# Stretching vibrations and structure of $(HF)_n$ ($n$ = 4—8) clusters

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IR spectra of 24 structural isomers of $(HF)_n$ ($n$ = 4—8) clusters were calculated in the framework of semiempirical theory of polyatomic molecule vibrations. Based on the results obtained and available experimental data it is proposed that $(HF)_n$ associates comprising 3—5-membered cycles with attached monomeric HF units are present in molecular beams and gas phase. *Ab initio* calculations performed by the SCF method show the existence of local minima corresponding to such structures on the potential energy surface of $(HF)_n$ clusters ($n$ = 4—6).

**Key words:** $(HF)_n$ clusters, hydrogen bond cooperativity, vibrational spectrum, structural isomers, potential energy surface.

Clusters of hydrogen fluoride molecules have been the subject of active theoretical and experimental investigations for several decades.[1—14] Being simple enough, these systems are very convenient for studying the properties of hydrogen bonding. In addition, the high degree of self-association in the HF vapor provides its unusual thermodynamic properties.

The results of experimental investigations[3—6] permitted reliable determination of the geometric structures of the HF dimer and trimer, which were supported by the *ab initio* calculations.[7,8] According to the measurements of molecular beam depletion in an electric field,[2] the clusters consisting of more than two HF molecules are non-polar, *i.e.*, can have a cyclic structure. The *ab initio* calculations on the cyclic and open (chain) configurations of the $(HF)_n$ clusters demonstrated that the cyclic isomers are more stable energetically at least for $n \le 6$.[8—12] These findings served as a foundation for the concept of HF gas phase, which takes into account only the cyclic $(HF)_n$ isomers.

Until recently, there was no experimental technique that would allow one to assign the observed spectral features to a cluster of definite mass. For this reason, theoretical results obtained for the particular $(HF)_n$ associate were usually compared with arbitrarily chosen experimental frequencies. Moreover, the calculated values of ΔνHF frequency shifts for the same clusters reported in different works markedly differ from each other.[8—14] In this situation neither the understanding of the nature of these shifts, nor the interpretation of the observed spectra were unambiguous. Some authors rationalized the large frequency shifts in the $(HF)_n$ spectra by the cooperativity effects,[13] while the others tend to explain them by the vibrational anharmonicity.[14] In the latter case the key role is played by the hypothesis that the intense bands belonging to the combination transitions in the cyclic associates exist in the observed spectra.

Interpretation of IR spectra of the $(HF)_n$ polymers has became reliable since the advent of the size-selective cluster vibrational predissociation technique in molecular beam.[15,16] The molecular-beam depletion spectroscopy with size-selection makes it possible to determine the size of a cluster that absorbs a photon at each point of the measured spectrum. In the experiments on vibrational predissociation[15,16] an optical parametric oscillator (OPO) with pulse energy of 4 mJ and linewidth $\Gamma \le 0.25$ cm$^{-1}$ was used as a tunable source of infrared radiation. The properties of the OPO nonlinear element ($LiNbO_3$ crystal) made it possible to perform spectral measurements in the whole region of νHF stretching vibrations except the 3590—3470 cm$^{-1}$ interval.

With the help of the molecular-beam depletion spectroscopy with size-selection, it was possible to make justified assignment of observed absorption bands to the $(HF)_n$ oligomers of definite size for $n \le 8$. It was found that if the number of molecules in a cluster increases, the shift of stretching vibrational frequency ΔνHF steeply grows from 94 cm$^{-1}$ for the dimer to 740 cm$^{-1}$ for the octamer.[16]

None of the *ab initio* methods was able to reproduce the measured values of ΔνHF for the clusters of different masses. It might be explained by the fact that the adiabatic approximation tends to overestimate signifi-

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cantly the vibrational frequencies of any molecular system.[17,18] Thus, the matching of experimental frequencies by means of non-empirical quantum-chemical calculations is complicated by the necessity to apply expensive methods of electronic correlation treatment as well as by difficulties with scaling of the calculated frequencies by a single parameter.[18] It is therefore expedient to compare the experimental data on the IR spectra of the $(HF)_n$ clusters[16] with those predicted by the semiempirical theory of polyatomic molecule vibrations.

In this paper we attempt to carry out such a calculation to obtain information on the structure of the $(HF)_n$ polymers in molecular beams and dynamical properties of the HF bonds. In the calculations on IR spectra of the $(HF)_n$ clusters the greatest attention was paid to the hydrogen bond cooperativity* effect, which was taken into account according to the mechanism suggested in Refs. 19—21.

To study the possibility of the formation of different $(HF)_n$ ($n$ = 3—6) structural isomers, the *ab initio* calculations were also carried out for the configurations corresponding to the local minima on the cluster potential energy surfaces (PES).

