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Calculation of structures, energetics and infrared absorption spectra of hydrogen-bonded dimers and trimers formed by formaldehyde with hydrogen fluoride

Motivation

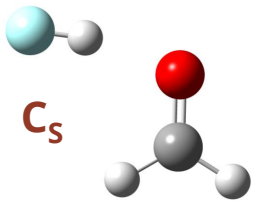
Complexes of H_2CO with HF are simplest H-bonded complexes of HF with carbonyl containing molecules. These complexes may be present in the Earth atmosphere.

Objects of investigations

- *Monomers*: formaldehyde H_2CO, hydrogen fluoride HF
- *Dimers* : $H_2CO\cdots HF$, planar and non-planar $(H_2CO)_2$
- *Trimers*: two stable $(HF)_2\cdots H_2CO$, four stable $(H_2CO)_2\cdots HF$

1

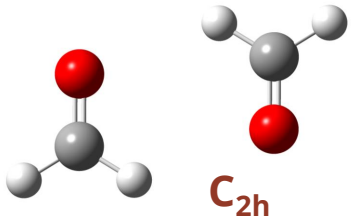
Heterodimer



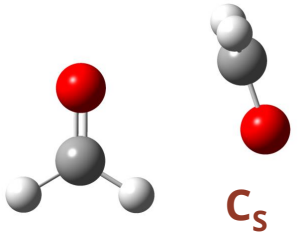
C_S

2

Homodimers



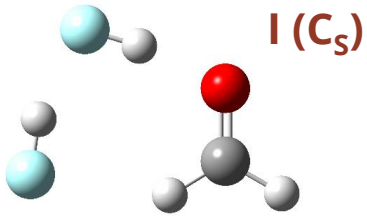
C_{2h}



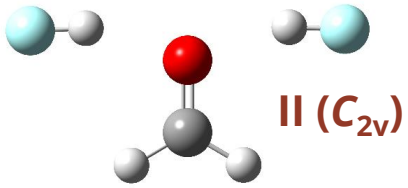
C_S

3

Trimers $(HF)_2\cdots H_2CO$



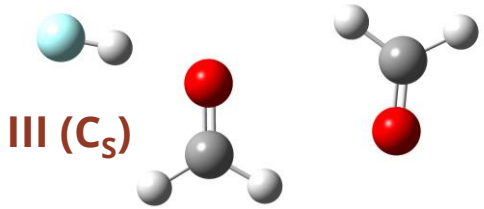
I (C_S)



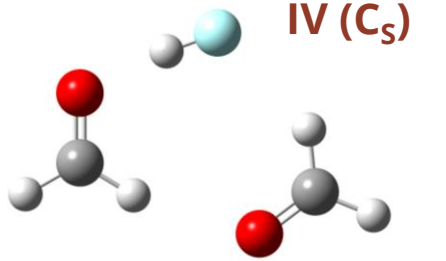
II (C_{2v})

4

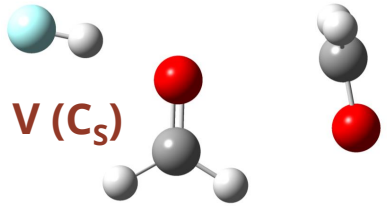
Trimers $\cdot(H_2CO)_2\cdots HF$



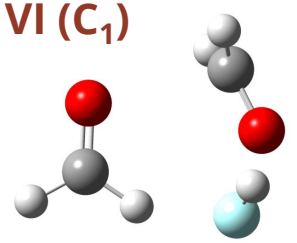
III (C_S)



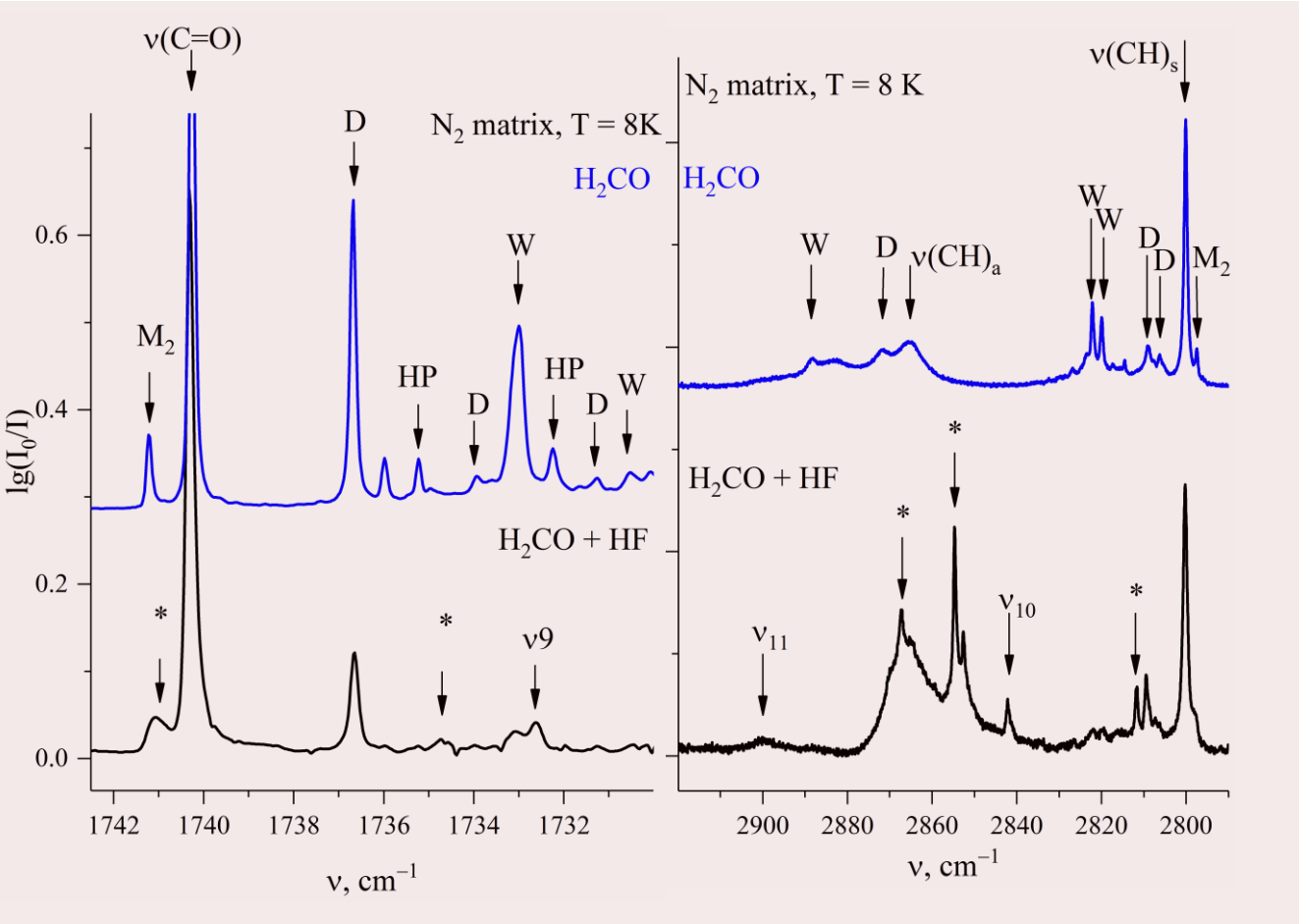
IV (C_S)



