

IR spectra of HF and its complexes with water under atmospheric conditions

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IR spectra of H₂O–HF mixture have been recorded in the spectral region from 700 to 4000 cm⁻¹ using a VECTOR-22 Fourier transform spectrometer. Analysis of the spectroscopic data enabled us to reveal some peculiarities in the spectra, in particular, a larger number of bands are observed as compared to that known from literature data. Based on *ab initio* quantum chemical calculations, experimental vibrational frequencies have been tentatively assigned. Our experiments show that in the atmosphere H₂O and HF form various complexes.

Solution of the problems in real-time monitoring of gas and aerosol emissions from chemical, radiochemical, and metallurgical plants requires reliable data on the concentration and molecular composition of the emissions. Today methods of remote laser sensing are most promising for this purpose. To implement these methods successfully, one needs detailed information on the absorption and emission spectra of molecular components and their interaction with water vapor and other atmospheric gases.^{1–3} Such an interaction may produce molecular complexes with the bond energy from several tens of calories to several kilocalories.⁴ The optical activity of such donor-acceptor or H-bonded complexes may be rather high, what can cause additional radiation losses in the atmosphere of industrial regions and variations of the solar radiation flux. Gas-phase complexes of water molecules are characterized, as a rule, by several types of large-amplitude motions.⁵ In the atmosphere, this, in its turn, leads to transformation of vibrational spectra of their components (shifts of spectral features relative to those of free molecules may range from several wave numbers to even hundreds of wavenumbers) and to appearance of new bands corresponding to intermolecular vibrations.⁴ These changes can be traced using the method of remote laser sensing. The aim of this paper is to study FTIR spectra of HF and (H₂O)_n(HF)_m complexes under nearly atmospheric conditions.

Experiment

The IR spectra were recorded with a VECTOR-22 Fourier transform spectrometer (manufactured by Bruker) in the spectral region from 700 to 4000 cm⁻¹ (resolution of 0.5 cm⁻¹). A multipass cell with the optical length of 4 m was filled with the mixture of gaseous HF with atmospheric air at room temperature. The HF concentration was 1·10¹⁷ cm⁻³, and the water vapor concentration was 1.3·10¹⁷ cm⁻³. In processing

the recorded spectra, water vapor absorption spectrum obtained by the same method on the same spectrometer was subtracted from the initial spectrum.

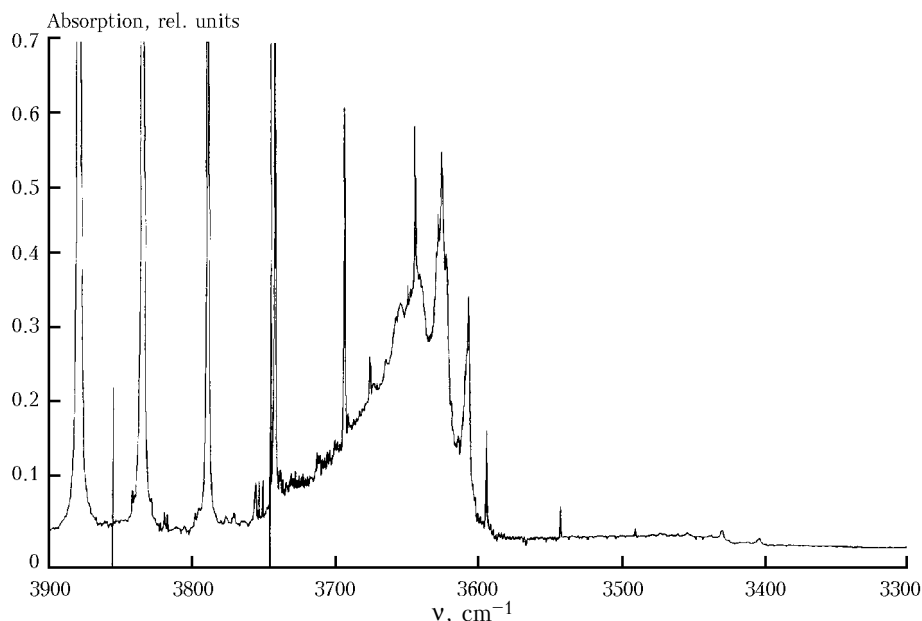
Calculations of IR bands of (H₂O)_n(HF)_m complexes

Potential energy surfaces and harmonic frequencies of (HF)_n(H₂O)_m complexes were calculated by Hartree–Fock–Roothaan (HFR) method with the use of the MONSTERGAUSS (Ref. 11) and GAUSSIAN 98 (Ref. 12) software packages adapted for use on Pentium IBM PCs. We used the 6-31G** Pople basis set including external polarization *d*- and *p*-functions at the atoms of F, O, and H, respectively. Table 1 gives vibrational frequencies of the hetero-dimer H₂O...HF. For a comparison Table 1 also presents, along with the experimental results, the corresponding data of more accurate calculations taking into account the effects of electron correlation by the Moller–Plesset (MP) perturbation theory.

