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Car–Parrinello Molecular Dynamics Study of the Blue-Shifted $F_3CH\cdots FCD_3$ System in Liquid N_2

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Fluoroform, as confirmed by both experimental and theoretical studies, can participate in improper H-bond formation, which is characterized by a noticeable increase in the fundamental stretching frequency ν(C–H) (so-called blue frequency shift), an irregular change of its integral intensity, and a C–H bond contraction. A Car–Parrinello molecular dynamics simulation was performed for a complex formed by fluoroform (F_3CH) and deuterated methyl fluoride (FCD_3) in liquid nitrogen. Vibrational analysis based on the Fourier transform of the dipole moment autocorrelation function reproduces the blue shift of the fundamental stretching frequency ν(C–H) and the decrease in the integral intensity. The dynamic contraction of the C–H bond is also predicted. The stoichiometry of the solvated, blue-shifted complexes and their residence times are examined.

1. Introduction

The hydrogen-bonded A–H···B system can be described as a donor part A–H interacting with an acceptor B, where A is an electronegative atom and B is either an electronegative atom or a group with a region of high electron density.[1–3] One of the most common features of the so-called regular H bonds, measured by IR spectroscopy, is the red shift of the fundamental stretching frequency ν(A–H), which is accompanied by an increase of the integrated intensity of the respective band. All these effects increase with the strengthening of the hydrogen bond.[4] Also, there is experimental (NMR spectroscopy, X-ray studies)[5] and theoretical[6,7] evidence for an elongation of the A–H bond during regular hydrogen bond formation.

A relatively wide class of H bonds with the participation of C–H groups (so-called C–H acids) are now of special interest due to their crucial role in the fine effects controlling some biomolecular processes.[8–10] Some features of this type of weak to modest H bond, revealed more than 30 years ago[11], suggest the possibility of a qualitative declination from the commonly accepted spectral and geometric characteristics of the regular H bonds. The most striking is the blue frequency shift of the fundamental stretching vibration ν(A–H), with the A–H bond length contracted. Also, the integrated intensity of this band can show irregular change with H-bond strengthening. All the mentioned features of the so-called blue-shifted or improper hydrogen bond have found wide experimental[12–21] and theoretical[22–38] support. The majority of the systems studied were naturally of the C–H type, but there are theoretical suggestions for the formation of blue-shifted hydrogen bonds with participation of Si–H, P–H, and N–H acids.[36,37] Most theoretical studies until now were based on either ab initio or DFT static calculations, which correspond to the conditions for the formation of an isolated complex, the most appropriate for treating the results of low-pressure gas-phase and molecular-beam experiments.

Thus, such calculations may become inadequate when considering the relevant part of the experimental results obtained in a high-density liquid state. In general, the systems studied in the liquid phase can be divided into two groups: one where the blue-shifted complex A–H···B is dissolved in weakly interacting liquefied rare gases,[12,13,16,19,38] and the other where the proton donor molecules are dissolved in molecular solvents, often acting as proton acceptors.[14,18,21] Usually the effect of liquefied rare gases on the spectroscopic parameters of the vibrational bands of interest is considered to be of secondary importance. In such a case, a theoretical analysis based on static ab initio calculations results in reasonable conclusions and truly reflects the experimental observations. On the contrary, the interactions of a proton donor molecule with more active low-temperature molecular solvents, such as N_2 or CO, can lead to the effects typical for weak hydrogen bond formation,[17,18,21] even in the absence of other proton acceptor molecules. Despite the more complicated character of interactions in this latter case, the results of static ab initio calculations are still considered as a more or less successful approximation. One could expect an even more complicated situation when the formation of a blue-shifted complex between proton donor and acceptor counterparts occurs in a molecular solvent,

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which acts as a weak proton acceptor. In this case, predictions based on static ab initio calculations should be treated rather only as a crude starting point for more realistic simulations, which take into account the dynamic nature of the liquid state.

Herein, a mixture of F_3CH and FCD_3 molecules in liquid N_2 (F_3CH/FCD_3//liq. N_2) has been chosen as a simple and simultaneously realistic model system for a Car–Parrinello molecular dynamics (CPMD)[39,40] simulation at a temperature of 100 K. Such a low-temperature system, which is characterized by a noticeable blue-shift effect, has not been studied experimentally before. However, a noticeable blue shift of the fundamental stretching frequency ν(C–H) of fluoroform has been recently found, both in mixtures with FCD_3 in liquid Kr (F_3CH/FCD_3//liq. Kr)[38] and in liquid N_2 (F_3CH//liq. N_2) used as a weak proton acceptor solvent.[18] The results of these experimental studies form a basis for the preparation of the initial conditions for molecular dynamics studies of the blue-shifted F_3CH/FCD_3 complex in liquefied N_2. CPMD is known to be a well-established tool for investigating liquid and disordered systems, and it has been applied to a variety of problems, including hydrogen-bonded systems and chemical reactions in water.[41–44] Recently, it has been shown that this method is also effective in studies of blue-shifted hydrogen bond formation.[45] In fact, CPMD gives a unique opportunity to study complex formation and its dynamic conformational changes practically under real conditions of hypothetical cryospectroscopic experiments in liquefied N_2 solvent (at the given temperature). The residence time and stoichiometry of the complexes can be derived in a natural way. Finally, the analysis of the Fourier transform (FT) of the dipole moment autocorrelation function enables the theoretical prediction of spectroscopic parameters and a direct comparison with available experimental spectroscopic data for separate systems, namely F_3CH//liq. N_2 and F_3CH/FCD_3//liq. Kr.