V (C_S)



VI (C_1)



Spectra of H_2CO (upper spectrum) and its mixture with HF (lower spectrum) recorded in N_2 matrices at T = 8 K in the region of the C=O (left) and the CH (right) stretching modes. Asterisks mark the bands that are found only in the spectra of mixtures of H_2CO and HF

Experiment

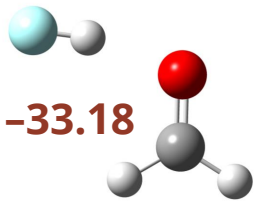
- The concentrations of components in $H_2CO/HF/N_2$ mixtures were within 0.07–0.6: 0.6–10: 1000
- The spectral range – 4500 – 560 cm^{-1}
- A resolution – 0.1 cm^{-1}

Binding energy (above) and $\Delta E_{nonadditivity}$ (below) (in kJ mol $^{-1}$)

Method of calculations. The electronic structure calculations were carried out by the MP2/aug-cc-pVTZ *ab initio* method.

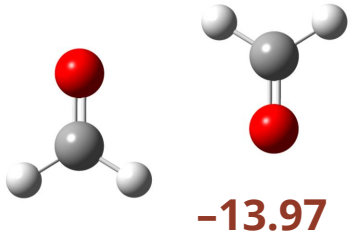
1

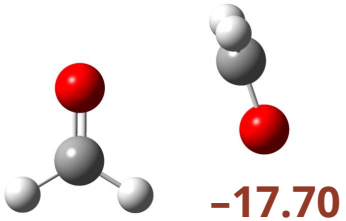
Heterodimer



2

Homodimers

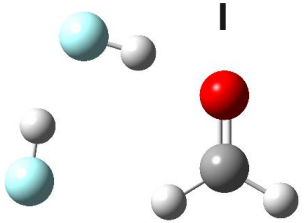




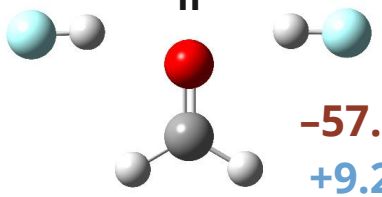
3

Trimers $(HF)_2\cdots H_2CO$

I



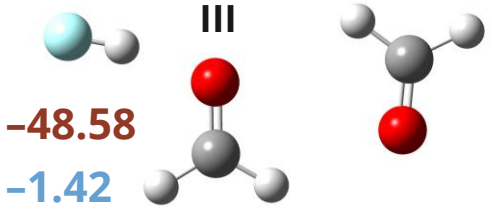
II



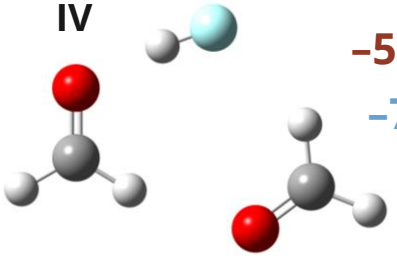
4

Trimers · $(H_2CO)_2\cdots HF$

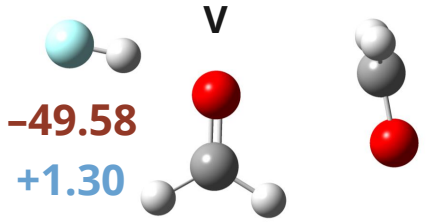
III



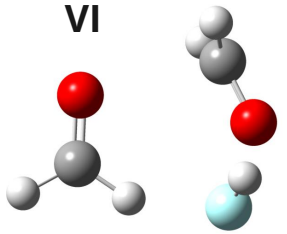
IV



V



VI

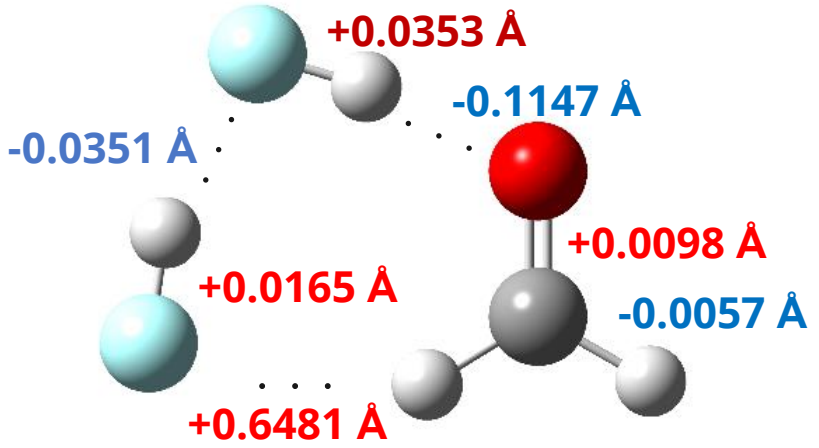


The difference between the trimer binding energy E_{bind} and the sum of pairwise dimerization energies of molecules constituent the trimer indicates the nonadditivity of hydrogen bonding ΔE_{nonadd} (blue color). Thus, from the energetic point of view, the nonadditivity of H-bonding is largest in trimer I. Two H-bonds in this strongest trimer helps each other. In contrast, H-bonds are anticooperative in trimers II and V.

