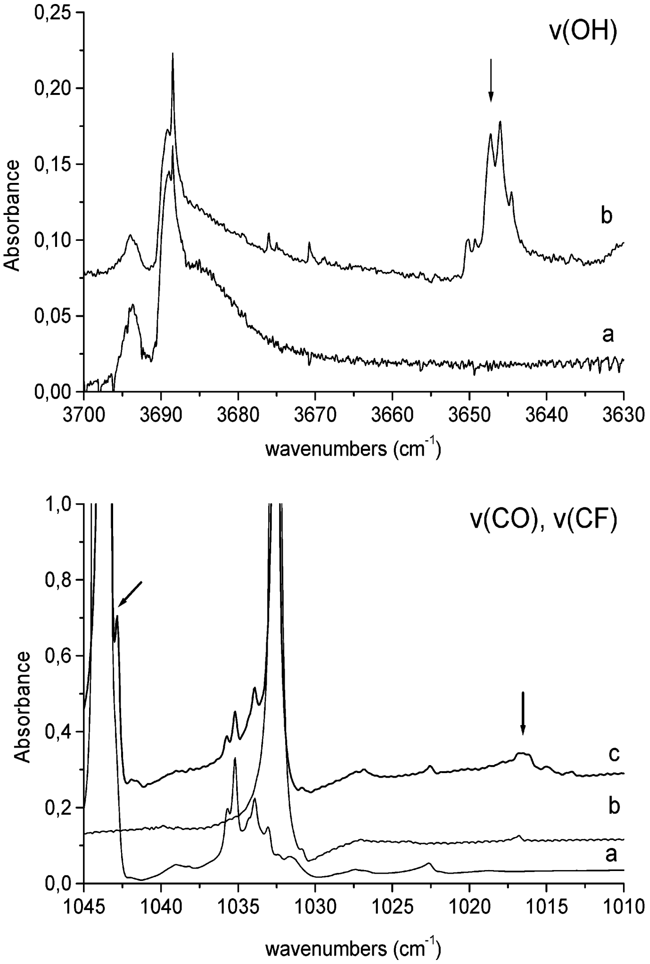

Figure 4. The spectra of the $CH_3OH/CH_3F/Ne = 1/1/500$ matrix in the OH stretching (b) and CO, CF stretching regions (c). The spectra of $CH_3OH/Ne = 1/1000$ and $CF_4/Ne = 1/500$ are presented for comparison. The bands due to complexes are indicated by arrows.

TABLE 2: The Comparison of the Calculated and Experimental Frequencies and Frequency Shifts (cm^{-1}) for the $CH_3OH\cdots CH_3F$ Complexes Isolated in Neon Matrixes

calculated			experimental			
CH_3F/CH_3OH	complex		CH_3F/CH_3OH	complex		assign-ment
ν	ν	$\Delta\nu$	ν	ν	$\Delta\nu$	
				3650.0		
				3647.2		
3923.0	3874	−49	3688.4	3646.0s	−42.4	ν(OH)
				3644.5		
1091.5	1057.7	−33.8	1043.7	1016.4	−27.3	ν(CF)
1066.4	1088.5	+22.1	1032.6	1041.7(?)	+9.1	ν(CO)

Methanol-Fluoromethane Complex. In Figure 4, the spectra of $CH_3OH/CH_3F/Ne$ matrix in the region of the OH stretching and FCF and CO stretching vibrations are presented; the experimental frequencies are compared to the calculated ones in Table 2. Three absorptions were identified for the $CH_3OH\cdots CH_3F$ complex isolated in neon matrixes. A product band with a characteristic structure appears in the OH stretching region at ca. 3646 cm^{-1}. The other band due to the complex is identified in the CF and CO stretching regions at 1016.4 cm^{-1}. A shoulder that occurs on the strong CF stretching band at 1041.7 cm^{-1} is also tentatively assigned to the $CH_3OH\cdots CH_3F$ complex.