## Semiempirical calculation of the vibrational spectra of the $(HF)_n$ clusters

It is known that anharmonic corrections to the νXH stretching vibrations of the hydrogen-bonded bridge X—H...Y amount *ca.* 2—5% and do not correlate with the H...Y bond strength.[22,23] For this reason the vibrational spectra of all clusters studied here were investigated within the harmonic approximation[24] using the program.

The geometric parameters of $(HF)_2$ dimer ($r$HF = 0.922 Å, $r$H...F = 1.780 Å, ∠F...H—F = 165°, and ∠H—F...H = 122°) were taken from Refs. 4 and 5. For simplicity, other $(HF)_n$ clusters were assumed to have planar configurations and their bond lengths were chosen to be the same as in the dimer. This choice of geometric parameters did not affect the accuracy of calculated νHF frequencies discussed below since both kinematic and dynamical couplings between stretching vibrations appear to be small enough for the cluster of any structure.[19,25]

Therefore, it is reasonable to assume that the variety of νHF values observed experimentally arises only from the difference in the force constants $K_{HF}$ of the HF molecules involved in the cluster. The lowering of the HF molecule force constant $\Delta K_{HF} = K^{free} - K^{bound}$ characterizes the strength of the hydrogen bond formed by the molecule. The cooperative effects (mutual enhancement of H-bonds in a system) increase $\Delta K_{HF}$, whereas the deformation (*i.e.*, weakening) of the H-bond decreases it.

The evaluation of the $(HF)_n$ force constants needed for the calculations took into account the non-additivity of interactions between different H...F bonds and the degree of their deformation. These effects were described within the semiempirical model of dynamical and electrooptical parameters of molecular complexes[19,20] and by the method allowing for the H-bond cooperativity and deformations.[21]

The calculated vibrational frequencies of the cyclic $(HF)_n$ ($n$ = 4—8) polymers, which are thought to be the most probable component of HF vapor and molecular beams (see above), are presented in Fig. 1. The comparison with experimental data[16] shows that the frequency of degenerate (IR-active) tetramer vibration (3492 cm$^{-1}$), which, according to the calculations, falls in the region of OPO nonlinear element absorption (3550—3450 cm$^{-1}$), differs from the experimentally observed frequency (3636 cm$^{-1}$) by *ca.* 150 cm$^{-1}$ (Fig. 1). For the cyclic pentamer, the results of the calculations (3451 cm$^{-1}$) and experiments (3453 cm$^{-1}$) are in very good agreement. The difference between observed and calculated frequencies monotonically increases and reaches hundreds wave numbers with further increase of the $(HF)_n$ cluster size ($n$ = 6—8); see Fig. 1.

Such a gradual deviation of the calculated frequencies of the $(HF)_n$ ($n$ = 4, 6—8) polymers from the measured ones[16] and, more importantly, the monotonic dependence of $\Delta\nu_n$ on the cluster size cannot be explained by the approximate nature of vibrational calculations or by the inaccuracy of input parameters. As was noted above, the results of other works, whose authors restricted themselves to a consideration of the cyclic $(HF)_n$ structures only, did not agree with the assignment of the frequencies in the mass-selective measurements despite the fact that strong vibrational anharmonicity and scaling factors were taken into account (see, for instance, Ref. 14). It is therefore reasonable to suggest that this disagreement is related to the formation of the clusters of distinct, non-cyclic, structures at low temperatures and non-equilibrium conditions in molecular beams. This hypothesis was also supported by the data on the cooperativity of hydrogen bonds, which reveal that the vibrational frequencies of unstrained cyclic clusters can drop significantly only upon the attachment of outer ("tail") molecules.[19,23] It should be noted that the formation of specific structures consisting of the $(HF)_{n-m}$ cycles and the fragments of the $(HF)_m$ chains upon sudden cooling of HF vapor was first predicted by the Monte-Carlo method in Ref. 13. Hereafter we will call such structures of the $(HF)_n$ polymers branched.

In order to check the above hypothesis, the IR spectra of 19 branched $(HF)_n$ ($n$ = 4—8) isomers consisting of 3—6-membered rings with one or more "tails" of various lengths were calculated here in addition to those of five cyclic associates; see Table 1 and Fig. 1.

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*Cooperativity, *i.e.*, the dependence of the strength of each H-bond on their number and mutual orientation, manifests itself in the changes of the force constants, and, in turn, of the vibrational frequencies of the HF molecules participating in these bonds.

