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1991

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Theoretical vibrational study of FX...NH_3 (X = H, D, Li) complexes

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(Received 29 March 1990; accepted 23 October 1990)

This paper presents the first *ab initio* attempt to construct the stretching fundamentals ν_{FX} and $\nu_{F...N}$ (X = H, D, Li) in the FX...NH_3 complexes taking into account the mechanical anharmonicity. A potential-energy surface $V(r_{FX},R_{F...N})$ grid was generated at the self-consistent-field and second-order Møller–Plesset levels. The coefficients fitting the potential-energy surface up to the fourth order have been used to compute the ν_{FX} and $\nu_{F...N}$ stretching modes. The vibrational problem is solved by means of a variational treatment which includes the effects of mechanical anharmonicity. The results are compared with the available experimental data.

I. INTRODUCTION

The hydrogen fluoride–ammonia complex and its deuterated analog have been the subject of several experimental[1–3] and theoretical electronic *ab initio*[4–15] studies. For the FLi...NH_3 complex there is no available experimental data to our knowledge. In recent theoretical studies[12,13] on these complexes, electronic calculations have been performed at the self-consistent-field (SCF) and correlated level by using the split valence 6-31G** basis set. Potential energy surfaces (PES) and the related coefficients of the PES, up to the fourth order, have also been previously reported.[12,13] In the present work, new and more extensive potential-energy surfaces have been computed and expanded as a polynomial in two dimensions up to the fourth order, in double precision. This has been used to determine the ν_{FX} and $\nu_{FX...N}$ (X = H, D, Li) stretching modes by means of a two-dimensional variational method. This method has been proven[16] to be suitable in the case of strong anharmonic coupling between the two stretching modes under consideration.

The purpose of the present paper is to estimate the correlation effects of FX...NH_3 (X = H, D) and FLi...NH_3 complexes and to attempt a detailed analysis of the mechanical anharmonicity of the ν_{FX} and $\nu_{FX...N}$ stretching modes of such complexes. The results are also compared with the available experimental data.[1–3]

II. VIBRATIONAL CALCULATIONS

A. The method

In the first step a grid of points for the two-dimensional potential-energy surface was derived from the *ab initio* calculations performed at the SCF and the second-order Møller–Plesset (MP2) perturbation levels. The split-valence 6-31G** basis set was used in the electronic calculations. For both complexes the optimized geometrical structures were adapted from previously reported results.[12,13]

The ν_{FX}, ν_{FLi}, and $\nu_{FX...N}$ stretching modes have been calculated by using a previously reported variational method.[16] The nuclear Schrödinger equation $H\Psi(r,R) = E\Psi(r,R)$ is solved for the internal degrees of freedom r and R where r is related to the F–X distance and R to the F...N distance. The eigenfunctions $\Psi(r,R)$ are written as an expansion of products of the eigenfunctions of the harmonic oscillator.

In the Hamiltonian, the potential function $V(r,R)$ is expanded as a polynomial in two dimensions up to the fourth order which ensures a good representation of $V(r,R)$ with respect to the electronic calculation. Grids of $V(r,R)$ have been constructed involving a number of points depending on the complex considered. The expansion coefficients have been computed by using the method of orthogonal polynomials and the results are reported in Table I. The coefficients

TABLE I. Expansion coefficient[a] of the PES for FH...NH_3 and FLi...NH_3 complexes calculated with the 6-31G** basis set. $V(r,R) = \Sigma\Sigma a_{pq} r^p R^q$.

	FH...NH_3		FLi...NH_3	
	SCF	MP2	SCF	MP2
a_{20}	4.6425	3.5784	1.6364	1.6294
a_{11}	0.1599	0.1875	−0.4843	−0.4847
a_{02}	0.1582	0.1941	0.3006	0.2727
a_{30}	−13.0427	−11.4167	−2.2027	−2.0719
a_{21}	0.7973	0.2862	−1.6495	−1.4621
a_{12}	−0.0386	0.1244	1.4908	1.3125
a_{03}	−0.2314	−0.3725	−0.4292	−0.4013
a_{40}	19.9476	20.0697	4.9782	4.0205
a_{31}	1.0506	1.3278	−2.2424	−2.0724
a_{22}	−0.9821	0.3185	2.8570	2.4411
a_{13}	−0.0511	−0.4424	−1.7716	−1.5327
a_{04}	0.2034	0.2778	0.0704	0.3112

[a] The results are given in mdyn/$Å^{p+q-1}$.