2. Results and Discussion

Table 1 shows the most relevant structural and spectroscopic properties (I^c and I^{free} denote intensities of the band attributed to the complex and monomer, respectively) of F_3CH/FCD_3, F_3CH/N_2, and $F_3CH/(FCD_3, 3N_2)$ complexes obtained with static calculations at the MP2(full) level of theory. The calculated structures for F_3CH/FCD_3, $F_3CH/(FCD_3, 3N_2)$, and F_3CH/N_2 complexes are shown in Figure 1. In the case of the F_3CH/FCD_3 complex, structures a and b are characterized by a very similar binding energy, whereas structure c, with a noninteracting C–H bond of F_3CH, seems to be of secondary importance. All the structures are characterized by features which are typical for so-called improper hydrogen bonds. Namely, the C–H bond contracts, the C–H stretching frequency is blue-shifted, and the integrated intensity of the respective bond decreases with respect to the values of free F_3CH. However, the non-H-bonded structure c reveals rather weak changes of these geometric and spectroscopic parameters. Due to the similarity of

Table 1. Geometric and spectroscopic features of different $F_3CH/FCD_3/N_2$ complexes at the MP2/6-31+G(d,p) level. All distances are in Å, energy values in kJ mol^{-1}, frequencies in cm^{-1}, and intensities in km mol^{-1}.

System	F_3CH and FCD_3	F_3CH/FCD_3	F_3CH/FCD_3	F_3CH/FCD_3	$F_3CH/FCD_3//3N_2$	F_3CH/N_2 linear	F_3CH/N_2 nonlinear	$F_3CH/2N_2$	$F_3CH/3N_2$
Structure	Free	Figure 1 a	Figure 1 b	Figure 1 c	Figure 1 d	Figure 1 e	Figure 1 f	Figure 1 g	Figure 1 h
$r(C_1–F_1)$	1.3489	1.3517	1.3537	1.3483	1.3517	1.3497	1.3495	1.3502	1.3509
$r(C_1–F_2)$	1.3489	1.3517	1.3503	1.3485	1.3517	1.3497	1.3495	1.3502	1.3509
$r(C_1–F_3)$	1.3489	1.3501	1.3503	1.3513	1.3517	1.3497	1.3496	1.3501	1.3510
$r(C_1–H)$	1.0838	1.0816	1.0820	1.0836	1.0804	1.0834	1.0830	1.0824	1.0813
$\Delta r(C_1–H)$	–	−0.0022	−0.0018	−0.0002	−0.0034	−0.0004	−0.0008	−0.0014	−0.0025
$r(C_2–F_4)$	1.4035	1.4100	1.4103	1.4047	1.4095	–	–	–	–
$r(C_2–D_1)$	1.0850	1.0848	1.0847	1.0854	1.0854	–	–	–	–
$r(C_2–D_2)$	1.0850	1.0848	1.0848	1.0854	1.0854	–	–	–	–
$r(C_2–D_3)$	1.0850	1.0848	1.048	1.0852	1.0854	–	–	–	–
$R(H–F_4)$	–	2.4245	2.3367	–	2.4133	–	–	–	–
$R(F_1\cdots D_1)$	–	3.1442	2.9018	3.3847	–	–	–	–	–
$R(H\cdots N_1)$	–	–	–	–	2.7402	2.7410	2.8432	2.8432	2.7805
$R(F_2\cdots D_2)$	–	3.1440	–	3.3273	–	–	–	–	–
$R(H\cdots N_2)$	–	–	–	–	2.7435	–	–	2.8354	2.7809
$R(F_3\cdots D_3)$	–	–	–	3.1034	–	–	–	–	–
$R(H\cdots N_3)$	–	–	–	–	2.7426	–	–	–	2.7788
E_e^{corr}	–	-11.52	-11.49	−3.15	−16.50	−3.29	−3.52	−7.38	−11.5
ν_1	3273.0	3307.5	3305.8	3277.2	3327.4	3285.5	3286.4	3297.6	3316.2
I_1	24.9	9.8	5.8	23.6	5.5	10.9	20.4	16.8	10.1
$\Delta\nu$	–	+34.5	+32.8	+4.2	+54.4	+12.5	+13.4	+24.6	+43.1
I_1^c/I_1^{free}	–	0.394	0.233	0.948	0.221	0.438	0.819	0.675	0.406
ν_1	2253.1	2255.1	2255.4	2251.7	2250.5	–	–	–	–
I_1	26.2	22.4	23.9	27.8	23.6	–	–	–	–
ν_4	2428.9	2434.6	2434.3	2427.9	2429.5	–	–	–	–
		2435.1	2436.5	2428.4	2429.6				
I_4	35.4	14.9	14.1	15.4	12.6	–	–	–	–
		12.1	12.3	15.9	12.6				