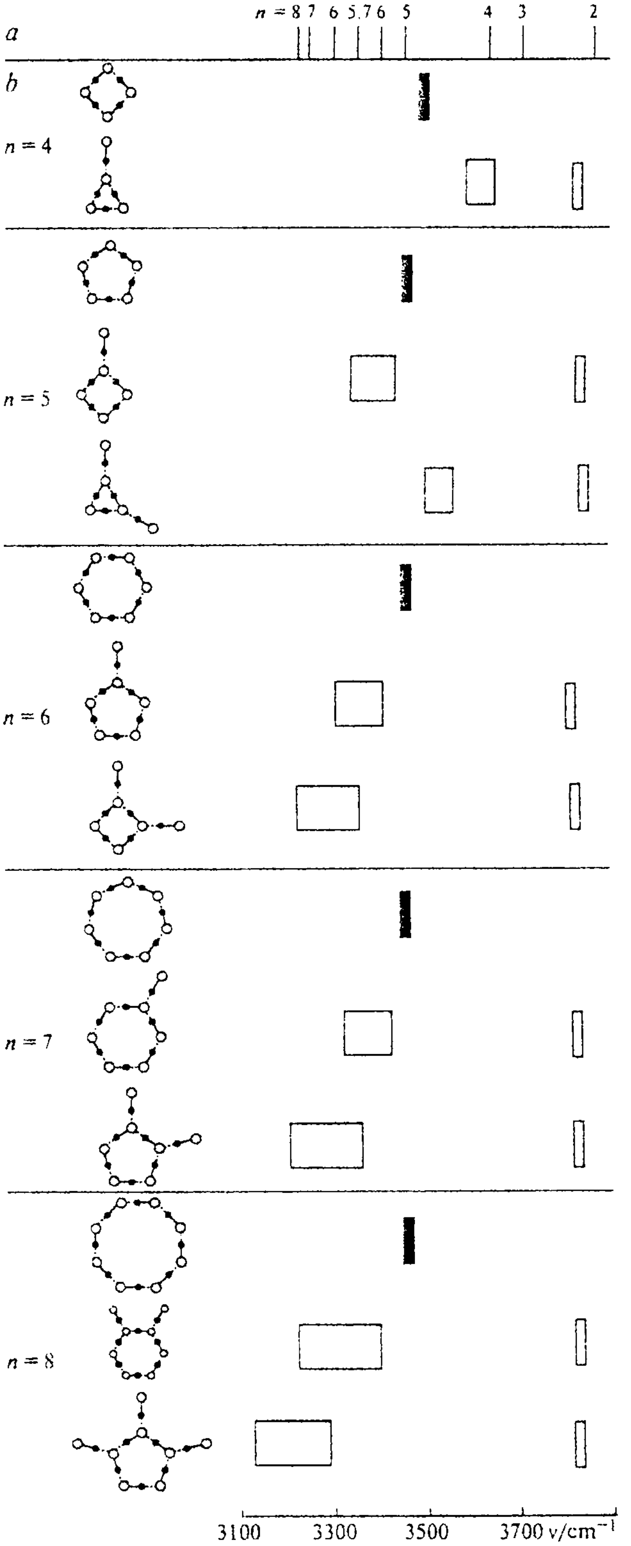


**Fig. 1.** The absorption regions of the various $(HF)_n$ ($n$ = 4—8) clusters: *a* — experimental.[16] *b* — calculated.

The frequencies of two of these branched structures were calculated previously.[13]

Analysis of calculated data shows that the attachment of the first "tail" molecule to the cycle leads to the lowering of the mean value of $\nu$HF vibrational frequencies of the cycle by *ca.* 100 cm$^{-1}$. The attachment of each next "tail" molecule at any site further lowers the "center of gravity" of cycle absorption by 80—100 cm$^{-1}$ (Table 1). This correlation between the absorption frequencies of the cyclic part of the cluster and the number of "tail" molecules is a consequence of the hydrogen bond cooperativity. The cooperativity effect also manifests itself in the non-equivalence of the force constants (and, in turn, the vibrational frequencies) of different members of the cycle upon the attachment of "tail" molecules. The less uniform is the distribution of "tail" molecules around the $(HF)_n$ cycle, the larger is the difference of these frequencies (60—240 cm$^{-1}$).

Hence, owing to these features of branched isomer spectra, the bands of hexamer and larger clusters are shifted toward the very same region (3460—3100 cm$^{-1}$), in which the absorption of the $(HF)_n$ ($n$ = 6—8) associates were detected.[16] These data (Table 1, Fig. 1) also allow us to explain the experimental fact that several absorption bands with significant energy separations may be due to the vibrations of one or several clusters of the same mass.