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of the expansion have been used to restore the original data. The points of the PES have been reproduced with an average precision which is always better than 10 cm^{-1}.

The variational method has been applied by using a 22×22 size of the vibrational basis set. Good enough convergence of the variational method has been attained for the FH...NH_3 complex. For this complex the first ten eigenvalues and transitions corresponding to the overtones of the $\nu_{FH...N}$ stretching mode change by less than 1 cm^{-1} in increasing the size of the basis set from 20×20 to 22×22. The eigenvalues corresponding to the ν_{FX} transitions change by less than 5 cm^{-1} for all calculations under the same condition, except in the case of the FH...NH_3 complex at the SCF level where the convergence is 15 cm^{-1}.

The same vibrational basis set has been used for the FLi...NH_3 complex. As the ν_{FLi} and $\nu_{FLi...N}$ stretching modes are closer than the corresponding stretching modes for the FH...NH_3 complex, only three or four overtones of the $\nu_{FLi...N}$ stretching mode may readily be assigned. Those overtones change by less than 1 cm^{-1} at the SCF level by passing from the 20×20 to 22×22 size of the vibrational basis set. The corresponding change is less than 1 cm^{-1} at the correlated level of calculation. The ν_{FLi} stretching mode changes by 15 cm^{-1} with a change of the same size of the vibrational basis set at the SCF level of calculation. The corresponding change is 7 cm^{-1} at the correlated level.

For the FH...NH_3 complex, it may be seen from Table I that the a_{20} coefficient is decreased by passing from the SCF to the correlated level while there is little change noted in the FLi...NH_3 complex.

On the other hand, the a_{02} coefficient is increased under the same circumstance for the FH...NH_3 complex. This kind of change has been observed previously for hydrogen-bonded complexes[17] and is consistent with reported results for the equilibrium geometry.[12,13] The a_{02} coefficient is slightly decreased for the FLi...NH_3 complex.

For the FH...NH_3 complex, the anharmonic coefficients a_{30}, a_{03}, a_{40}, and a_{04} undergo small changes when the electron correlation effects are taken into account. The changes are more important concerning the anharmonic coupling coefficients, the signs of which eventually change when these effects are under consideration.

Neither the anharmonic coefficients, nor the anharmonic coupling coefficients related to the PES of the FLi...NH_3 complex undergo a significant change in passing from the SCF to the correlated level of calculation.

B. Comparison of ν_{FX} and $\nu_{FX...N}$ stretching fundamentals with experimental data

In Table II are reported the calculated values of the fundamental transitions for FX...NH_3 hydrogen-bonded and lithium-bonded complexes at the SCF and correlated level of calculation as well as the corresponding available experimental values. Concerning the hydrogen-bonded complex, the role of the electron correlation effect is clearly shown by the ν_{FX} stretching vibration and is consistent with the observed changes in the PES coefficients.

The ν_{FH} stretching mode is decreased by 442 cm^{-1} in passing from the SCF to the correlated level of calculation. A similar decrease of 554 cm^{-1} was noted previously for H_3N...HCl, using the harmonic approximation.[18] The decrease is 325 cm^{-1} for the deuterated analog. Such a decrease has been observed previously when correlation effects are accounted for in electronic calculations.[17] From the argon matrix infrared spectrum,[1] ν_{FH} stands at 3041 cm^{-1} and ν_{FD} at 2278 cm^{-1}. The present calculated values of 3331 and 2427 cm^{-1} for FH...NH_3 and its deuterated analog represent shifts of 290 and 149 cm^{-1}, respectively, in comparison with matrix results. If it is assumed that the gas-phase calculated values are subject to a typical error of about 3%, mainly due to incomplete basis set and partial treatment of correlation effects in the electronic calculations, the ν_{FH} transition would be located near 3230 cm^{-1} and its deuterated analog near 2355 cm^{-1}. The gas-phase infrared spectrum has not yet been observed though results are expected[19] near 3215 cm^{-1}.

The calculated 1.372 isotopic ratio is close to the 1.335 experimental value. As observed[17] earlier, the $\nu_{FX...N}$ transitions increase in passing from the SCF to the correlated level of calculation. No comparison is possible with the experimental data because these transitions have been observed neither in matrix infrared spectra nor in the gas phase.