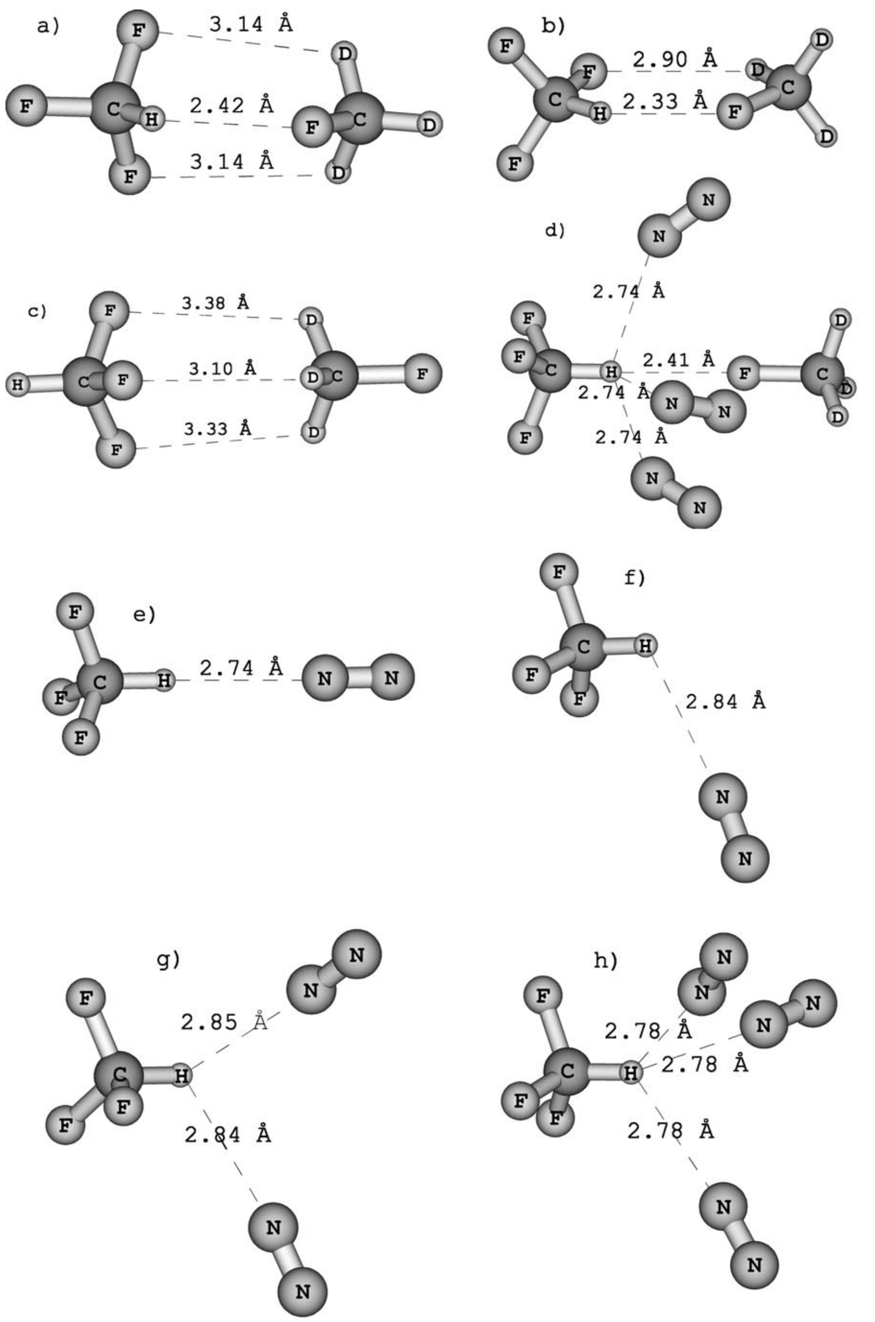

Figure 1. MP2(full)/6-31+G(d,p) predicted structures for $F_3CH/(FCD_3, 3N_2)$ and F_3CH/N_2 complexes.

the values of the binding energy, the C–H bond contraction, and the frequency shift for the most stable structures a and b, it is quite reasonable to suggest the possibility of its mutual dynamic equilibration in the CPMD simulation. Notably, a possible linear structure for the F_3CH/FCD_3 complex, although characterized by only a slightly smaller binding energy, possesses one imaginary frequency for a motion of nuclei corresponding to a recovery to structures a or b. Thus, this linear structure should be ascribed to a transition state, at least in the case of the isolated complex.

Taking into account the possibility of interactions of the F_3CH molecule with several nitrogen molecules, the different types of complexes ($F_3CH/n N_2$) with stoichiometry varying from 1:1 to 1:3 are examined (see Figure 1 e–h). The results collected in Table 1 clearly show that the blue frequency shift, the decrease of the intensity, and the C–H bond contraction grow quickly with the addition of N_2 molecules. Clearly this result is strictly true only at a very low temperature and in the absence of other intermolecular interactions. In the case of the F_3CH/N_2 complex with 1:1 stoichiometry, a linear structure e as well as a bent structure f have been predicted. However, both structures have similar binding energies and blue frequency shifts. They differ only in the C–H bond contraction, namely the C–H bond of F_3CH in the nonlinear structure is more contracted than that in a linear one.

An interesting conclusion can be drawn when analyzing the interaction of the F_3CH/FCD_3 complex with an additional three nitrogen molecules. The mutual competition between the FCD_3 and N_2 molecules results in the formation of a blue-shifted hydrogen-bonded complex with linearly placed F_3CH and FCD_3 counterparts (see Figure 1 d), which is characterized by a remarkable growth of the blue shift and C–H bond contraction. This finding suggests the possibility of stabilization of a linear-like structure when the complex is immersed in liquid nitrogen, which would cumulate the improper H-bond effects.