Comparison of the calculated and measured vibrational frequencies of the $(HF)_n$ polymers indicates that the pentamer $(HF)_5$ has the cyclic structure in the molecular beam, while the larger clusters have the branched one. It is also found that the branched isomers having the "tails" of one HF unit should absorb in the 3850—3800 cm$^{-1}$ range. If the "tails" consist of two or three members, additional absorption should be observed in the 3750—3700 cm$^{-1}$ range and nearby 3650 cm$^{-1}$. The question of the tetramer $(HF)_4$ structure remains less clear. According to the calculations, the frequency of the cyclic isomer (~3490 cm$^{-1}$) lies in a region so far inaccessible for experimental measurements, whereas the frequencies of branched isomer (3648, 3624, and 3583 cm$^{-1}$) are in reasonable agreement with the doublet (3636 and 3625 cm$^{-1}$) observed for the four-membered cluster.[16]

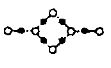
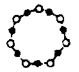
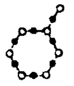
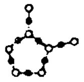
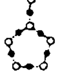
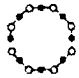
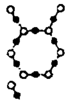
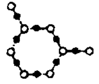
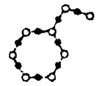
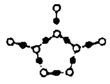
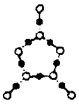
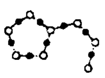
Let us now consider the spectral density distributions of the $(HF)_n$ polymers under study. The vibrational transition intensities needed for their simulation were calculated using the following initial data. The values of bond dipole moments were taken from the literature.[26] The values of particular combinations of the dipole moment derivatives with respect to the natural coordinates $\partial\mu X...HF/\partial qHF - \partial\mu X...HF/\partial qX...H$, which determine the band intensity of each stretching vibration, were evaluated from the experimental dependence (Fig. 2) taken from Refs. 27 and 28. This procedure made it possible to take into account contribution of the hydrogen bond cooperativity effect (whose magnitude varies depending on the mutual orientation of the H-bonds) not only to the vibrational frequencies, but also to the intensities of the HF vibrational bands in the clusters under study.

The spectral density distributions for all $(HF)_n$ structural isomers were simulated under the assumption that the absorption bands have Gaussian profile with the half-width $\sigma = 20$ cm$^{-1}$. Several most characteristic examples of such spectra are presented in Fig. 3. They exemplify the main features of the spectra of different $(HF)_n$ $(4 \le n \le 8)$ structural isomers as well as the characteristic regions where the clusters of different masses absorb.

Obviously, the overlapping of neighboring absorption bands reduces the number of maxima on the spectral density distributions. If the spectra are recorded under conditions of significant line broadening ($\sigma > 20$ cm$^{-1}$), the number of resolved spectral features should decrease further. It is worth noting that the intensity of isolated vibrational bands of the "tail" HF molecules is an order of magnitude smaller than the integrated intensity of the molecules in the cycle. It is likely the reason why the vibrational bands of "tail" molecules have not been detected so far.

Calculated spectra of different $(HF)_n$ isomers allow one to simulate the observed vibrational predissociation spectrum of clusters in molecular beam[16] (Fig. 4, *a*). To model this spectrum, the relative contents of the clusters

**Table 1.** Frequencies of the stretching vibrations of the $(HF)_n$ clusters calculated within the framework of semiempirical theory of molecular vibrations

| Cluster $(HF)_n$ *n* | Isomer | ν/cm$^{-1}$ |
|---|---|---|
| 4 |  | 3494 3492 3492 3490 |
| |  | 3837 3648 3624 3589 |
| 5 |  | 3453 3451 3451 3447 3447 |
| |  | 3831 3433 3411 3381 3340 |
| |  | 3837* 3562 3524 3499 |
| |  | 3830 3740 3603 3559 3499 |
| 6 |  | 3456 3454 3454 3449 3449 3447 |
| |  | 3826 3413 3398 3378 3350 3310 |
| |  | 3832* 3355 3302 3281 3227 |
| |  | 3832* 3324 3324 3258 3258 |
| |  | 3832 3735 3393 3355 3302 3227 |
| |  | 3865* 3432 3432 3432 |
| 7 |  | 3455** |
| |  | 3826 3426 3418 3401 3386 3356 3322 |
| |  | 3826* 3361 3325 3275 3271 3204 |
| |  | 3826* 3340 3312 3296 3256 3235 |
| |  | 3826 3724 3386 3361 3325 3275 3205 |
| 8 |  | 3455** |
| |  | 3826* 3394 3366 3337 3292 3286 3225 |
| |  | 3826* 3376 3351 3330 3306 3286 3253 |
| |  | 3826 3725 3407 3393 3366 3337 3286 3225 |
| |  | 3826* 3287 3221 3217 3165 3127 |
| |  | 3826* 3258 3237 3195 3179 3149 |
| |  | 3826 3724 3367 3333 3287 3221 3127<br>3650 |

*Several "tail" molecules in the cluster have the same frequency.