For the FLi...NH_3 complex, the ν_{FLi} stretching frequency increases by 15 cm^{-1} in passing from the SCF to the correlated level of calculation. The $\nu_{FLi...N}$ stretch decreases

TABLE II. ν_{FX} and $\nu_{FX...N}$ vibrational transitions for FX...NH_3 (X = H, D, Li) complexes.

	FH...NH_3			FD...NH_3			FLi...NH_3	
	Calc.		Expt.	Calc.		Expt.	Calc.	
	SCF	MP2		SCF	MP2		SCF	MP2
ν_{FX}	3773	3331	3041[a] 3215[b]	2752	2427	2278[a]	932	947
$\nu_{F...N}$	240	263	...	236	255	...	292	281
ν_{FH}/ν_{FD}	1.371	1.372	1.335					

[a] Reference 1.
[b] Reference 19.

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TABLE III. Isotopic substitution for FX...NX_3 complexes (X = H, D).

	NH_3 + HF	$^{15}NH_3$ + HF	NH_3 + DF	$^{15}NH_3$ + DF	ND_3 + HF	ND_3 + DF
Expt.	3041	3042(+ 1)[a]	2278	2277(− 1)	3017(− 24)	2269(− 9)
Calc.	3331	3328(− 3)	2427	2425(− 2)	3324(− 7)	2420(− 7)

[a] The numbers in parentheses represent the difference with the nonsubstituted species.

from 292 to 281 cm^{-1} under the same condition. This 11 cm^{-1} decrease matches quite closely the 10 cm^{-1} drop noted in ClLi...NH_3.[18] The correlation effects are weaker than in the case of the FH...NH_3 hydrogen-bonded complex. This trend has been outlined previously in a study of the electronic properties of lithium-bonded complexes.[14] No comparison with experiment is possible at the present time because there is still no data available on this complex.

C. Isotopic substitutions in the hydrogen-bonded complex

Experimental data have been recorded with several isotopic substitutions using ^{15}N and deuterium for the hydrogen-bonded complex FX...NH_3. Those isotopic substitutions have been undertaken to support the assignments of the matrix infrared spectra. The ν_{FX} stretching mode is then allowed to vary slightly under these substitutions. The ν_{FX} stretching mode has been recorded for the following hydrogen-bonded complexes: FH + $^{15}NH_3$, FD + $^{15}NH_3$, FH + ND_3, FD + ND_3. Calculations have been performed in an attempt to reproduce at least the trends of such fine effects. The experimental data as well as the calculated results are reported in Table III. From experimental data it is seen that the ^{15}N substitution produces an increase of 1 cm^{-1} and a decrease of 1 cm^{-1} on ν_{FH} and ν_{FD} with the ^{15}N-substituted atom, respectively, in comparison with the equivalent nonsubstituted complexes. The trend is partly reversed in the calculations with a decrease of 3 and 2 cm^{-1} for both complexes. Several reasons can be responsible for the discrepancy between observed and calculated trends of the frequency shifts due to the ^{15}N substitution. Effects observed in experimental studies are extremely small, on the order of 1 cm^{-1}, so it cannot be precluded that the matrix effect in this case can disturb the tendency for the gas-phase experiment which corresponds strictly to the results of calculations. On the other hand, application of a more flexible basis set in the *ab initio* calculations as well as the inclusion of higher-order corrections in the Møller–Plesset expansion of electron correlation can change the computed values.

A second type of substitution is the D substitution which experimentally produces a decrease of 24 and 9 cm^{-1} in ν_{FH} and ν_{FD} with the NH_3 molecule, respectively, in comparison with the nonsubstituted complexes. The calculations obey this trend, with a decrease of 7 cm^{-1} for both stretching modes. The discrepancy between the experimental and calculated results could be caused by the reasons discussed above.

D. Mechanical anharmonicity effects on ν_{FX} and $\nu_{FX...N}$ stretching fundamentals

To gain further insight into the nuclear motion in the complexes, the ν_{FH} and $\nu_{FH...N}$ stretching fundamentals are reported in Table IV along with an analysis of the mechanical anharmonicity effects at the correlated level of calculation. The results were obtained using the correlated PES.