As mentioned in the Computational Methods section, additional DFT calculations with both hybrid B3LYP and exchange-correlation BLYP functionals were performed to check if the most important geometric and spectroscopic parameters differ from those calculated by using the MP2(full) method. Indeed, the DFT method does not describe properly the van der Waals interactions. However, the complexes investigated here are characterized by weak hydrogen bonds, whose description has been proven to be correct utilizing DFT methods. In Table 2, we report the most important geometric and spectroscopic parameters for the F_3CH/N_2 complex only. This complex has been chosen from the test calculations as one of the weakest

Table 2. Geometric and spectroscopic features of the linear F_3CH/N_2 complex obtained at the different levels of theory. All distances are in Å, energy values in kJ mol^{-1}, frequencies in cm^{-1}, and intensities in km mol^{-1}. Both a priori and a posteriori basis set superposition errror (BSSE) correction method have been used.

	MP2/6-311 ++G(3df,3pd) a posteriori BSSE	MP2/6-31 +G(d,p) a posteriori BSSE	MP2/6-31 +G(d,p) a priori BSSE	DFT/B3 LYP6-311 ++G(3df,3pd) a posteriori BSSE	DFT/B3 LYP6-31 +G(d,p) a priori BSSE	DFT/BLYP6-31 +G(d,p) a priori BSSE
$r(C_1{-}H)$	1.0835	1.0829	1.0834	1.0882	1.0907	1.0982
$\Delta r(C_1{-}H)$	−0.0010	−0.0009	−0.0004	−0.0008	−0.0006	−0.0006
$R(H\cdots N)$	2.516	2.621	2.741	2.730	2.807	2.911
E_e^{corr}	−4.8	−3.4	−3.3	−1.5	−1.9	−1.2
ν_1	3231	3292	3286	3144	3176	3084
I_1	5	7	11	11	14	14
$\Delta\nu$	+31	+19	+13	+17	+12	+11
I_1^c/I_1^{free}	0.21	0.29	0.44	0.39	0.52	0.52

of all possible complexes formed, and therefore theoretically it should be the most influenced by different computational methods. The collected DFT results (with B3 LYP and BLYP functionals) suggest that the trends for the C–H fundamental stretching frequency shifts and the values of C–H bond contraction are reproduced satisfactorily in comparison to previously performed MP2 calculations.

Thus, on the basis of this MP2/DFT comparison, one might expect a proper description of the blue-shifted system by CPMD where the BLYP functional has been used. One of the most characteristic features of an improper hydrogen bond is the blue shift of the fundamental stretching frequency ν(A–H). Table 3 presents the calculated theoretical frequencies (CPMD) for the following systems: F_3CH/FCD_3//liq. N_2, F_3CH/FCD_3 complex, and F_3CH in the gas phase. Experimental data (FTIR) for F_3CH//liq. N_2 and F_3CH/FCD_3//liq. Kr are also given. In the case of the F_3CH/FCD_3//liq. N_2 system, experimental values have not yet been reported, and so a direct comparison with theoretical results is not possible.

Table 3. Experimental (FTIR) and theoretical (CPMD) frequencies [cm^{-1}] for selected F_3CH/FCD_3 complexes.

Band symmetry	νCH (stretch)	νCH (bend)	νCF (stretch) asym	νCF (stretch) sym
experiment[18,38]				
F_3CH, gas	3035.2	1377.9	1158.3	1141.5
F_3CH//liq. N_2	3047.4	1376.5	1146.3	1140.0
$\Delta\nu$	+12.2	−1.4	−12.0	−0.5
F_3CH//liq. Kr	3033.0	1373.1	1138.5	1132.2
F_3CH/FCD_3//liq. Kr	3057.0	1378.7	1133.2	1130.3
$\Delta\nu$	+24.0	+5.6	−5.3	−1.9
CPMD				
F_3CH,	2889.0	1271.0	1123.9	1077.9
F_3CH/FCD_3,	2925.7	1280.1	1123.9	1077.9
$\Delta\nu$	+36.7	+9.1	0.0	0.0
F_3CH/FCD_3//liq. N_2	2945.0	1274.3	1113.0	1075.0
$\Delta\nu$	+56.0	+3.3	−10.9	−2.3
F_3CH//liq. N_2	2926.2	1281.6	1106.6	1071.6
$\Delta\nu$	+37.2	+10.6	−17.3	−6.3

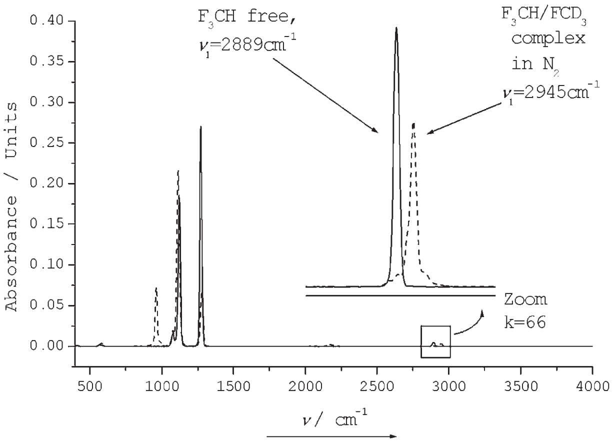

Figure 2. Theoretical spectrum (CPMD) obtained from the FT of the dipole moment autocorrelation function for both F_3CH/FCD_3 complex dissolved in N_2 and F_3CH in the gas phase.