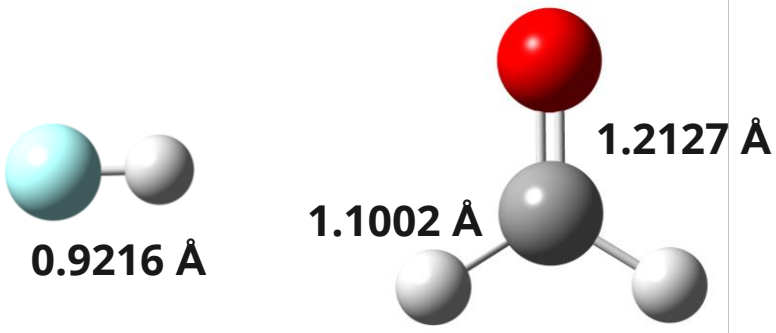
Structures of monomers, heterodimer HF···H_2CO, and trimers $(HF)_2$···H_2CO

The numbers indicate bond length values in H_2CO, H-bond length in HF···H_2CO and bond length changes upon dimerization, and changes of interatomic distances upon trimerization.

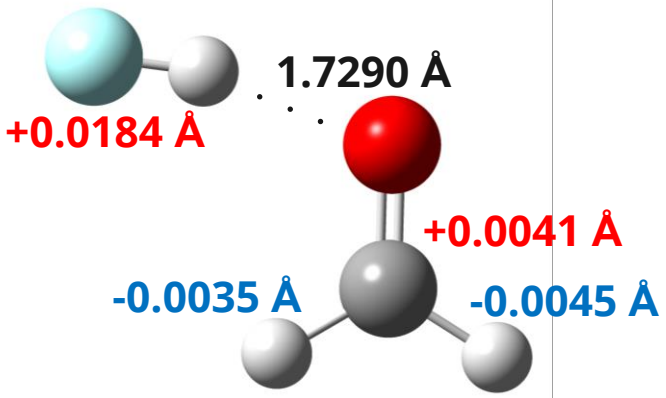
I



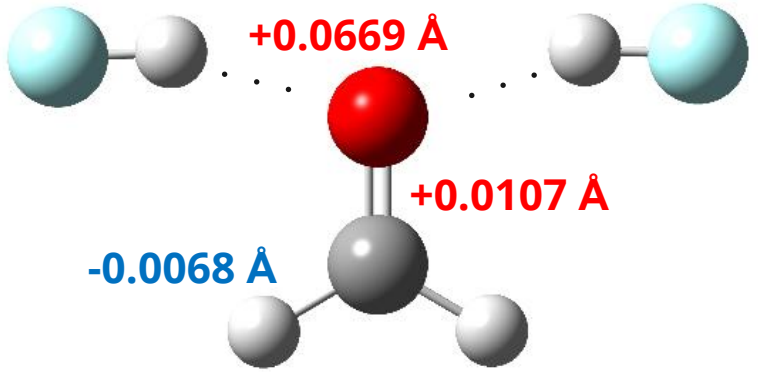
Monomers



Heterodimer



II

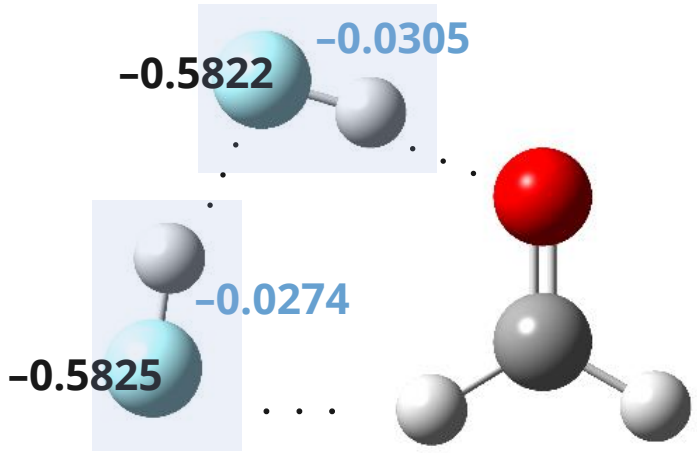


NBO charges on F atoms and the charges transferred from H_2CO in HF ··· H_2CO and trimers I and II

Comparison of NBO charges calculated for molecular complexes and monomers can provide valuable information on the nature of intermolecular interactions.

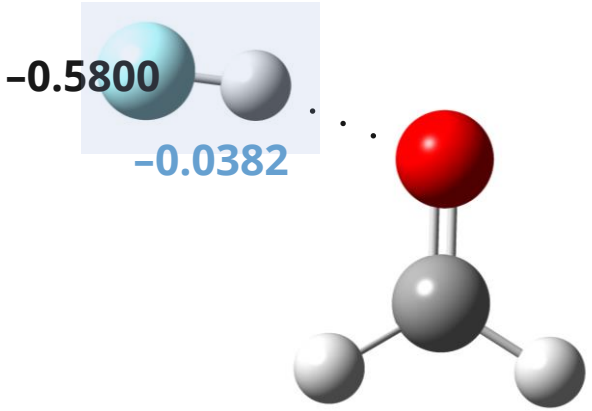
The NBO charges calculated by the MP2 method with the option “density = current”