TABLE IV. Anharmonicity effects[a] for FX...NH_3 (X = H, D, Li) complexes at the correlated level.

	FX...NH_3				FLi...NH_3	
	ν_{FH}	$\nu_{FH...N}$	ν_{FD}	$\nu_{FD...N}$	ν_{FLi}	$\nu_{FLi...N}$
Full[b]	3331	263	2427	255	947	281
Harmonic[c]	3514	265	2527	262	1010	272
Full ($a_{11}=0$)	3357(+ 26)	257(− 6)	2449(+ 22)	253(− 2)	1049(+ 102)	291(+ 10)
Full ($a_{21}=0$)	3336(+ 5)	260(− 3)	2429(+ 2)	254(− 1)	844(− 103)	288(+ 7)
Full ($a_{12}=0$)	3329(− 2)	261(− 2)	2425(− 2)	254(− 1)	929(− 8)	229(− 52)
Full ($a_{31}=0$)	3339(+ 8)	263(0)	2431(+ 4)	256(+ 1)	958(+ 11)	284(+ 3)
Full ($a_{22}=0$)	3328(− 3)	261(− 2)	2426(− 1)	255(0)	932(− 15)	274(− 7)
Full ($a_{13}=0$)	3288(− 43)	264(+ 1)	2385(− 42)	257(+ 2)	1000(+ 53)	289(+ 8)

[a] The numbers in parentheses represent the difference with the full treatment in the first row.
[b] Calculated with all the coefficients of the expansion $V(r,R)$.
[c] Calculated in the harmonic approximation; i.e., including only a_{20}, a_{02}, and a_{11}.

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The results concerning the FH...NH_3 hydrogen-bonded complex and the deuterated analog are analyzed first.

It is seen from the first two rows of Table IV that the ν_{FH} stretching mode of FH...NH_3 is decreased by 183 cm^{-1} and ν_{FD} by 100 cm^{-1}, when the overall anharmonicity is taken into consideration, which represents a relative decrease of 5.5% and 4.1%, respectively. On the other hand, there is a decrease of 2 and 7 cm^{-1} for the $\nu_{FH...N}$ and $\nu_{FD...N}$ stretching modes, respectively. By examining individual contributions to anharmonicity in the last several rows of Table IV, it is evident that none of the anharmonic coupling coefficients produces a large relative change in the transitions except the a_{11} and a_{13} coefficients. These results clearly show that the ν_{FH} and $\nu_{F...N}$ modes are not very strongly coupled though FH...NH_3 hydrogen-bonded complex is of medium strength.

The general trends for the FLi...NH_3 complex are not the same at all, though the 1010–947 cm^{-1} decrease of the ν_{FLi} mode represents a 6.6% anharmonicity effect, quite comparable to the corresponding decrease in ν_{FH}. The low $\nu_{FLi...N}$ stretching mode increase of 9 cm^{-1}, when anharmonicity effects are taken into consideration, is reversed in comparison with the $\nu_{FH...N}$ mode decrease. By examining the individual contribution to the anharmonicity coming from the expansion coefficients, it is seen that the a_{21} and a_{11} coefficients have very important relative effects on the ν_{FLi} transition. For this complex, each coefficient has a more important relative effect than the corresponding coefficient in the FH...NH_3 complex. Though the individual effects of the a_{pq} coefficients of the PES are not strictly additive, the whole set of anharmonic coupling coefficients (i.e., $a_{21}, a_{12}, a_{31}, a_{22}, a_{13}$) produces a decrease of 40 cm^{-1} for the FLi...NH_3 complex and an increase of 9 cm^{-1} for the FH...NH_3 complex. On the other hand, by subtracting the ν_{FX} anharmonic value (first row of Table IV) from the ν_{FX} harmonic one (second row of Table IV), one obtains a decrease of 63 cm^{-1} for the FLi...NH_3 complex and 183 cm^{-1} for the FH...NH_3 complex. The effect due to the pure anharmonic part of the PES (i.e., a_{30}, a_{40}), deduced from both calculations above, is a decrease of 192 cm^{-1} for ν_{FH} and 23 cm^{-1} for ν_{FLi}. Accordingly, the pure anharmonic effect is relatively stronger for FH...NH_3 than for FLi...NH_3. This fact might be directly seen in Table I.