Ab Initio Calculations. Three optimized structures (I-1, I-2, I-3) of the $CH_3OH\cdots CF_4$ complex are presented in Figure 5. In Table 3, the selected structural parameters and interaction energies are collected for the three structures. The whole set of

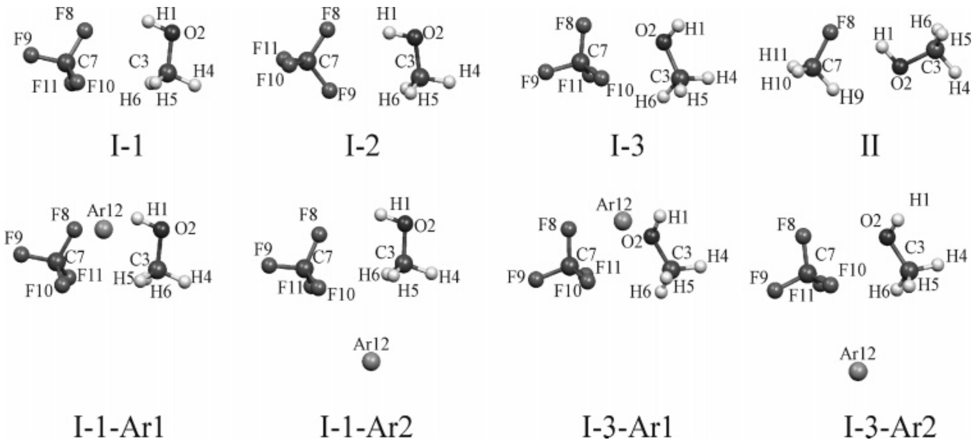

Figure 5. The optimized structures of the binary $CF_4\cdots CH_3OH$, $CH_3F\cdots CH_3OH$ complexes and ternary $CF_4\cdots CH_3OH\cdots Ar$ complexes.

TABLE 3: The Selected Structural and Spectroscopic Parameters for the $CF_4\cdots CH_3OH$ and $CH_3F\cdots CH_3OH$ Complexes

	α (F⋯H−O) [deg]	r(F⋯H) [Å]	r(O⋯C) [Å]	Δr (O−H)[a] [Å]	ΔE(BSSE)[c] kcal mol^{-1}
I-1	147.50	2.3391	4.0148	0.0001	−0.59
I-1[b]		2.3511		−0.0004	−0.19
I-2	172.62	2.2735	4.0185	−0.0001	−0.51
I-1−Ar1	146.23	2.3439	4.0211	0.0002	−1.04 (−0.05)
I-1−Ar2	143.16	2.3879	4.0492	0.0002	−0.99 (−0.05)
I-3			3.1897	0.0003	−1.02
I-3−Ar1			3.1848	0.0004	−1.44 (−0.10)
I-3−Ar2			3.1927	0.0004	−1.36 (−0.06)
II	148.86	1.9702	3.2090	0.0032	−3.54

[a] The difference between the complex and methanol monomer, $\Delta r = r_{comp} - r_{mon}$. [b] Data from ref 4. [c] The cooperative effect for the ternary complexes is given in the brackets.

TABLE 4: The Calculated Frequencies (ν, cm^{-1}), Frequency Shifts upon Complexation ($\Delta\nu$, cm^{-1}), and Intensities (km mol^{-1}) for the Optimized Structures of the $CH_3OH\cdots CF_4$ Complexes

I-1		I-2		I-3		
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	assignment
3929 (61)	+6	3933 (87)	+10	3919 (44)	−4	ν(OH)
3197 (22)	−2	3196 (23)	−3	3201 (17)	+2	$\nu_{as}(CH_3)$
3139 (36)	−1	3138 (40)	−2	3142 (39)	+2	$\nu_{as}(CH_3)$
3066 (49)	−2	3066 (50)	−2	3069 (51)	+1	$\nu_s(CH)_3$
1537 (6)	+2	1534 (5)	−1	1533 (5)	−2	$\delta_{as}(CH_3)$
1525 (3)	+2	1523 (4)	0	1524 (4)	+1	$\delta_{as}(CH_3)$
1493 (4)	−1	1494 (5)	0	1494 (4)	0	$\delta_s(CH_3)$
1385 (12)	+7	1387 (33)	+9	1379 (32)	+1	δ(COH)
1309 (463)	+10	1313 (410)	+14	1313 (383)	+14	$\nu_{as}(CF_4),\nu_3$
1305 (384)	+6	1303 (474)	+4	1300 (378)	+1	$\nu_{as}(CF_4),\nu_3$
1280 (415)	−19	1278 (394)	−21	1277 (489)	−22	$\nu_{as}(CF_4),\nu_3$
1190 (0)	+2	1190 (0)	+2	1189 (0)	+1	$\rho(CH_3)$
1103 (4)	+2	1104 (8)	+3	1101 (8)	0	$\rho(CH_3)$
1071 (117)	+5	1072 (90)	+6	1066 (97)	0	ν(C−O)
925 (1)	0	925 (1)	0	924 (0)	−1	$\nu_s(CF_4),\nu_1$
640 (3)	+1	641 (6)	+2	640 (5)	+1	$\delta_{as}(CF_4),\nu_4$
640 (7)	+1	639 (4)	0	640 (4)	+1	$\delta_{as}(CF_4),\nu_4$
639 (5)	0	638 (6)	−1	636 (6)	−3	$\delta_{as}(CF_4),\nu_4$
442 (40)	+1	443 (0)	+2	443 (0)	+2	$\delta_s(CF_4),\nu_2$
441 (0)	0	440 (0)	−1	441 (0)	0	$\delta_s(CF_4),\nu_2$
332 (97)		347 (99)		301 (110)		τ_{OH}