**All molecules of the cyclic part of the cluster have frequencies close to this frequency.

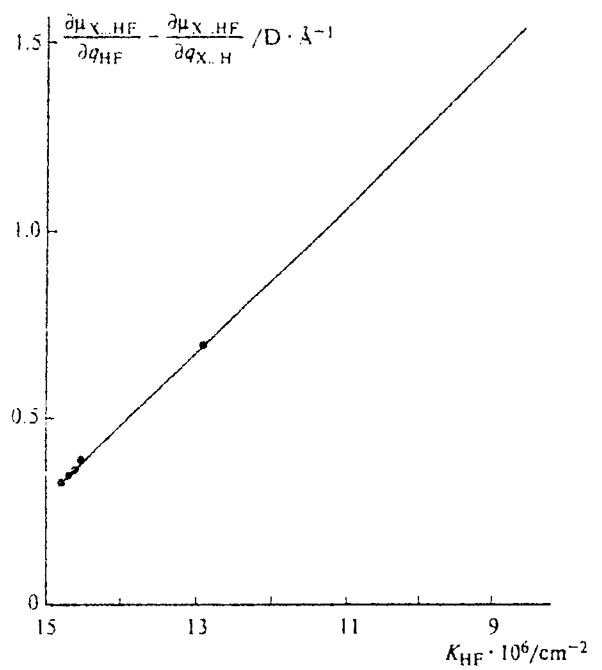


**Fig. 2.** Dependence of the electrooptical parameter of the X...H—F hydrogen bridge on the strength of the hydrogen bond (according to Refs. 27 and 28).

of different masses in a beam at $T = 5$ K were estimated from the percentage of beam depletion at the mass 21. The estimations point out that the main fraction in such a beam consists of hexa- and heptamers, whereas the pentamer concentration is quite insignificant.[16]

The attempts to model the experimental spectral density distribution revealed that it can be simulated from the spectra of a definite set of $(HF)_n$ clusters. The equally good fits can be obtained with several sets of the clusters, which differ from each other both in the sizes and the concentrations of isomers. It is, however, necessary that the polymers forming the main fraction in each set consist of cycles no larger than five molecules and "tails" no longer than one molecule. It is interesting to note that all the considered sets of clusters, which provide the best fit to experimental data, almost completely (by ~95%) consist of the branched isomers.

Let us discuss for example the integrated spectral density distributions obtained for two such sets (Fig. 4, *b*). It is evident that the experimental positions and relative intensities of absorption maxima are reproduced quite correctly in both cases. The main difference is that the calculated spacing between two bands of 3630 cm$^{-1}$ doublet is four times greater than the measured one.

To summarize, the consideration of the branched structures of the $(HF)_n$ polymers permitted an adequate explanation of the features of cluster molecular beam vibrational predissociation spectrum[16] including the large red shifts of HF stretching vibrational bands, the existence of several bands assigned to the clusters of the same size, the characteristic spacings between the maxima of spectral density distribution (~50—100 cm$^{-1}$), and the coincidence of frequencies for some clusters of different size.