E. Progressions

In Table V are reported the studies of the $\nu_{FX} \pm n\nu_{FX...N}$ progressions for both hydrogen-bonded and lithium-bonded complexes at the correlated level of calculation. The successive transitions show nearly equally decreasing progressions due to the mechanical anharmonicity effect for correlated calculations. This trend is slightly more pronounced for FD...NH_3 than for FH...NH_3, implying that in excited vibrational states, the deuterated species is slightly more strongly coupled than the nondeuterated one, as previously indicated by Stepanov.[20] This type of progression has been described earlier.[21]

For FLi...NH_3 only the first three overtones of the $\nu_{FLi...N}$ stretching mode have been computed. Other overtones are not recognizable because the two stretching modes are close together, though vibrational overtones of the $\nu_{FLi...N}$ stretching mode are mixed with combination modes of the ν_{FLi} stretching mode with $\nu_{FLi...N}$ modes. The progression is anharmonic as in the case of the FH...NH_3 complex.

TABLE V. Overtones of $\nu_{FX...N}$ and combinations bands of ν_{FX} in FX...NH_3 (X = H, D, Li) at the correlated level.

Transitions $mn \rightarrow m'n'$ [a]	FH...NH_3	FD...NH_3	FLi...NH_3
00→01	263	255	281
00→02	509 (246)	494 (239)	557 (276)
00→03	739 (230)	717 (223)	829 (272)
00→04	958 (219)	931 (214)	1096 (267)
00→05	1172 (214)	1141 (210)	
00→10	3331	2427	947
00→11	3644 (313)	2735 (308)	1272 (325)
00→12	3921 (277)	2995 (260)	1551 (279)
00→13	4180 (259)	3239 (244)	1822 (271)
00→14	4425 (245)	3470 (231)	
00→15	4658 (233)	3691 (221)	

[a] The subscripts m and n describe the fundamental state while m' and n' describe the excited states; m and n refer to the ν_{FH} (or ν_{FLi}) and the $\nu_{FX...N}$ (or $\nu_{FLi...N}$) stretching modes, respectively.

[b] The numbers quoted in parentheses represent the increase relative to the transition listed directly above.

III. CONCLUSIONS

The results presented here demonstrate clearly that the vibrational method is suitable for the study of coupled vibrational modes. The comparison between calculated frequencies derived from PES and available experimental data indicates that electron correlation plays a very important role in a description of the interaction and its contribution for the hydrogen-bonded complex is more pronounced than for the lithium-bonded systems as shown in Table VI. The ν_{FH} stretching mode in FH...NH_3 in the harmonic approximation is decreased by 497 cm^{-1} in passing from the SCF to the correlated level. An additional decrease of 183 cm^{-1} is ob-

TABLE VI. Influence of anharmonicity and electron correlation on vibrational transitions.

	FH...NH_3		FLi...NH_3	
	ν_{FH}	$\nu_{FH...N}$	ν_{FLi}	$\nu_{FLi...N}$
SCF				
Harm.	4011	230	953	286
Anharm.	3773	240	932	292
MP2				
Harm.	3514	265	1010	272
Anharm.	3331	263	947	281
Expt.	3041[a]			
	3215[b]			

[a] Reference 1, from Ar matrix spectrum.

[b] Reference 19, expected for the gas-phase spectrum.

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tained by incorporation of anharmonicity effects into the MP2 result. By combining both effects, i.e., electron correlation and anharmonicity, the ν_{FH} frequency decreases from 4011 to 3331 cm^{-1}, which represents an improvement of 20%, bringing the result in better accord with experimental data. For the lithium-bonded FLi...NH_3 complex, a more complicated situation is noted. The MP2 contribution increases by 57 cm^{-1} the ν_{FLi} stretching mode calculated at the SCF level, whereas the anharmonicity has an opposite effect and further reduces the MP2 value by 63 cm^{-1}. Because both effects represent opposite shifts the total improvement of the ν_{FLi} stretching mode from the SCF harmonic value to the MP2 anharmonic one is in this case very small and equal to only -6 cm^{-1}.

Analysis of individual effects of the a_{pq} coefficients of the PES provides a second important conclusion that mechanical anharmonicity coupling effects are more important for FLi...NH_3 than for FH...NH_3.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Institutes of Health (Grant No. GM36912) and by the Polish Academy of Sciences (Grant No. CPBP-01.12).

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