structural parameters for the three structures are presented in the Supporting Information. The complexes I-1 and I-2 are stabilized by a very weak hydrogen bond between the OH group of methanol and F atom of tetrafluoromethane; they differ with the orientation of CF_4 with respect to methanol. The complex I-3 is stabilized by van der Waals interaction. The optimized structure, II, of the $CH_3OH\cdots CH_3F$ complex is also presented in Figure 5; it is stabilized by the hydrogen bond between the OH group and F atom. The formation of a hydrogen bond has a negligible effect on the O−H bond length of methanol in the I-1, I-2 complexes; larger lengthening of the OH bond (0.0003 Å) is calculated for the I-3 complex than for the I-1, I-2 ones. The non-hydrogen-bonded complex I-3 is also more stable than the I-1, I-2 complexes (−1.02 kcal mol^{-1} versus −0.59, −0.51 kcal mol^{-1}, respectively). The complex II between methanol and fluoromethane ($\Delta E = -3.54$ kcal mol^{-1}) is much more stable than the I-1, I-2 complexes. The formation of a relatively strong hydrogen bond is accompanied by lengthening of the OH bond by 0.0032 Å.

The calculations indicate two true minima for the ternary CH_3OH-CF_4-Ar systems in which an Ar atom is attached to the binary I-1 or I-3 structures (see Figure 5 and Table 3). In the complexes I-1−Ar1 and I-3−Ar1, the argon atom is placed above the C(7)F(8)H(1)O(2) plane and above the F(8)⋯H(1) bond, whereas in the complexes I-1−Ar2 and I-3−Ar2 the argon atom is placed below the F(11)F(10)H(6)H(5) plane. The attachment of one argon atom to the binary complex slightly stabilizes it; however, the cooperative effects in the ternary I-1−Ar1, I-1−Ar2, I-3−Ar1, and I-3−Ar2 complexes are very small (−0.05, −0.06, and −0.10 kcal mol^{-1}). The whole set of the structural parameters for the ternary $CH_3OH\cdots CF_4\cdots Ar$ complexes are presented in the Supporting Information.

In Table 4 are presented the calculated frequencies and intensities for the binary I-1, I-2, and I-3 complexes (the frequencies of the ternary complexes are presented in the Supporting Information). As one can see, the I-1, I-2, and I-3 structures are characterized by a very similar set of frequencies. Slightly larger differences occur for the COH group vibrations (as may be expected). The calculations indicate a small blue shift of the OH stretching vibration in the I-1, I-2 complexes (+6, +10 cm^{-1}) and red shift in the I-3 complex (−4 cm^{-1}) with respect to the CH_3OH monomer vibration. The COH bending and C−O stretching vibrations are calculated to shift +7, +5 cm^{-1} and +9, +6 cm^{-1} toward higher frequencies in the I-1, I-2 complexes, respectively, whereas a negligible shift is calculated for the two vibrations in the I-3 complex (+1 and 0 cm^{-1}). It is also interesting to note relatively strong perturbations of the $\nu_{as}(CF_4)$ vibrations in all three complexes I-1, I-2, and I-3 (see Table 4). The attachment of an argon atom to the I-1 complex in the I-1−Ar1 position or attachment of an argon atom to I-3 in positions I-3−Ar1, I-3−Ar2 shows no effect or negligible effect on the frequencies of the binary complexes