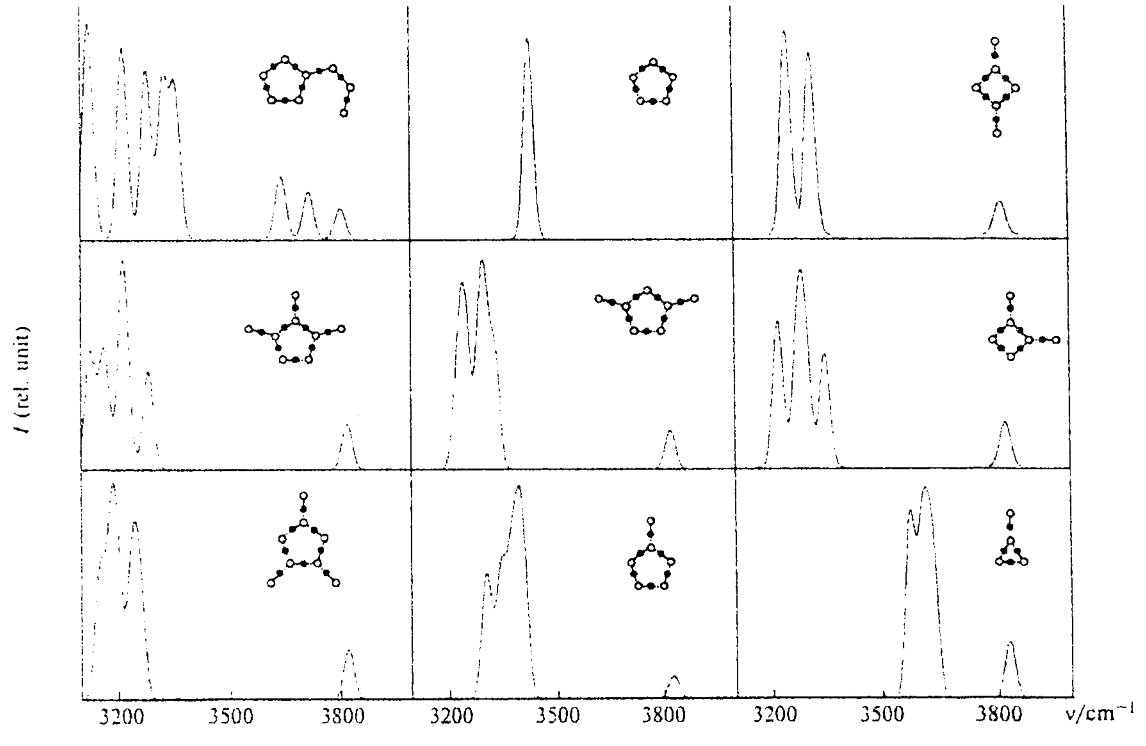


**Fig. 3.** Spectral density distributions of some isomeric $(HF)_n$ clusters.

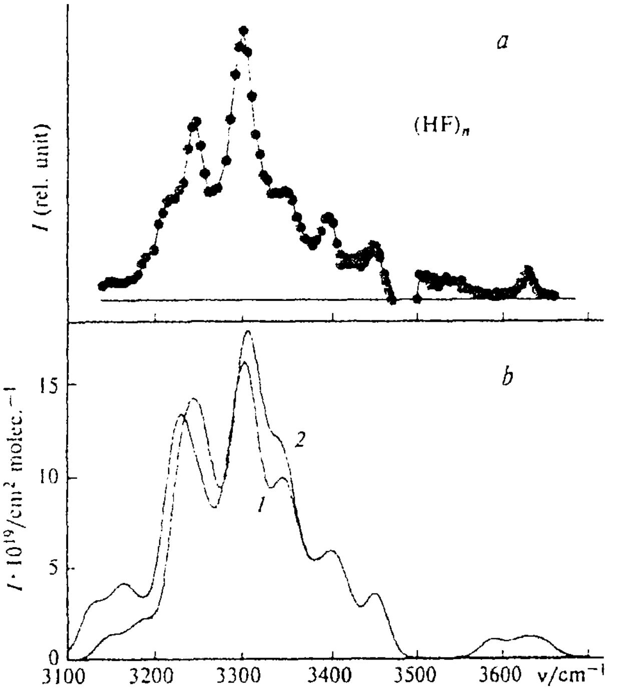
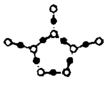
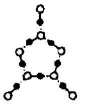
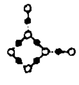
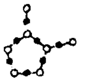
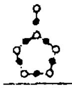


**Fig. 4.** Vibrational predissociation spectra of the $(HF)_n$ ($n \le 8$) clusters in molecular beam ($T$ = 5 K); *a* — experimental;[16] *b* — simulated:

| Oligomer | Oligomer content (%) 1 | Oligomer content (%) 2 | Oligomer | Oligomer content (%) 1 | Oligomer content (%) 2 |
|---|---|---|---|---|---|
|  | 11.4 | 0.0 |  | 0.0 | 7.0 |
|  | 5.8 | 5.5 |  | 14.0 | 14.0 |
|  | 28.0 | 33.0 |  | 5.8 | 5.5 |
|  | 21.0 | 21.0 |  | 14.0 | 14.0 |

The calculated data and their good agreement with the measured results suggest the following. The unexpectedly low cyclic pentamer concentration (relative to that of the larger clusters) detected experimentally[16] may be caused by the effective formation of branched $(HF)_n$ ($n$ = 6—8) isomers from the pentamer units. It is likely that for this reason as well as because of the shift of relative cluster stability from $n$ = 4 under the equilibrium conditions to $n$ = 5—6 in a molecular beam,[21,29] the concentration of cyclic tetramers may be also relatively low.