I

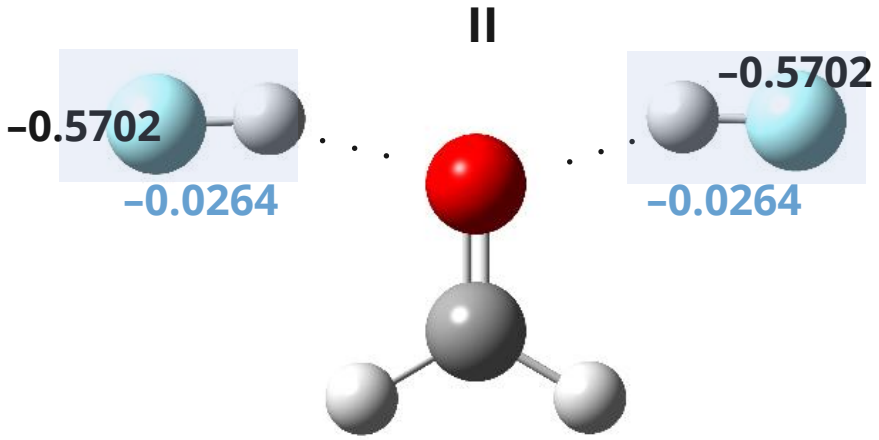


Monomer

Heterodimer



II



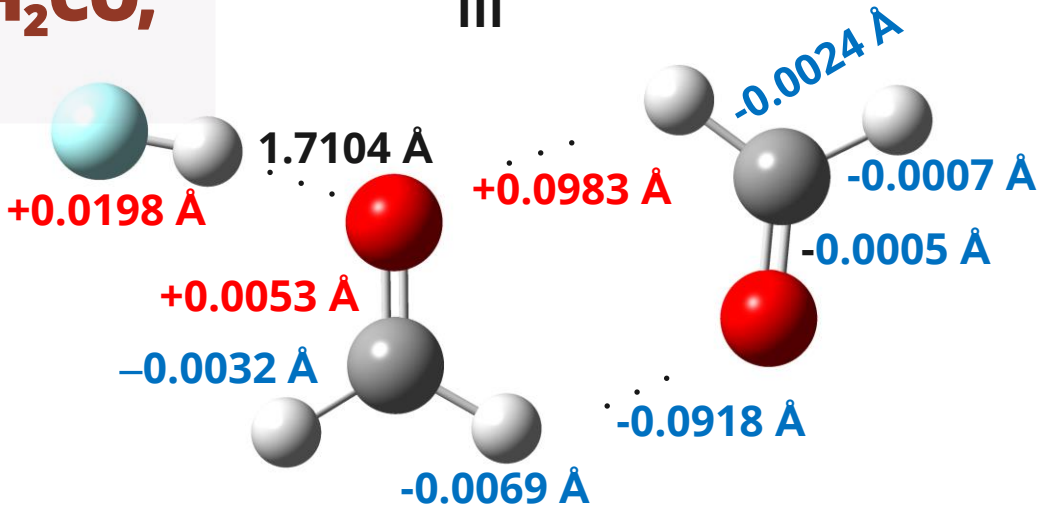
Structures of monomers, heterodimer HF···H_2CO, and trimers $(HF)_2$···H_2CO

Here, as in slide 5, the bond lengths and their changes upon complexation are shown.

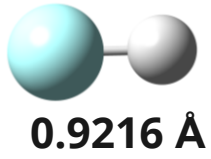
Upon formation of trimer IV, the HF molecule breaks one of H-bonds in the planar homodimer and becomes a proton donor in the strong O···HF bond and a proton acceptor in the weaker F···HC bond.