TABLE 5: Topological Properties, Charge Density $\rho(r)$ (in au), and Laplacian of Charge Density $\nabla^2\rho(r)$ (in au) of O−H, F⋯H Bonds for Hydrogen-Bonded I-1, I-2, II Complexes and O−H, O⋯F Bonds for I-3 Complex

	ρ(O−H)	$\nabla^2\rho$(O−H)	ρ(F⋯H)	$\nabla^2\rho$(F⋯H)	ρ(O⋯F)	$\nabla^2\rho$(O⋯F)
I-1	0.3749	−2.8191	0.0082	0.0356		
I-2	0.3749	−2.8223	0.0090	0.0396		
I-1−Ar1	0.3747	−2.8169	0.0082	0.0353		
I-1−Ar2	0.3747	−2.8155	0.0075	0.0324		
II	0.3702	−2.8225	0.0199	0.0818		
I-3	0.3743	−2.8052			0.0062 (O2⋯F8)	0.0287
					0.0068 (O2⋯F10)	0.0265
					0.0067 (O2⋯F11)	0.0300
I-3−Ar1	0.3743	−2.8049			0.0064 (O2⋯F8)	0.0269
					0.0068 (O2⋯F10)	0.0293
					0.0068 (O2⋯F11)	0.0298
I-3−Ar2	0.3743	−2.8047			0.0060 (O2⋯F8)	0.0260
					0.0069 (O2⋯F10)	0.0290
					0.0069 (O2⋯F11)	0.0307
CH_3OH	0.3750	−2.8111				

(0, ±2 cm^{-1}). The frequencies are slightly more modified when an argon atom is attached to the I-1 complex in position I-1−Ar2. The OH stretching, COH bending, and C−O stretching are 7, 4, and 3 cm^{-1} red shifted upon complex formation (see the Supporting Information for the full set of frequencies).

Table 5 presents topological properties of the electronic charge density at a bond critical point (BCP) found for the O−H bond and F⋯H interactions in the I-1, I-2, II complexes and for the O⋯F(8), O⋯F(10), and O⋯F(11) interactions in the I-3 complex. The values of the density $\rho(r)$ and the Laplacian of the density $\nabla^2\rho(r)$ at the BCP are equal to 0.0082, 0.0356 au, respectively, for the F⋯H interaction in the I-1 complex, and to 0.0090, 0.0396 au in the I-2 complex, confirming the presence of hydrogen bonding in these two structures (for hydrogen bonds $\rho(r)$ and $\nabla^2\rho(r)$ values usually lie within the range 0.002−0.04 and 0.02−0.15 au, respectively[22]). There is a negligible change of charge density of the O−H bond upon complexation in these two complexes. An attachment of an argon atom to I-1 has no or negligible effect on the $\rho(r)$ and $\nabla^2\rho(r)$ values of the F⋯H interaction in the I-1−Ar1 structure, whereas it slightly decreases both $\rho(r)$ and $\nabla^2\rho(r)$ values of F⋯H in the I-1−Ar2 structure. In the complex II, the $\rho(r)$ and $\nabla^2\rho(r)$ values of the F⋯H interaction are equal to 0.0199 and 0.0818 au, larger than in the I-1, I-2 complexes, which is in agreement with a higher interaction energy of this complex with respect to the I-1, I-2 complexes. The charge density of the O−H bond shows a distinct change upon complexation for complex II (from 0.3750 for the monomer to 0.3702 for the complex). In the I-3 complex, BCP were found between the oxygen atom of the methanol molecule and three fluorine atoms (F8, F10, and F11) of CF_4 and between one of the hydrogen atoms of methanol, H6, and the fluorine, F11, atom.