In the case of F_3CH/FCD_3//liq. N_2 in a CPMD run, the frequency shift is +56 cm^{-1}, calculated as the difference between the C–H stretching frequency of a free F_3CH molecule in the gas phase and the complex in liquid N_2 (see Figure 2). For comparison, the frequency shift calculated as the difference between the C–H stretching frequency of the F_3CH/FCD_3 complex and the F_3CH molecule, both in the gas phase, is +36 cm^{-1}. One supposes that such a noticeable increase of the blue frequency shift in the case of F_3CH/FCD_3//liq. N_2 is due to the mutual interaction of FCD_3 and N_2 molecules with the F_3CH proton donor. The effect observed in a CPMD run is similar to the supermolecular static MP2 calculations mentioned earlier, when an addition of three N_2 molecules into the F_3CH/FCD_3 complex stabilizes it and gives rise to a higher value of the blue shift. Nevertheless, one should remember that the results of static calculations for such five-particle supermolecular systems are not directly applicable to real systems at a temperature of 100 K. A direct comparison of theoretical results for F_3CH/FCD_3 and F_3CH/FCD_3//liq. N_2 systems with experimental values cannot be done due to the lack of such data. However, a crude comparison with the available FTIR results for F_3CH/FCD_3//liq. Kr and F_3CH//liq. N_2 comes to the conclusion that the calculated frequency might be somewhat overestimated. The reliability of these CPMD results can also be confirmed by the analysis of other vibrational bands. For example, opposite to the blue shift of the C–H stretching frequency, both symmetric and antisymmetric C–F stretching frequencies are red-shifted, which is in accordance with available experimental values. Thus, the CPMD method truly reflects the spectroscopic features of the studied systems with unusual hydrogen bonds.

Apart from the C–H stretching frequency shift itself, the character of the change in the integral intensity of this band should be considered as another important feature of the improper hydrogen bond. The analysis in the C–H stretching frequency region shows a decrease in the integrated intensity in the case of F_3CH/FCD_3//liq. N_2 in comparison to F_3CH in the gas phase. The calculated I^c/I^{free} is 0.74, whereas the experimental values in the cases of F_3CH/FCD_3//liq. Kr and F_3CH// liq. N_2 reach 0.32 and 0.63, respectively.

The C–H bond contraction of the proton donor molecule cannot be observed directly in the spectroscopic experiment, but can be quite easily gained from the CPMD simulation as the difference between the expectation value of the C–H bond length in the simulation of F_3CH/FCD_3//liq. N_2 and the same value in the run of F_3CH in the gas phase. Table 4 displays all the calculated bonds lengths of proton donor and acceptor molecules in both the free (noninteracting) gas state and in F_3CH/FCD_3//liq. N_2. In the case of F_3CH, the C–H bond reveals a contraction of −0.0018 Å (±9.4E-05 Å) as a result of F_3CH/FCD_3 complex formation in liquid nitrogen. Contrary to the C–H bond, an elongation of all the C–F bonds in F_3CH is obtained with an average value of +0.0019 Å (±9.8E-05 Å). In the proton acceptor FCD_3 molecule, the C–F bond also lengthens by a value of +0.0082 Å (±1.2E-04 Å) and all C–D bonds contract with an average value of −0.0014 Å (±7.8E-05 Å). Thus, the character of changes in the bond lengths of both F_3CH and FCD_3 molecules upon mutual interaction calculated by CPMD is in agreement with both DFT and ab initio static calculations.

Table 4. Calculated (CPMD) average distances [Å] for F_3CH and FCD_3 molecules in the gas phase and in solution.

	Free molecules in the gas phase	F_3CH/FCD_3//liq. N_2	
	F_3CH	F_3CH	Δr
r(CH)	1.0940±2.6E-05	1.0922±6.8E-05	−0.0018±9.4E-05
$r(CF_1)$	1.3977±4.0E-05	1.3996±6.2E-05	+0.0019±1.2E-04
$r(CF_2)$	1.3977±4.0E-05	1.4005±4.8E-05	+0.0028±8.8E-05
$r(CF_3)$	1.3977±4.0E-05	1.3987±4.6E-05	+0.0010±8.6E-05
	FCD_3	FCD_3	
$r(CF_4)$	1.4563±3.1E-05	1.4645±8.6E-05	+0.0082±1.2E-04
$r(CD_1)$	1.0955±3.8E-05	1.0940±3.6E-05	−0.0015±7.4E-05
$r(CD_2)$	1.0955±3.8E-05	1.0942±3.4E-05	−0.0013±7.2E-05
$r(CD_4)$	1.0955±3.9E-05	1.0941±3.9E-05	−0.0014±7.8E-05

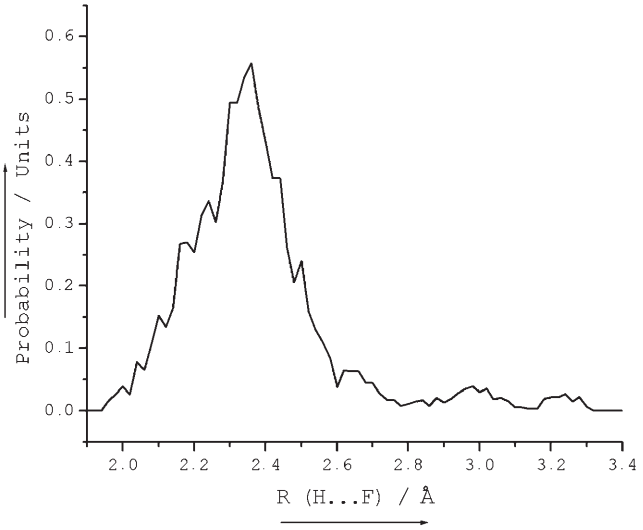

Figure 3. RDF for H···F distance. The increment value for the distance is 0.02 Å.