Trimers

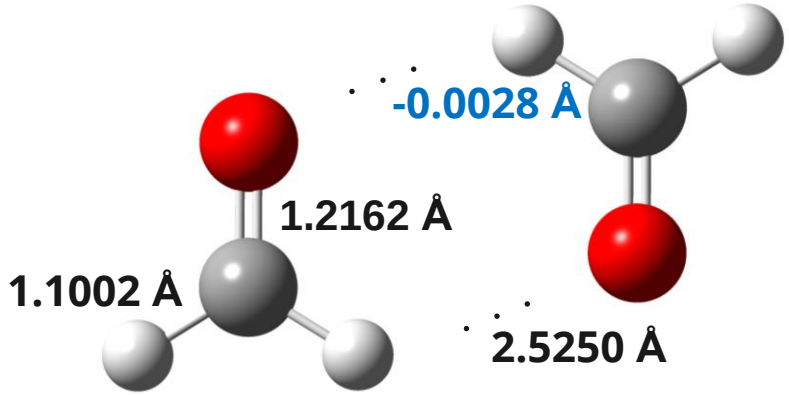
III



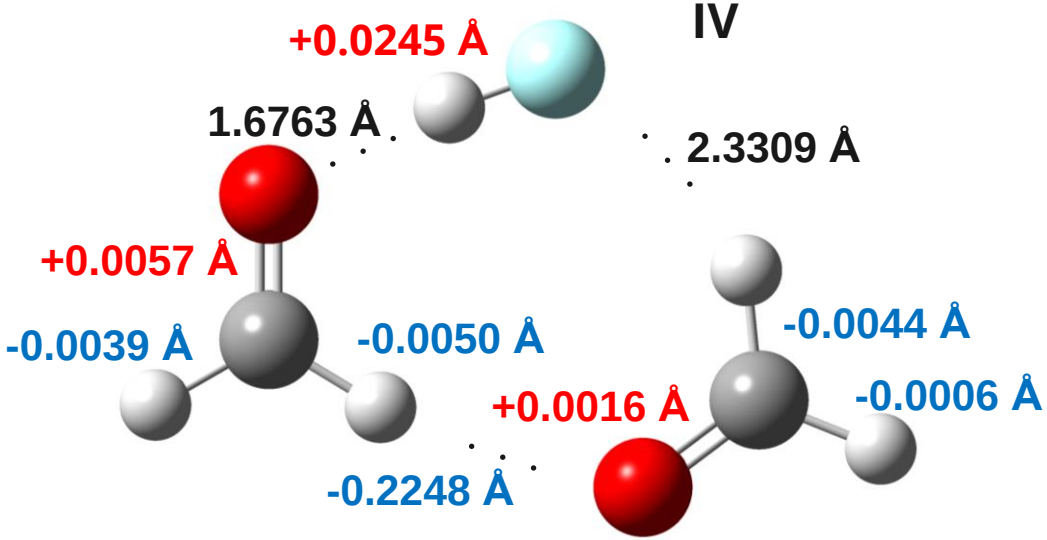
Monomer



Homodimer



IV

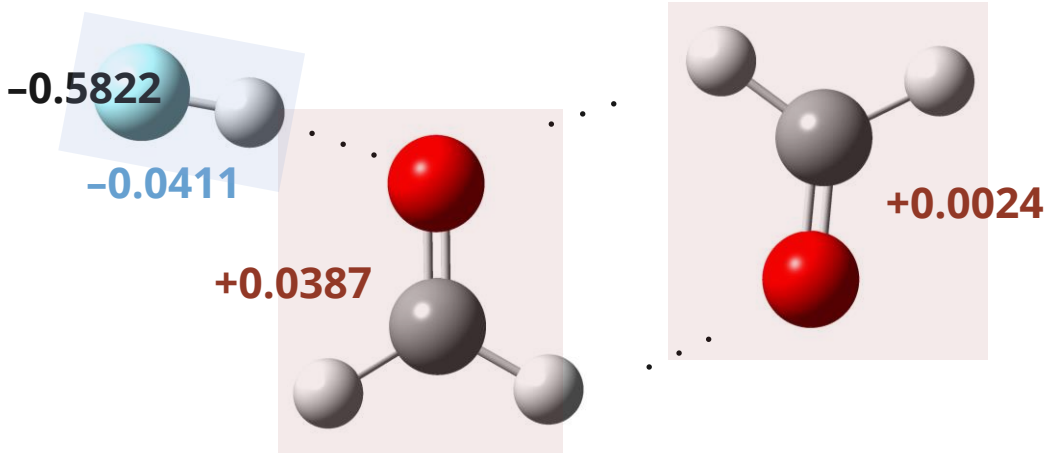


NBO charges on F atoms and the charges transferred from H_2CO in $HF\cdots H_2CO$ and trimers III and IV

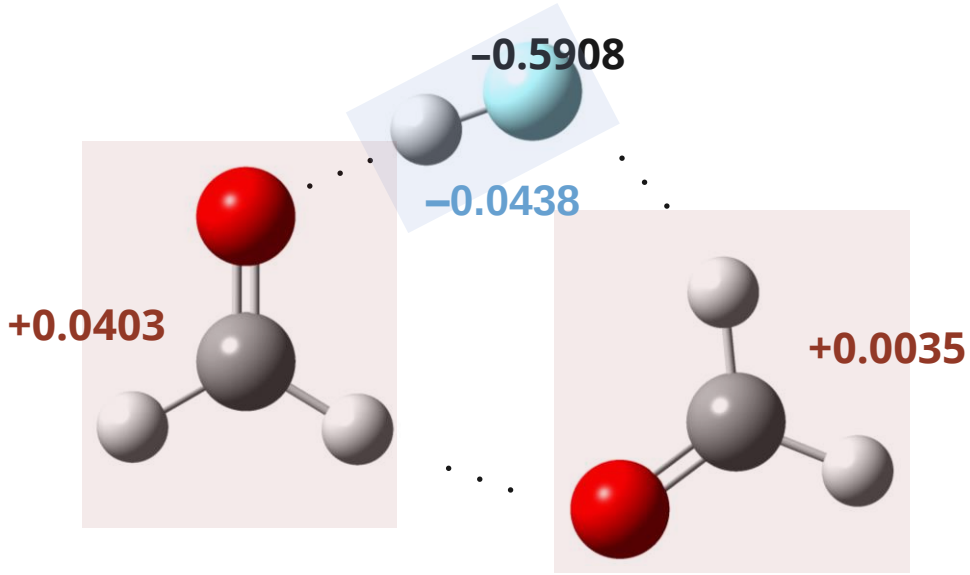
In trimers III and IV the electron charge is transferred primarily from the H_2CO molecules involved in the O···HF bonds.

Trimers

III

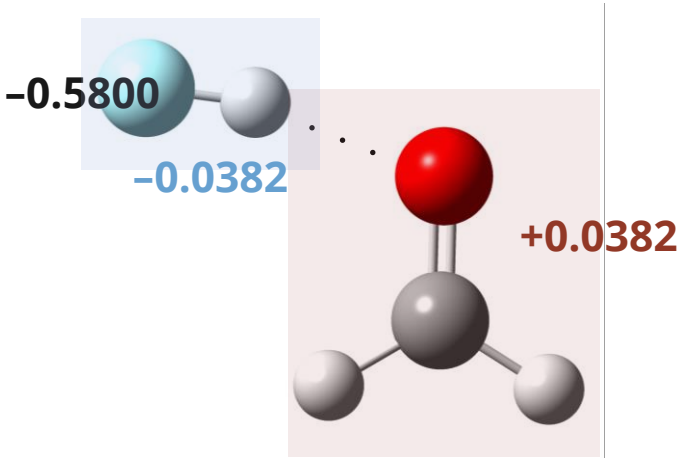


IV



Monomer

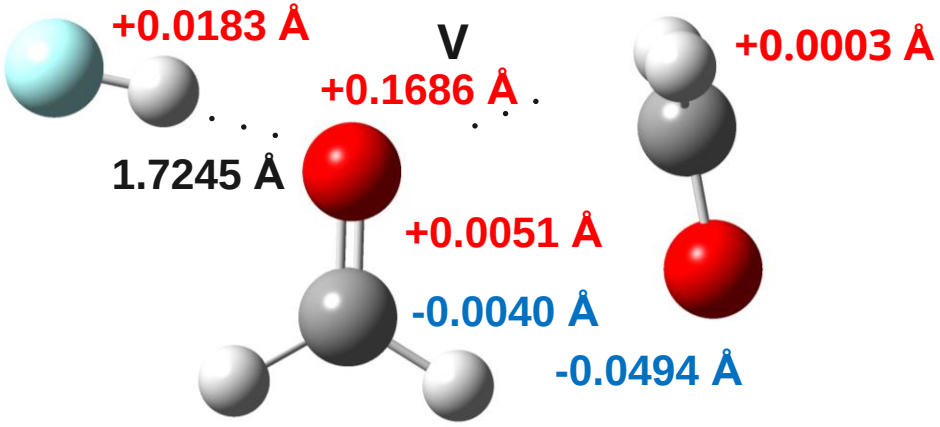
Heterodimer



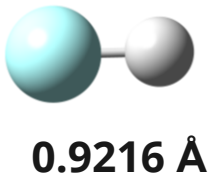
Structures of monomers, heterodimer HF···H_2CO, and trimers $(H_2CO)_2$···HF

Upon formation of the relatively weak trimer V, HF approaches the H_2CO unit lying in the symmetry plane.