As is seen from Table 1, the partial allowance for the effects of electron correlation within the Moller–Plesset perturbation theory up to the second order inclusive (MP2) leads to a decrease in the frequencies of the intramolecular normal vibrations thus improving the agreement with the experimental data. However, for intermolecular vibrational modes, the smallest deviation from the experimental frequencies results from calculation with the use of the 6-31G** basis set and the Hartree–Fock–Roothaan method. The calculated harmonic frequencies ω_i may differ markedly from the experimentally observed frequencies ν_i of the fundamental vibrational transitions. This discrepancy may be caused by significant contributions of the anharmonic terms to ν_i in description of vibrational spectra of complexes with H-bonds.

Table 1. Vibrational frequencies, cm^{-1} , of the $\text{H}_2\text{O}\dots\text{HF}$ hetero-dimer

HFR/6-31G**	MP2/6-31G**	HFR/6-31++ G**	MP2/6-31++ G**	HFR/aug-cc-pVDZ	MP2/aug-cc-pVDZ	Exp., Ref. 6	Assignment
4258	4012	4261	3991	4231	3919	3756	$\nu_{as}(\text{OH})$
4270	3908	4209	3728	4172	3664	3608 ± 2	$\nu(\text{H}_b\text{F})$
4142	3869	4142	3854	4124	3792	3657	$\nu_s(\text{OH})$
1765	1675	1745	1641	1746	1626	1595	$\delta(\text{HOH})$
760	821	795	886	775	852	666 ± 30	$\delta_o(\text{OH}_b\text{F})$
626	702	648	731	661	733	696 ± 30	$\delta_i(\text{OH}_b\text{F})$
236	269	217	222	216	236	180 ± 30	$\nu(\text{O}\dots\text{H}_b\text{F})$
206	208	224	276	230	268	145 ± 50	$\delta_o(\text{HOH}_b)$
194	212	162	281	186	280	170 ± 50	$\delta_i(\text{HOH}_b)$

**Fig. 1.** IR absorption spectrum of the HF mixture with air in the region of $3300\text{--}3900\text{ cm}^{-1}$.

An efficient model rather accurately and simply allowing for the anharmonic contributions to the frequencies ν_i of the stretching vibrations of a monomer Y, when it produces a complex $\text{H}_2\text{O}\dots\text{Y}$ with the quasi-linear hydrogen bond under atmospheric conditions, was developed and justified in Ref. 13. In this paper, the vibrational frequencies of complexes with the nonlinear bond were corrected with the use of linear calibration function

$$\nu_{\text{cor}} = b\omega_{\text{calc}} + a, \quad (1)$$

where ω_{calc} are the harmonic vibrational frequencies calculated *ab initio*; ν_{cor} are the corrected values of the vibrational frequencies; a and b are the calibration coefficients, which are determined from the least-squares fitting to the experimental data⁶ for the $\text{H}_2\text{O}\dots\text{HF}$ complex. These coefficients b and a proved to be equal to 0.84 and 108 cm^{-1} , respectively, and the correlation coefficient between the experimental and calculated frequencies was 0.998 . In this case, the mean absolute deviation of ν_{calc} from ν_{exp} was 58 cm^{-1} .

Discussion

For the first time, the existence of $\text{H}_2\text{O}\dots\text{HF}$ complex in the gas phase under equilibrium conditions

at 315K temperature was found experimentally by Thomas⁶ with the use of the method of traditional IR spectroscopy. In Thomas' opinion, three bands pointed to the existence of the complex: one corresponding to the stretching vibrations of the HF molecule, the second corresponding to the bending vibrations of the water molecule, and the third corresponding to two bending vibrations of the hydrogen bond itself. The energy for the formation of the complex with the allowance for zero vibrations was determined from the spectroscopic data as $7\text{ kcal}\cdot\text{mol}^{-1}$. The rotational spectrum of this complex was studied in Refs. 7 and 8. Under equilibrium conditions in the gas phase, intensities of rotational transitions were measured in the ground state of the molecules H_2O and HF and the complex $\text{H}_2\text{O}\dots\text{HF}$ and the equilibrium constant of complex formation was calculated, as well as the energy of the formation with the allowance for zero vibrations, which proved to be equal to $10.2\text{ kcal}\cdot\text{mol}^{-1}$ (Ref. 8).