The total frequency shift calculated on the basis of the dipole moment autocorrelation function is a superposition over all possible structures of F_3CH/FCD_3//liq. N_2. Thus, it is worth deriving some characteristic complexes between F_3CH as a proton donor and both FCD_3/N_2 molecules acting as proton acceptors. To check which complexes are formed during the simulation, the radial distribution functions (RDFs) for H···F (Figure 3), F···D (Figure 4), and H···N (Figure 5) contacts were calculated. The peaks at distances of 2.35 Å in Figure 3, 2.90 and 3.30 Å in Figure 4, and 2.85 Å in Figure 5 correspond to the equilibrium distances of particular structures. With the support of both a visualization of trajectory and the results of static DFT and ab initio calculations, peaks were attributed to

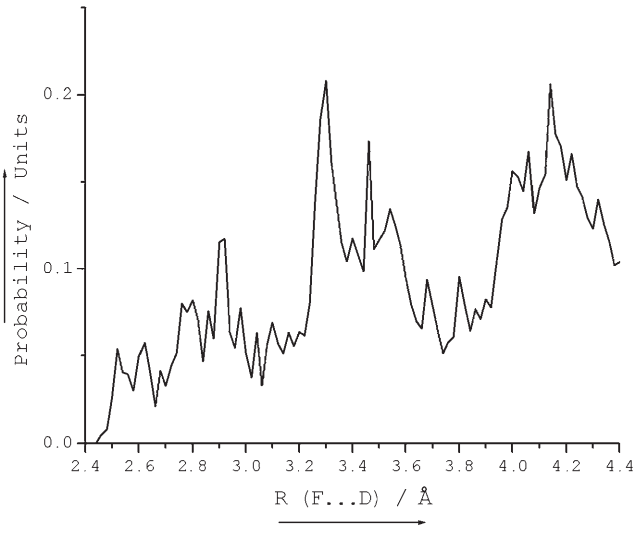

Figure 4. RDF for F···D distance. The increment value for the distance is 0.02 Å.

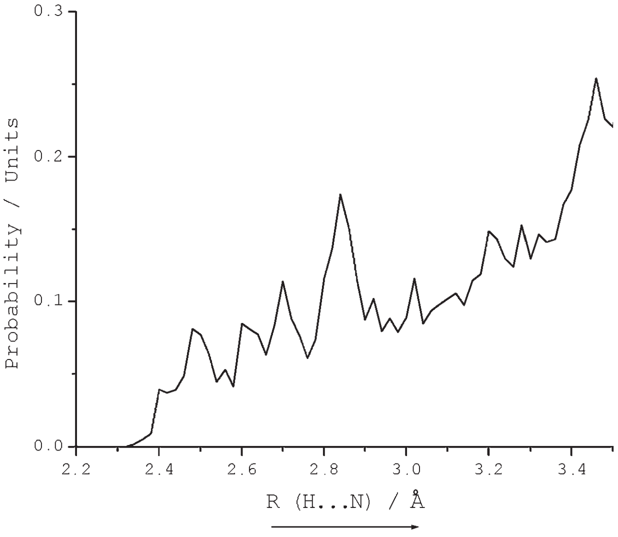

Figure 5. RDF for H···N distance. The increment value for the distance is 0.02 Å.

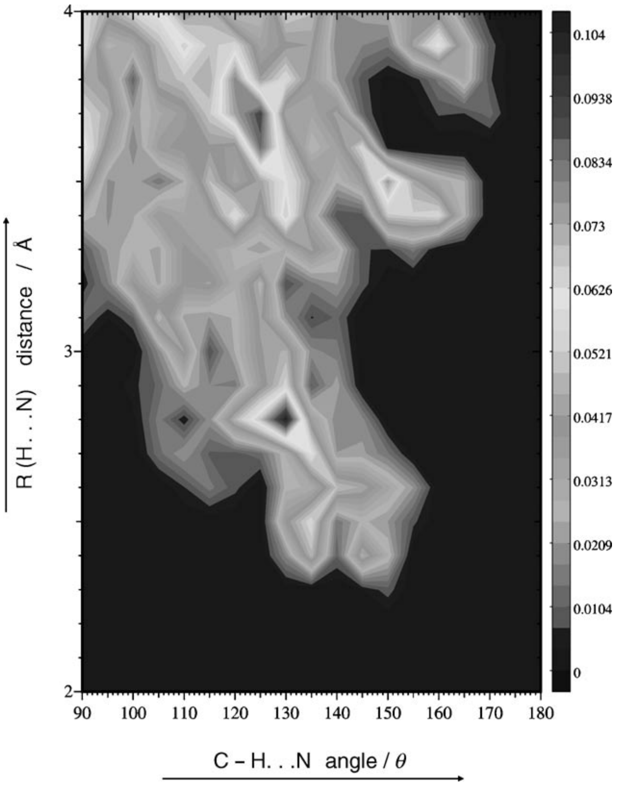

Figure 6. Two-dimensional histogram showing the probability of finding $F_3CH\cdots N_2$ interactions in a F_3CH/FCD_3//liq. N_2 system within a given range of H···N distance and C–H···N angle. The increment values for the distance and the angle are 0.1 Å and 5°, respectively.