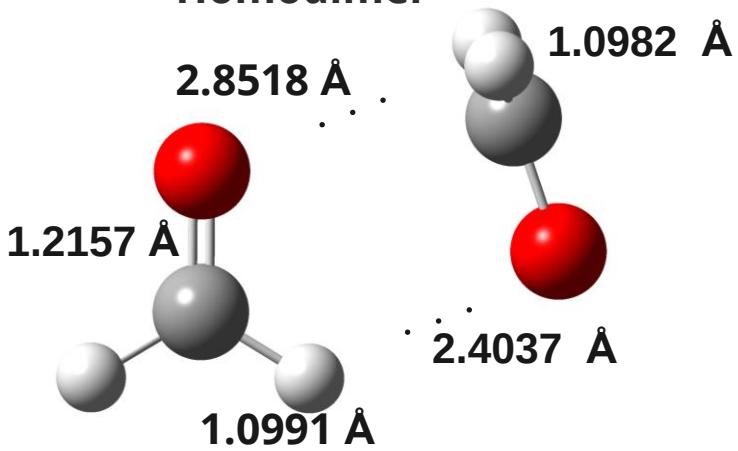
In trimer VI the HF molecule forms an H-bond with the H_2CO fragment that is approximately perpendicular to the symmetry plane of the non-planar homodimer. Judging from the R(H–F) and R(O···HF) values, this trimer is almost as strong as trimer IV.



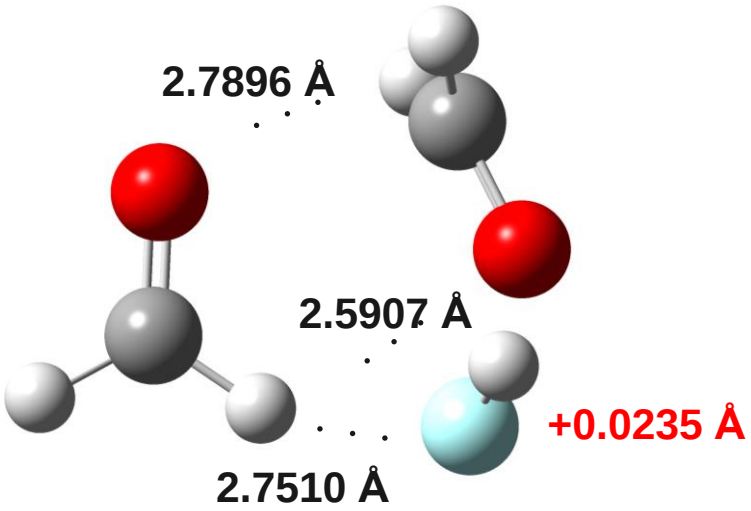
Monomer



Homodimer



VI

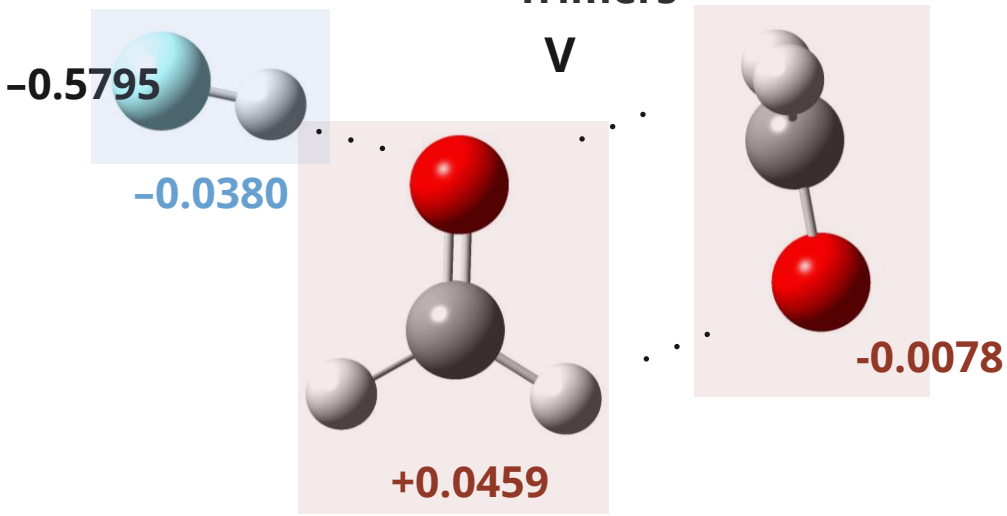


NBO charges on F atoms and the charges transferred from H_2CO in HF···H_2CO and trimers V and VI

Upon formation of trimer VI the natural charge of an HF subunit becomes –0.0466. The charge value is largest in all the trimers considered.