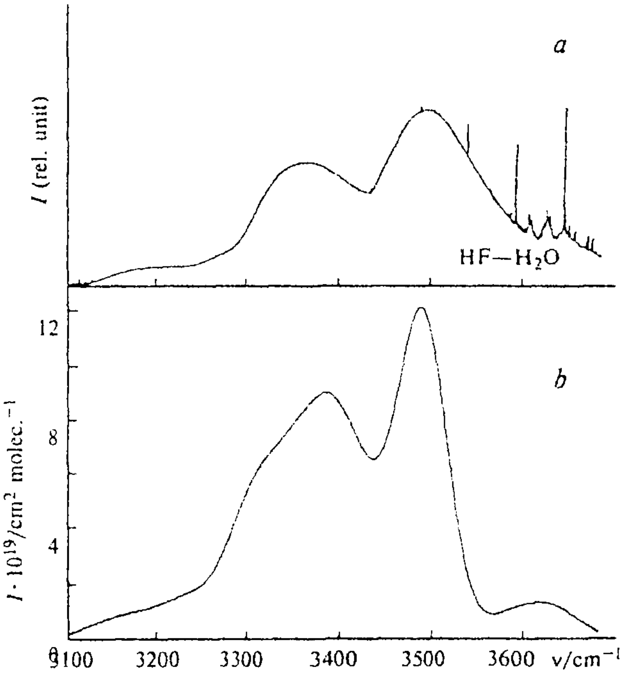
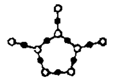
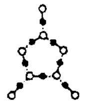


**Fig. 5.** IR spectra of the $(HF)_n$ clusters in the gas phase ($T$ = 273 K): *a* — experimental;[12] *b* — simulated:

| Oligomer | Oligomer content (%) | Oligomer | Oligomer content (%) |
|---|---|---|---|
|  | 1.6 |  | 4.1 |
|  | 1.6 |  | 41.0 |
|  | 3.2 |  | 16.2 |
|  | 32.3 | | |

Assuming that the branched $(HF)_n$ polymers also can be formed in the equilibrium systems, we attempted to apply a similar description to the IR spectrum of HF vapor at the temperature 273 K obtained in Ref. 12. According to the theoretical estimations,[29] the cyclic $(HF)_4$ tetramer should have the maximum concentration under these conditions. Indeed, the spectrum of this cluster allowed us to explain the most intense band at ~3500 cm$^{-1}$; see Fig. 5, *a*. In the higher frequency range, where, as follows from our calculations, the bands of the branched tetramer take place, the authors of Ref. 12 predicted the absorption not only due to the $(HF)_n$ clusters, but also to the $H_2O—HF$ ones (see Fig. 5, *a*). Hence, in this range the most striking disagreement between simulated and measured spectra should be expected (and really exists). The absorption in the rest of the frequency region can be successfully described by the set of the spectra of cyclic pentamer and branched clusters formed from the former upon the attachment of one, two, or three "tails". The resulting spectral density distribution, in which the widths of all bands were set to 40 cm$^{-1}$ (Fig. 5, *b*), provides a quite acceptable description of the experimental curve.

Thus, the hypothesis of the coexistence of the branched $(HF)_n$ clusters with their cyclic isomers as well as consideration of the cooperativity of conjugated hydrogen bonds provide an explanation for the specific features of hydrogen fluoride spectra in the gas phase[12] and in molecular beams[16] and indicate which structural isomers and why are formed under the equilibrium and non-equilibrium conditions.

This hypothesis is supported not only by the results of Monte-Carlo simulations.[13] The special calculations on the thermodynamic functions of the $(HF)_n$ clusters based on the data of this spectroscopic study demonstrated the relative stability of the branched isomers.[21] It is likely that the stabilities of some of them (in which the numbers of molecules in the cycle and in the "tails" are in the ratios 3 : 1, 4 : 2 and 5 : 1) is comparable to those of pure cyclic structures. This observation make it interesting to perform the direct search for the branched $(HF)_n$ ($n$ = 4—6) structures within the *ab initio* methods.

### *Ab initio* SCF calculations on the stable configurations of the $(HF)_n$ clusters

The calculations were performed by the self-consistent field (SCF) method in the double-zeta atomic orbital basis augmented by the polarization orbitals using the GAMMES program package.[30] The energies at the stationary points of a system were calculated within the second-order Møller-Plesset perturbation theory (MP2). It should be noted that this approximation does not reveal rigorous quantitative conclusions since the latter require more grounded treatment of electron correlation effects.

The results of the calculations demonstrated that the branched clusters with the ratios of cycle to "tail" units 3 : 1, 3 : 2, 3 : 3, 4 : 1, 4 : 2, and 5 : 1 are really stable. None of the stable clusters with the dimeric "tail" was observed. The geometry optimization always transforms such configurations to structures corresponding to either cycle or a cycle with a monomer "tail".