Discussion

The Structure of the Complex Trapped in Argon and Neon Matrixes. The calculations show that the three complexes I-1, I-2, and I-3 are characterized by a very similar set of frequencies (Table 4), the largest differences in frequencies occurring for the COH group vibrations as discussed earlier. For the $CH_3OH\cdots CF_4$ complex trapped in neon and argon matrixes, three bands due to the OH and CO stretches and to the FCF asymmetric stretching, ν_3 (CF_4), vibration were observed (Table 1). The C−O stretching and ν_3 (CF_4) vibrations exhibit very similar perturbations in neon and argon matrixes. The C−O stretch is red shifted 2 and 3.4 cm^{-1}, and the doublet observed for the ν_3 (CF_4) is red shifted 25.3, 28.8 cm^{-1} and 27.3, 23.8 cm^{-1} in neon and argon matrixes, respectively, with respect to the corresponding vibrations of CH_3OH or CF_4 monomers. However, the band assigned to the OH stretch exhibits different behavior in neon and argon; it is 8.5 cm^{-1} red shifted in neon and 5.3 cm^{-1} blue shifted in argon with respect to the OH stretch of CH_3OH. The questions arise about the structure of the complex trapped in neon and argon matrixes and about the nature of the different behavior of the OH stretch in the two matrixes. As is well known, solid neon provides a more neutral environment than solid argon, so, one may expect that the complex isolated in neon will be less perturbed by the environment than the complex isolated in argon. The observed shifts of the OH and CO stretching vibrations with respect to the corresponding monomer vibrations suggest that the complex trapped in neon has the non-hydrogen-bonded structure I-3. The CO stretching vibration is particularly informative as far as the structure of the complex is concerned. First, it is less sensitive to matrix environment than the OH stretching vibration. Second, the vibration exhibits different perturbation in hydrogen-bonded I-1, I-2 complexes and in the non-hydrogen-bonded I-3 complex. For the two hydrogen-bonded structures, the calculations predict a distinct blue frequency shift of the CO stretch, whereas a small red frequency shift is observed. The identified overtone of the CO stretching vibration, 2ν(CO), is also red shifted (3.4 cm^{-1}) with respect to the 2ν(CO) of the CH_3OH monomer (Table 1).

The identified FCF vibrations provide no information on the complex structure; for all three structures the calculations indicate similar perturbation of the ν_3 (CF_4) mode. Failure to observe other complex vibrations may be due to their negligible perturbations from monomers vibrations as indicated by calculations (Table 4).

The Nature of the Blue Shift of the OH Stretch in an Argon Matrix. There are known examples of weak complexes[23] whose structures depend on the matrix material in which the complex is trapped. However, very similar perturbations of the CO stretching vibration in the complex isolated in neon and argon matrixes suggest that the complex of the same structure is trapped in the two matrixes. Both in the complex trapped in solid neon and in solid argon the CO stretch shows a downward frequency shift, so, one may conclude that the complex in the two matrixes has the I-3 structure.

The blue shift of the OH stretch in solid argon as compared to the red shift of this vibration in solid neon may be explained by different effects of these two matrix materials on the OH stretching vibration in the CH_3OH monomer and in the $CH_3OH\cdots CF_4$ complex. The typical effect of various matrixes on the vibrational spectrum of individual molecule or van der Waals and hydrogen-bonded complex consists of the vibrational frequency shift appropriate to the selected vibrational mode and to the type of the matrix. Luck et al.[24] have shown that between the matrix-induced frequency shifts of the OH, OD groups of methanol or water and the square root of the critical temperature, $\sqrt{T_c}$, of the matrix material there exists a linear correlation. Later, Huisken et al.[25] have demonstrated that matrix-induced frequency shifts of the HF monomers, hydrogen-bonded HF, and H_2O aggregates also show a linear dependence on $\sqrt{T_c}$, and they have described the nature of this simple empirical correlation. We found a similar correlation for the OH stretching frequency of the *trans*-HONO isomer and its complex with N_2 trapped in various matrixes.[26] The analysis of the matrix-induced frequency shifts of the CH_3OH, H_2O, HF, HCl, HONO monomers and their complexes shows that matrix material induces larger perturbation of the HX (X═O, F, Cl) stretching vibration for the monomer than for the complex. For example, the HF stretch of the hydrogen fluoride monomer shows ca. 33.5 cm^{-1} frequency shift when going from neon to argon matrix, whereas the stretching vibrations of "free" and bonded HF molecules in $(HF)_2$ dimer show, respectively, 18.4 and 15.4 cm^{-1} shifts from neon to argon. The larger sensitivity of the OH stretch of the HONO monomer to the matrix material with respect to the corresponding vibration of the HONO complex with N_2 is a reason the OH stretching frequency of $N_2\cdots$HONO is red shifted for the complex isolated in solid argon and blue shifted for the complex isolated in solid xenon.[26]