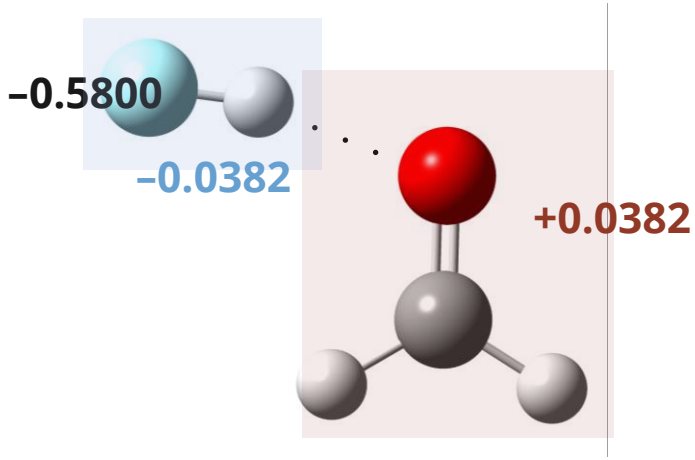
Trimers

V

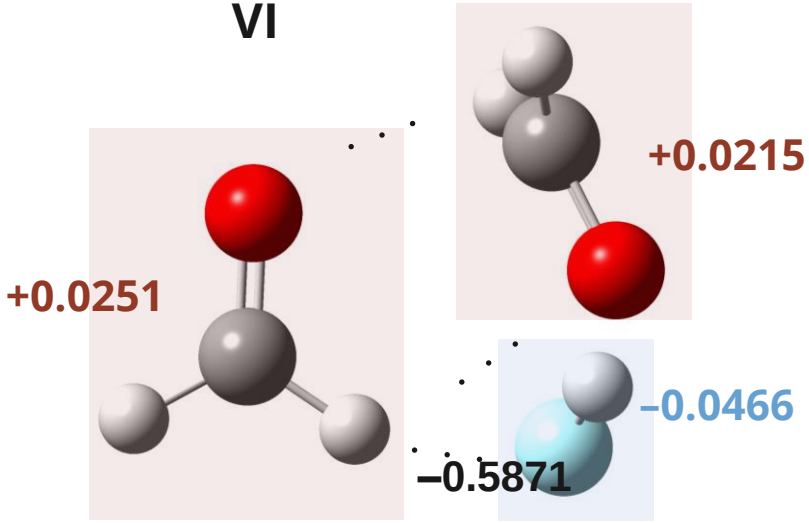


Monomer

Heterodimer



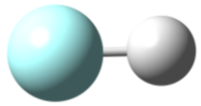
VI



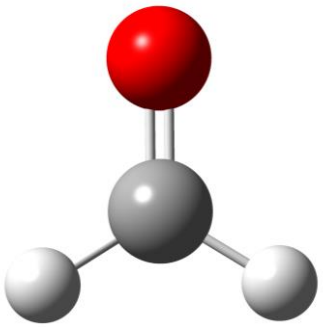
Calculation of frequencies and intensities of absorption bands

The table lists the harmonic and anharmonic values of frequencies and intensities (in parentheses).

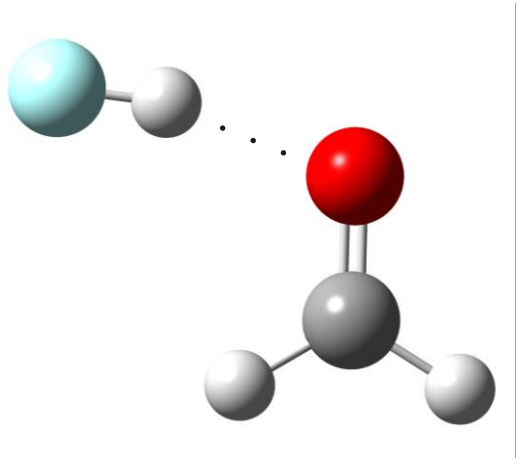
The spectral parameters of all compounds were also calculated in the harmonic and anharmonic approximation using the second-order perturbation theory.



HF		
Mode	harmonic	anharmonic
ν (H–F str)	4123 (121)	3952 (118)



H_2CO		
Mode	harmonic	anharm
ν (CH_2 wag)	1197 (7)	1180 ()7
ν (CH_2 rock)	1267 (9)	1247 (10)
ν (CH_2 sci)	1540 (11)	1508 (9)
ν_{18} (C=O str)	1753 (68)	1721 (69)
ν (CH_2 str. sym)	2973 (67)	2827 (65)
ν (CH_2 str. asym)	3047 (88)	2863 (77)



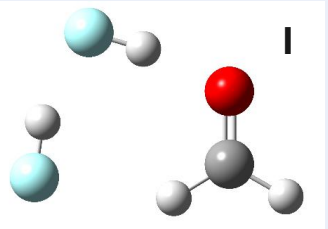
$H_2CO\cdots HF$		
Mode	harmonic	anharm
ν_5(HF libr ip)	763	639
ν_{12}(H–F str)	3720	3580

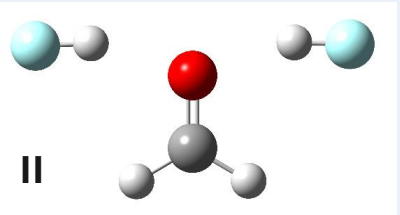
Spectral parameters of strongest bands of $(HF)_2\cdots H_2CO$ trimers

The table lists the harmonic and anharmonic values of frequencies and intensities (in parentheses)

- The H–F frequency shift of the ν_{17} mode in trimer I relative to the frequency of an isolated HF molecule equals 735 cm^{-1} both in the harmonic and anharmonic calculations.
- The intensity of H-F stretching mode increases by a factor of about 9 upon trimerization (modes ν_{17})
- Librational bands of HF are also strong and lie in the IR region.