A fragment of the IR spectrum of the HF mixture with air in the region of $3300\text{--}3900\text{ cm}^{-1}$ is shown on Fig. 1. The values of the experimental and calculated (with allowance for the systematic error) vibrational frequencies for the complexes of HF with H_2O and their tentative assignments are tabulated below in

Table 2. For a comparison, Table 2 also gives the experimental vibrational frequencies for the complex HF...H₂O taken from Ref. 6.

Table 2. Experimental (v_{exp}) and calculated (v_{theor}) vibrational frequencies for the complexes (HF)_m...(H₂O)_n and their tentative assignments

v_{exp} , cm ⁻¹	v_{exp} , (Ref. 1), cm ⁻¹	v_{theor} , cm ⁻¹	Tentative assignment
3726 w	3756	3740 3720 3740, 3750	HF...H ₂ O, (HF) ₂ ...H ₂ O (HF) ₂ ...(H ₂ O) ₂ , (HF) ₃ ...(H ₂ O) ₃
3676 ar		3670 3690	(HF) ₂ ...(H ₂ O) ₂ (HF) ₂ ...H ₂ O
3665 ar		3670	(HF) ₂ ...(H ₂ O) ₂
3655 ar	3657	3650	HF...H ₂ O
3643 m		3645, 3635	(HF) ₂ ...H ₂ O
3625 s		3623	HF...(H ₂ O) ₂
3607 s	3608	3610	HF...H ₂ O, (HF) ₂ ...H ₂ O
3471 ar		3534	(HF) ₂ ...(H ₂ O) ₂
3453 w		3527	(HF) ₂ ...(H ₂ O) ₂
3429 w		3430	(HF) ₂ ...H ₂ O
3403 w		3425	HF...(H ₂ O) ₂
1620 ar	≈ 1600	1622, 1628	(HF) ₃ ...(H ₂ O) ₃ ,
1612 m		1607, 1610	HF...(H ₂ O) ₂
1594 ar		1601, 1600	(HF) ₂ ...H ₂ O, (HF) ₂ ...(H ₂ O) ₂
		1595	(HF) ₂ ...(H ₂ O) ₂
		1590 1591	(HF) ₂ ...(H ₂ O) ₂ HF...H ₂ O, (HF) ₂ ...H ₂ O

Note. s means strong band, m means medium band, and w means weak band; ar denotes an arm.

The analysis of obtained spectroscopic data (see Table 2) revealed some peculiarities in the spectra. Thus, the number of the observed bands is larger than that known from the literature data.⁶ In the region of 3600–3750 cm⁻¹, four new bands were found, while only two bands were observed in Ref. 6. In the region of bending vibration of the water molecule (1550–1650 cm⁻¹), three allowed spectral bands were observed, but only one band was found in Ref. 6. In addition, new, not reported earlier, bands were found in the region of 3400–3450 cm⁻¹. Structures possibly connected with the rotation of one of the complex fragments were observed nearby 3700 and 3600 cm⁻¹.

It follows from Table 2 that the bands in the region of 3750–3600 cm⁻¹ can be tentatively assigned to the stretching vibrations of HF and H₂O in such complexes as HF...H₂O (1:1), (HF)₂...H₂O (2:1), HF...(H₂O)₂ (1:2), (HF)₂...(H₂O)₂ (2:2), (HF)₃...(H₂O)₃ (3:3). The gas phase complex of the composition 1:1 was observed experimentally in the gas medium only in Ref. 6, and the complexes of the composition 1:2 and 2:1 were observed only under conditions of low-temperature matrix isolation.⁹ The energy, structure, and vibrational spectra of complexes of HF with H₂O up to the composition 3:3 were calculated in Ref. 10. The bands in the region of 1650–1550 cm⁻¹ can be

tentatively assigned to the bending vibrations of H₂O in the complexes mentioned above. As to the bands in the region of 3400–3450 cm⁻¹, according to quantum chemical calculations, they can be assigned to the vibration of HF in the complexes with the composition 1:2, 2:1, and 2:2.

Thus, the experiments conducted evidence that HF produces in the atmosphere various complexes with water. More strict assignment of bands in the IR spectra will likely become possible after recording of spectra with a higher resolution.

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