The ν(OH) band position of the methanol monomer changes from 3688.5 cm^{-1} in neon to 3666.4 cm^{-1} in argon. The effect of neon on methanol is nearly zero as compared to the CH_3OH vapor-phase frequency, so, the induced frequency shift in an argon matrix equals ca. 22.1 cm^{-1}. In turn, the ν(OH) stretching frequency of the $CH_3OH\cdots CF_4$ complex changes from 3680.0 cm^{-1} in neon to 3671.7 cm^{-1} in argon, the frequency shift from neon to argon equal to 8.3 cm^{-1} being less than the OH stretch shift of the methanol monomer. As discussed earlier, the attachment of an argon atom to the I-1 complex in the I-1−Ar1 position or attachment of an argon atom to I-3 shows a negligible effect on the frequencies of the binary complexes. The frequencies are slightly more modified when an argon atom attaches to the I-1 complex in position I-1−Ar2; small red frequency shift (and not the blue one) of the OH stretching frequency with respect to the CH_3OH monomer is calculated. The ternary complexes with one argon atom attached to the binary $CH_3OH\cdots CF_4$ ones do not model the environment of an argon matrix. However, the calculations predict negligible perturbation of the OH stretching frequency of the I-3 complex by an argon atom, supporting our suggestion that the blue shift of the OH stretching vibration in the complex isolated in argon is due to the fact that the OH stretch of the I-3 complex, which is trapped in the matrix, is less sensitive to the argon environment than the OH stretch of the CH_3OH monomer.

Are the I-1 and I-2 Complexes Improper or Classic Hydrogen-Bonded Complexes? The MP2(full)/6-311+G(2df,2pd) calculations performed for $CH_3OH\cdots CF_4$ result in slightly different complex characteristics than those obtained earlier by Alabugin et al.[4] using the MP2(FC)/6-31+G* level of theory. Some of the parameters obtained by the two levels of theory are compared in Table 3. The higher level of theory predicts interaction energy equal to −0.59, −0.51 kcal mol^{-1} for I-1, I-2 complexes and −3.54 kcal mol^{-1} for complex II, which can be compared to −0.19 kcal mol^{-1} for I-1 reported by Alabugin et al. The MP2(full)/6-311+G(2df,2pd) calculations result in elongation of the O−H bond by 0.0001 Å, which is however accompanied by a small blue shift (+6 cm^{-1}) of the OH stretching frequency. On the other hand, the MP2(FC)/6-31+G* level of theory predicts contraction of the OH bond by 0.0004 Å after I-1 complex formation. So, the structural and vibrational parameters obtained by a higher level of theory do not indicate univocally whether the I-1 complex involves the improper hydrogen bond. For the complex I-2, the MP2/6-311+G(2df,2pd) calculations predict contraction of the OH bond by 0.0001 Å, which is accompanied by 10 cm^{-1} blue shift of the OH stretching vibration. For comparison, for the classical hydrogen bond that is present in the $CH_3F\cdots CH_3OH$ complex II, the calculations predict a distinct elongation of the OH bond (by 0.0032 Å) accompanied by a distinct red shift of the OH stretching vibration (by 49 cm^{-1}). An attachment of an argon atom to the I-1 complex in the I-1−Ar1 or in the I-1−Ar2 positions leads to further elongation of the OH bond as compared to I-1 and a negligible red shift of the OH stretching frequency (by ca. 2 cm^{-1}).

It has been shown for a series of C−H$\cdots$X complexes[27] that formation of improper hydrogen bond is accompanied by an increase of charge density values of the C−H bond. The calculated topological parameters for the I-1, I-2 complexes, similarly as the calculated structural and vibrational parameters, do not confirm the existence of improper hydrogen bond in the I-1, I-2 complexes. The analysis of the $\rho(r)$ and $\nabla^2\rho(r)$ shows that in complexes I-1, I-2 the charge density values of the OH bond slightly decrease on complexation when compared to that of the monomer (by 0.0001 au, Table 5). In fact, the calculated changes of $\rho(r)$ values after formation of the I-1, I-2 complexes are within calculation error. However, one should note that an attachment of an argon atom to I-1 results in a further $\rho(r)$ decrease by 0.0003 au as compared to the CH_3OH monomer. After formation of typical hydrogen-bonded complex II, a distinct decrease of the $\rho(r)$ value of the OH bond occurs (by 0.0047 Å, Table 5).