$H_2CO\cdots HF\cdots HF$ (I)		
Mode	harmonic	anharm
ν_8 (HF ip libr.)	679 (201)	582 (201)
ν_{10} (HF ip libr.)	1000 (155)	885 (119)
ν_{14} (C=O str.)	1731 (72)	1702 (65)
ν_{15} (CH_2 sym. str.)	3035 (68)	2891 (46)
ν_{17} (H–F iph. str.)	3388 (1335)	3217 (936)
ν_{18} (H–F ooph. str.)	3793 (608)	3637 (489)





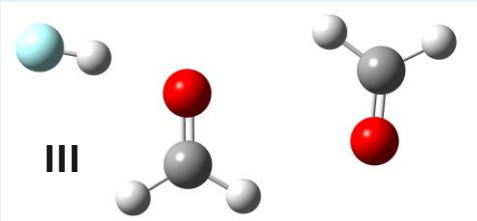
$FH\cdots H_2CO\cdots HF$ (II)		
Mode	harmonic	anharmonic
ν_8 (HF libr., B_2)	638 (221)	535 (215)
ν_{10} (HF libr., A_1)	707 (320)	568 (223)
ν_{14} (C=O str., A_1)	1730 (62)	1701 (62)
ν_{15} (CH_2 str., A_1)	3045 (25)	2896 (27)
ν_{17} (H–F str., B_1)	3815 (1285)	3671 (988)
ν_{18} (H–F str., A_1)	3844 (108)	3691 (101)

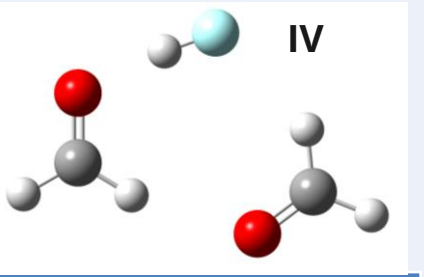
Spectral parameters of strongest bands of trimers III and IV

The table lists the harmonic and anharmonic values of frequencies and intensities (in parentheses)

- Judging from the binding energy, trimer III is weakest of all the trimers considered. The H–F stretch frequency is only slightly lower than in the $H_2CO\cdots HF$ heterodimer, while the HF libration frequencies are somewhat higher.
- Combined action of two H_2CO monomers on HF in trimer IV lowers the H–F stretching frequency by 528 and 506 cm^{-1} according to harmonic and VPT2 calculations. The HF absorption stretching band of trimer IV is sufficiently strong and is shifted from the H–F stretching band of the $H_2CO\cdots HF$ heterodimer, which makes it promising for an experimental detection of trimers in gas mixtures.
- The C-H stretching modes of trimers III and IV are blue-shifted relative to monomeric values.

$(H_2CO)_2\cdots HF$ (III)		
Mode	harmonic	anharmonic
ν_{10} (oop HF libr.)	745 (102)	636 (99)
ν_{11} (ip HF libr.)	787 (128)	660 (98)
ν_{18} (C=O inph str.)	1728 (28)	1701 (22)
ν_{19} (C=O ooph str.)	1747 (87)	1718 (89)
ν_{20} (CH_2 sym. str.)	2989 (66)	2835 (49)
ν_{21} (CH_2 sym. str.)	3022 (45)	2867 (36)
ν_{24} (H–F str.)	3688 (1058)	3545 (779)



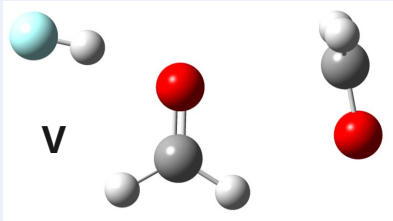


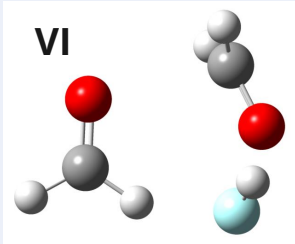
$H_2CO\cdots HF\cdots H_2CO$ (IV)		
Mode	Harmonic	anharmonic
ν_{10} (oop HF libr.)	796 (97)	804 (98)
ν_{11} (ip HF libr.)	821 (128)	714 (114)
ν_{18} (C=O inph str.)	1729 (35)	1707 (32)
ν_{19} (C=O ooph str.)	1741 (100)	1715 (97)
ν_{20} (CH_2 sym. str.)	2992 (97)	2835 (47)
ν_{21} (CH_2 sym. str.)	3018 (72)	2874 (83)
ν_{24} (H–F str.)	3595 (1100)	3446 (760)

Spectral parameters of strongest bands of trimers V and VI

- Recall that among the trimers with two H_2CO subunits, trimer V has the lowest binding energy of the O···HF bond and its system of H-bonds is anticooperative. The H–F stretching mode of trimer V has the highest frequency value, which is in accordance with the shortest value of R(H–F) and longest value of R(O···HF).
- As in other HF···$(H_2CO)_2$ trimers, librational bands of HF are strong and lie in the IR region.
- Trimer VI is second in the O···HF bond strength of $(H_2CO)_2$···HF trimers only to trimer IV. The ν_{24} H–F stretching frequency of trimer VI is red-shifted relative to a free HF molecule by 515 (harmonic value) and 505 cm^{-1} (anharmonic value) and almost coincides with the analogous parameter of trimer IV. Therefore, the H–F stretching bands of trimers IV and VI may overlap in experimental spectra.

$(H_2CO)_2$···HF (V)		
Mode	harmonic	anharmonic
ν_{10} (HF oop libr.)	723 (100)	634 (101)
ν_{11} (HF inp libr.)	765 (130)	660 (87)
ν_{18} (C=O inph str.)	1734 (38)	1707 (39)
ν_{19} (C=O ooph str.)	1752 (78)	1721 (76)
ν_{24} (H–F str.)	3719 (1008)	3564 (758)





$(H_2CO)_2$···HF (VI)		
Mode	harmonic	anharmonic
ν_{10} (HF libr.)	806 (170)	719 (115)
ν_{11} (HF libr.)	817 (90)	702 (125)
ν_{18} (C=O inph str.)	1738 (37)	1706 (22)
ν_{19} (C=O ooph str.)	1748 (97)	1730 (62)
ν_{24} (H–F str.)	3608 (996)	3447 (696)

Conclusion

- The calculations showed that H_2CO can form sufficiently strong H-bonded complexes with HF, which can exist under atmospheric conditions.
- The IR spectrum of the $H_2CO\cdots HF$ heterodimer was measured in an N_2 matrix at 8 K and identified with the help of calculated results.

- Frequency shift (up to 735 cm^{-1}) and intensity increase (up to a factor of 9) upon formation of complexes were predicted for the H-F stretching band.

- It was shown that the $H_2CO\cdots HF$ heterodimer and three sufficiently stable trimers have strong absorption bands remote from strong bands of monomers, which can facilitate the spectroscopic detection of these complexes.

Acknowledgments

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Thank you for your attention!