Table 2 shows the total energies of the global and local minima on the PES of the $(HF)_n$ ($n$ = 1—6) clusters as well as the energies of local minima with respect to those of the global ones. In keeping with the calculations by other authors, the minimum energies correspond to the cyclic structures. The local minima corresponding to branched structures with one or two "tails" lie higher in energy by 5—8 and 12—14 kcal mol$^{-1}$, respectively. The energy of the unique configuration with three "tails" (for $n$ = 6) exceeds that of the prime isomer by more than 20 kcal mol$^{-1}$. It is evident that the application of the more accurate *ab initio* methods will affect the absolute ΔE values but not the conclusions on the relative stabilities of the conformers.

Special attention should be paid to the fact that the calculated values of the harmonic frequencies for the cyclic and the stable branched $(HF)_n$ conformers fall within the same spectral region (Table 3). It provides implicit evidence that the local minima are relatively

**Table 2.** Total $E$ (a.u.) and relative $\Delta E$ (kcal mol$^{-1}$) energies of isomers calculated within the SCF and MP2 approximations

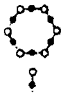
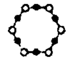
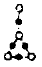
| $n$ | Isomer | SCF | | MP2 | | $n$ | Isomer | SCF | | MP2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $(HF)_n$ | $E$ | $\Delta E$ | $E$ | $\Delta E$ | | $(HF)_n$ | $E$ | $\Delta E$ | $E$ | $\Delta E$ |
| 1 |  | −100.047825 | | −100.229575 | | 5 |  | −500.273623 | 14.22 | −501.191041 | 17.90 |
| 2 |  | −200.103354 | | −200.468430 | | 6 |  | −600.357382 | 0.0 | −601.465065 | 0.0 |
| 3 |  | −300.167257 | | −300.718827 | | |  | −600.348997 | 5.26 | −601.455413 | 6.06 |
| 4 |  | −400.233202 | 0.0 | −400.971298 | 0.0 | |  | −600.338472 | 11.87 | −601.442421 | 14.21 |
| |  | −400.221201 | 7.53 | −400.955829 | 9.71 | |  | −600.338008 | 12.16 | −601.441991 | 14.48 |
| 5 |  | −500.296279 | 0.0 | −501.219566 | 0.0 | |  | −600.324592 | 20.58 | −601.424715 | 25.32 |
| |  | −500.286284 | 6.27 | −501.207439 | 7.61 | | | | | | |

**Table 3.** IR spectra of the $(HF)_n$ clusters

| $n$ | Isomer $(HF)_n$ | $\nu$/cm$^{-1}$ ($I_{rel}$ (%)) | $n$ | Isomer $(HF)_n$ | $\nu$/cm$^{-1}$ ($I_{rel}$ (%)) |
|---|---|---|---|---|---|
| 1 |  | 4511(4) | 5 |  | 4461(4), 4459(10), 4392(11), 4318(16), 4205(11) |
| 2 |  | 4473(4), 4427(11) | 6 |  | 4194(1), 4168(0), 4168(0), 4085(67), 4085(67), 3988(0) |
| 3 |  | 4344(14), 4344(14), 4275(0) | |  | 4457(7), 4264(9), 4199(15), 4142(31), 4080(32), 3947(21) |
| 4 |  | 4255(0), 4208(32), 4208(32), 4103(0) | |  | 4464(0), 4463(14), 4288(0), 4284(30), 4122(43), 4066(0) |
| |  | 4441(7), 4395(12), 4324(11), 4199(12) | |  | 4470(6), 4467(8), 4328(12), 4210(32), 4194(10), 4008(19) |
| 5 |  | 4199(0), 4199(0), 4124(51), 4124(51), 4015(0) | |  | 4477(0), 4475(10), 4475(10), 4332(18), 4332(18), 4276(0) |
| |  | 4453(7), 4309(12), 4236(21), 4167(20), 4030(16) | | | |

deep and, in turn, that the corresponding isomers are relatively stable.

Leaving aside the analysis of the absolute values of calculated νHF frequencies, we consider the main trends of their variations from one cluster to another. It is evident from the data of Table 3 that the *ab initio* results support the following trends found in the semiempirical studies of the spectra of the $(HF)_n$ clusters (Table 1). The frequencies of the "tail" molecules in all branched clusters are close to each other, being similar to the $(HF)_2$ dimer vibrational frequency. The band intensities associated with the vibrations of "tail" molecules are much weaker than those associated with the HF bonds in the cycles. The attachment of "tail" molecule to the cycle strongly splits out its stretching vibrations.

To summarize, the results of our calculations and critical analysis of the published data indicate that the association of HF molecules in the gas phase and molecular beams can form a significant fraction of the branched clusters. However, the existence of such structures can be rigorously proven only by the experimental detection of the bands of large ($n \geq 4$) $(HF)_n$ clusters in a 3850—3800 cm$^{-1}$ where, according to the calculations, the absorption by the "tail" molecules should take place.

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