Conclusions

The MP2(full)/6-311+G(2df,2pd) calculations indicate that CF_4 forms with CH_3OH three stable 1:1 complexes, two hydrogen-bonded complexes I-1, I-2, and one weak van der Waals complex I-3. The hydrogen-bonded complexes involve weak O−H$\cdots$F hydrogen bonds that differ with the orientation of CF_4 with respect to the CH_3OH subunit. The interaction energy ΔE^{CP} is equal to −0.59, −0.51, and −1.02 kcal mol^{-1} for the I-1, I-2, and I-3 complexes, respectively. The structural, vibrational, and topological parameters calculated for I-1 and I-2 do not support the formation of improper hydrogen bond in these complexes as suggested earlier on the basis of ab initio calculations at the lower level of theory.[4] The MP2(full)/6-311+G(2df,2pd) calculations performed for the $CH_3F\cdots CH_3OH$ indicate formation of a stable hydrogen-bonded O−H$\cdots$F complex with an interaction energy ΔE^{CP} equal to −3.54 kcal mol^{-1}. The structural, vibrational, and topological properties are characteristic for classic hydrogen bond.

The comparison of experimental frequencies of the $CF_4\cdots CH_3OH$ complex trapped in argon and neon matrixes to those predicted by calculations indicates that in matrixes the most stable non-hydrogen-bonded complex is trapped. The red frequency shift of the OH stretching vibration of methanol in neon matrix and blue frequency shift in argon matrix upon complex formation is due to the larger sensitivity of the OH stretch of the free methanol than that of bonded methanol to the matrix material. The identified frequencies of the $CH_3F\cdots CH_3OH$ complex trapped in neon matrix show a good agreement with the calculated ones for the complex.

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Supporting Information Available: Geometrical parameters, vibrational frequencies, and intensities of the CH_3OH, CF_4, and CH_3F monomers and $CH_3F{-}CH_3OH$, $CF_{4-}CH_3OH$, and $CF_{4-}CH_3OH{-}Ar$ complexes calculated at the MP2/6-311+G(2df,2pd) level. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Denpoh, K.; Nanbu, K. *J. Vac. Sci. Technol., A* **1998**, *16*, 1201.

(2) Tachikawa, H. *Chem. Phys*. **2001**, *273*, 149.

(3) Mack, H.; Oberhammer, H. *J. Chem. Phys.* **1987**, *87*, 2158 and references therein.

(4) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.

(5) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(6) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639.

(7) Barnes, A. J. *J. Mol. Struct.* **2004**, *704*, 3 and references therein.

(8) Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695.

(9) Fang, Y.; Fan, J.-M.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett.* **2002**, 116.

(10) Fan, J.-M.; Liu, L.; Guo, Q.-X. *Chem. Phys. Lett.* **2002**, *365*, 464.

(11) Meenakshi, P. S.; Biswas, N.; Wategaonkar, S. *J. Chem. Phys.* **2003**, *118*, 9963.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. M.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

(13) Krishnan, R.; Binkley, R.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(14) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265.

(15) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.

(16) Bieger-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1980**, *13*, 317.

(17) Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* **1970**, *66*, 1920.

(18) Bakkas, N.; Boutellier, Y.; Loutellier, A.; Perchard, J. P.; Racine, S. *Chem. Phys. Lett.* **1995**, *232*, 90.

(19) Coussan, S.; Bouteiller, Y.; Loutellier, A.; Perchard, J. P.; Racine, S.; Peremans, A.; Zheng, W. Q.; Tadjeddine, A. *Chem. Phys.* **1997**, *219*, 221.

(20) Coussan, S. Ph.D. Thesis, Universite Pierre et Marie Curie, Paris, 1997.

(21) Cherevatova, A.; Kolomiitsova, T. D.; Mielke, Z.; Shchepkin, D. N.; Tokhadze, K. G.; Coussan, S. *J. Mol. Spectrosc.*, submitted.

(22) Popelier, P. *Atoms in Molecules. An Introduction*; Prentice Hall: Upper Saddle River, NJ, 2000.

(23) Schriver-Mazzuoli, L.; Schriver, A.; Wierzejewska-Hnat, M. *Chem. Phys*. **1995**, *199*, 227.

(24) Behrens-Griesenbach, A.; Luck, W. A. P.; Schrems, O. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 579.

(25) Huisken, F.; Kaloudis, M.; Vigasin, A. A. *Chem. Phys. Lett.* **1997**, *269*, 235.

(26) Mielke, Z.; Talik, T.; Tokhadze, K. G. *J. Mol. Struct.* **1999**, *484*, 207.

(27) Kolondaivel, P.; Nirmala, V. *J. Mol. Struct.* **2004**, *694*, 33.