particular types of complexes. Namely, the following three most relevant structures have been suggested: i) one of the plausible dynamic situations corresponds to the single H···F (bond) interaction between fluoroform and methyl fluoride, which can be approximately represented by the structure shown in Figure 1 d; ii) F_3CH and FCD_3 form a cyclic structure with two main bonds, H–F and F–D (see Figure 1 b); and iii) the F_3CH/FCD_3 complex with three bonds (one H–F and two F–D) is also quite possible (see Figure 1 a). Thus, the CPMD results correspond well to the structures obtained from DFT and ab initio static calculations. It seems quite natural from steric reasons that the active solvent effect is the most decisive in the case of complex stabilization by single H···F bond formation, which resembles the structure shown in Figure 1 d.

The role of solvent molecules can be represented by the use of a two-dimensional histogram (see Figure 6), which shows the probability of finding $F_3CH\cdots N_2$ interactions in an F_3CH/FCD_3//liq. N_2 system within a given range of H···N distance and C–H···N angle, respectively. The clearly marked peak ($R(H\cdots N) = 2.8$ Å, $\sphericalangle(C{-}H\cdots N) = 130°$) corresponds to the strong prevalence of nonlinear interactions of the solvent molecules with the proton donor molecule over the linear type. In the case of solely F_3CH/N_2 interactions, the dynamically formed structure is similar to that in Figure 1 f, obtained from static ab initio calculations. Thus, the CPMD result, where the nonlinear F_3CH/N_2 structure is preferred, differs from that predicted by static calculations (ab initio/DFT), where both nonlinear and linear H-bond-like interactions between fluoroform and nitrogen are energetically equivalent (see Figure 1 e,f). The second peak, situated at $R(H\cdots N) \approx 3.7$ Å, $\sphericalangle(C{-}H\cdots N) = 130°$, most likely corresponds to N atoms of the N_2 molecule, which do not participate in H-bond formation directly. In fact N_2 molecules, as a noticeably weaker proton acceptor in comparison to FCD_3, interact with non-H-bonded F_3CH rarely. However, they are able to affect the H-bonded F_3CH/FCD_3 complex, thus making the quasi-linear structure with the single H···F bond more stable than the cyclic and three-bond structures (see Figures 1 a and b). Thus, the solvent molecules can dynamically stabilize such a quasi-linear structure of the F_3CH/FCD_3 complex, characterized by single H···F bond formation. It is worth remembering that static ab initio/DFT calculations give a stable linear F_3CH/FCD_3 structure only after addition of three N_2 molecules, nonlinearly attached to this complex. Another solvent effect predicted by the CPMD analysis is the additional blue shift of the fundamental stretching frequency ν(C–H) and a concomitant contraction of this bond.

The ratio between the time of the existence of a particular structure and the total length of the simulation was calculated on the basis of a trajectory analysis. To distinguish different structures, the maximum distances for the particular types of interactions were taken from corresponding RDF plots, namely $R(H\cdots F) = 2.6$ Å, $R(F\cdots D) = 3.3$ Å, and $R(H\cdots N) = 2.9$ Å. The analysis shows that for the F_3CH/FCD_3 complex, the F_3CH molecule interacting with FCD_3 via a single H···F bond occurs most frequently ($\approx 40\%$ of the total time). The F_3CH/FCD_3 complexes represented as structures in Figures 1 a and b occur 22 and 4% of the total time, respectively, with the noticeable predominance of a cyclic form. It is interesting to note the case of additional interaction between the H atom of fluoroform, already involved in cyclic complex formation with FCD_3 (compare with Figure 1 b), and a nitrogen molecule of the solvent (8% of the total time). The activity of the N_2 solvent is also revealed in the possibility of a total breaking of the F_3CH/FCD_3 complex and the formation of nonlinear $F_3CH/1\,N_2$ complexes without the FCD_3 proton acceptor (8% of the total time). Finally, the situation where all the distances (H···F, F···D, and H···N) are far from their equilibrium lengths occurs relatively seldom (1% of the total time). It corresponds to the situation where the fluoroform proton donor interacts with both proton acceptor and solvent molecules via van der Waals-type forces without H-bond complex formation.

Another important characteristic of all the possible $F_3CH/FCD_3/N_2$ structures found, which has a more physical meaning, is their residence time. This lifetime (τ) is estimated as the time period in which the lengths of particular bonds [R(H···F, F···D, H···N)] describing the type of complex do not exceed the values of the equilibrium distance from respective RDF functions. Thus, several values of lifetimes for different stoichiometries are calculated. Naturally, this is only a rough estimation, which takes the average time as the most probable value. The quasi-linear structure (see Figure 1 d) seems to be the most stable one with a maximum lifetime observed of 1.2 ps. Other frequently detected structures are less stable; for example, in the case of a cyclic form of F_3CH/FCD_3 (see Figure 1 b) and a structure with three main bonds (see Figure 1 a), the lifetimes are of the order of $\tau \approx 200$ and ≈ 70 fs, respectively. In fact, the CPMD simulation predicts a mutual dynamic transformation between these two structures. However, the N_2 molecules often destroy them, thus giving rise to the longest living structure with a single H···F bond or sometimes to interactions between fluoroform and nitrogen molecules only, taking the FCD_3 proton acceptor away.

3. Conclusions

1. CPMD simulations for the F_3CH/FCD_3//liq. N_2 system predict complex formation with an unusual (improper) hydrogen bond, where the C–H fundamental stretching frequency is blue-shifted with its intensity decreased. The comparison of this theoretical prediction with data obtained for the isolated F_3CH/FCD_3 complex shows that the additional interactions with N_2 molecules of the low-temperature solvent can result in an increase of the blue frequency effect.
2. Hydrogen bond formation results in structural changes, in particular the C–H bond of F_3CH is contracted. Also, a weak variation in the C–D bond lengths is observed.
3. A variety of possible structures of the $F_3CH/FCD_3/N_2$ system have been found. Three of them, namely, F_3CH/FCD_3 with a single H···F bond (40%), cyclic F_3CH/FCD_3 with two bonds (H···F, F···D; 22%), and the F_3CH/FCD_3 complex with three bonds (H···F, F···D, F···D; 4%) occur frequently (66% of the total time). Occasionally a weaker F_3CH/N_2 complex with nonlinear structure can be temporarily formed (8%). The remaining time of the simulation ($\approx$24%) corresponds to the dynamically formed intermediate-type structures of secondary importance.
4. The lifetimes of the basic structures have been derived on the basis of the CPMD trajectory. The longest lifetime is found for the quasi-linear structure of the F_3CH/FCD_3 complex with a single H···F bond, which is dynamically stabilized by the N_2 solvent molecules. This finding explains the lack of this structure in the case of the isolated complex, as predicted by static ab initio calculations, and confirms the importance of an explicit inclusion of the solvent for a realistic description of the system.

Computational Methods

The theoretical description of the analyzed system consists of several parts. Ab initio calculations at the MP2(full) level of theory using the 6-31+G(d,p) basis set with diffuse functions on heavy atoms and a set of polarization functions, both on hydrogen and heavy atoms, were performed first using the Gaussian 98 A.11.1 quantum mechanical program package.[46] The geometries, interaction energy, and vibrational frequencies of the F_3CH/FCD_3 and F_3CH/N_2 complexes were obtained using the a priori basis set superposition error (BSSE) correction method, namely CP-corrected gradient optimization. Then the possible effect of additional N_2 molecules on the spectroscopic and geometric features of the F_3CH/FCD_3 complex was examined at the same level of theory by adding from one to three nitrogen molecules. In the case of the $F_3CH/(FCD_3, 3\,N_2)$ complex, the CP-corrected gradient optimization was not used due to the large computational effort. The choice of MP2, which is a truly ab initio method, as a starting point for calculations was because of some doubts related to the use of density functional theory (DFT) in the description of the weak hydrogen-bonded complexes.[47] Thus, additionally, the DFT calculations utilizing the 6-31+G(d,p) basis set were performed for selected complexes to check if the geometric and spectroscopic parameters obtained within hybrid (B3LYP) and exchange-correlation (BLYP) functionals were compatible with the MP2 results. Geometry optimization was performed without any constraint and each optimized structure was checked to be a real minimum by a frequency calculation. All of the structures found exhibited a negative binding energy and a blue shift in the C–H stretching frequency, with the C–H bond noticeably contracted. Geometries obtained within the DFT method, as well as spectroscopic parameters, were consistent with the MP2 results, although quantitative differences were observed.

First-principles molecular dynamics simulations were performed using the Car–Parrinello approach as implemented in the CPMD program.[40] Static DFT calculations showed that the gradient-corrected BLYP exchange-correlation functional properly described the blue-shift effect on the systems studied. Therefore, this functional was used in CPMD runs (as a reasonable compromise between the quality of the results and the time of calculations). The primary MD simulations were carried out at 100 K using a system of F_3CH/FCD_3 surrounded by 25 N_2 molecules in a cubic box of length 12.45 Å with periodic boundary conditions (which corresponds to the density of liquid nitrogen at $T \approx 100$ K). The density of the solution and the temperature were set up according to the experimental conditions.[18,38] Martins–Troullier pseudopotentials were used along with the Kleinman–Bylander decomposition, and the plane-wave expansions were truncated at 50 Ry. Test calculations previously performed for isolated F_3CH using different energy cutoffs proved that a value of 50 Ry was a good compromise between efficiency and quality in the description of the system. The fictitious electronic mass was set at 400 a.u. and the equations of motion were integrated with a time step of 5 a.u. ($\approx$0.12 fs). The system was equilibrated under the canonical ensemble (NVT) conditions for 8 ps before accumulating statistics for an additional period of 6 ps. Simulations of an F_3CH/FCD_3 complex as well as single F_3CH and FCD_3 molecules in the gas phase were performed in a cubic box of length 12.45 Å at 100 K using previously described settings. The total length of the simulation run for each system was 6 ps. The frequencies for all the systems studied were derived on the basis of FT of the dipole moment autocorrelation function derived on-the-fly from the CPMD simulation. Autocorrelation functions were calculated using the program package developed by Kohlmeyer.[48] A visualization of a trajectory was performed by use of the VMD program package.[49]

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