



XXV ISSSMC-2021

FTIR EXPLORE OF THE $\text{CH}_3\text{CN}\cdots\text{HF}$ COMPLEX IN GAS PHASE AND COMPUTATIONAL METHODS

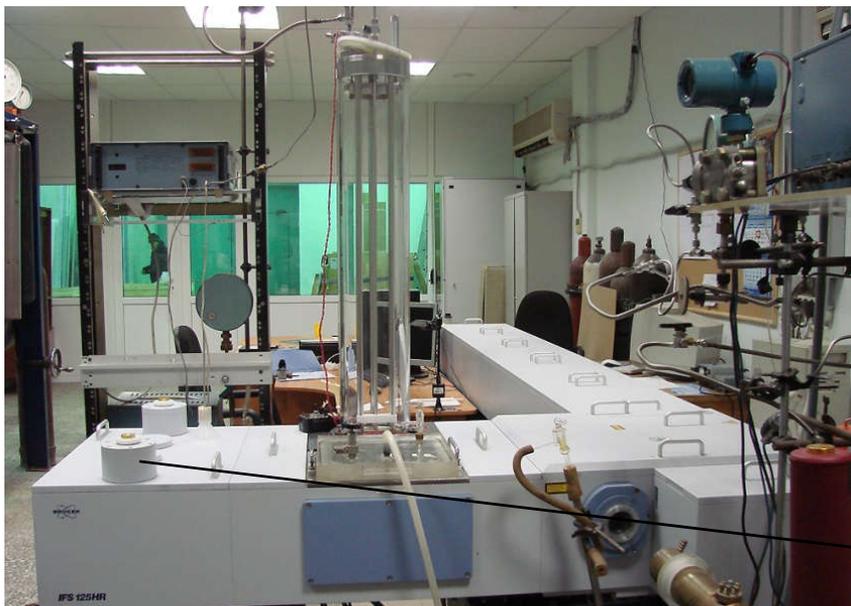
A.Amonov¹, K.G.Tokhadze², G.Murodov¹, A.Jumabaev¹, G.Nurmurodova¹

¹Department of Physics, Samarkand State University, Samarkand, Uzbekistan

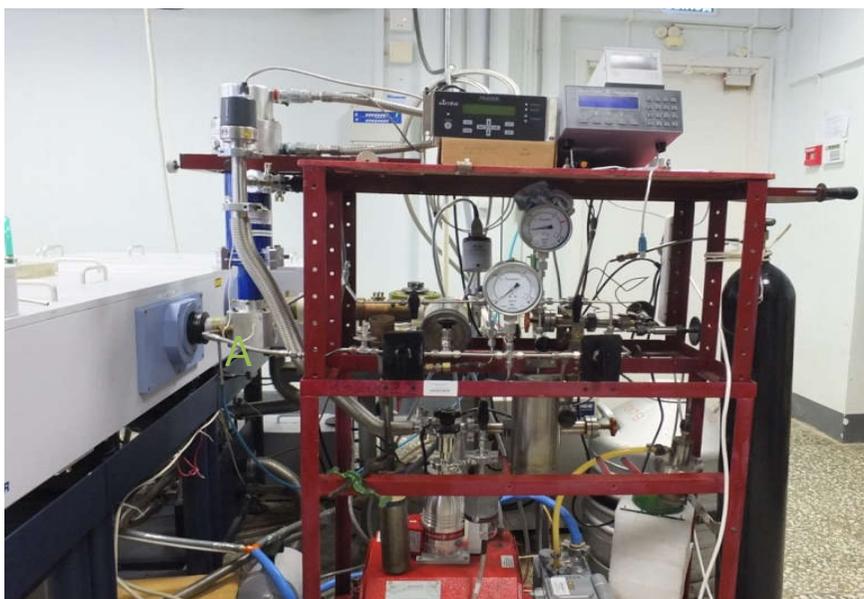
²Department of Physics, Saint Petersburg State University, Russia

*Corresponding author: akhtamul@gmail.com

**DEPARTMENT OF PHYSICS, SAMARKAND STATE UNIVERSITY,
REPUBLIC OF UZBEKISTAN**

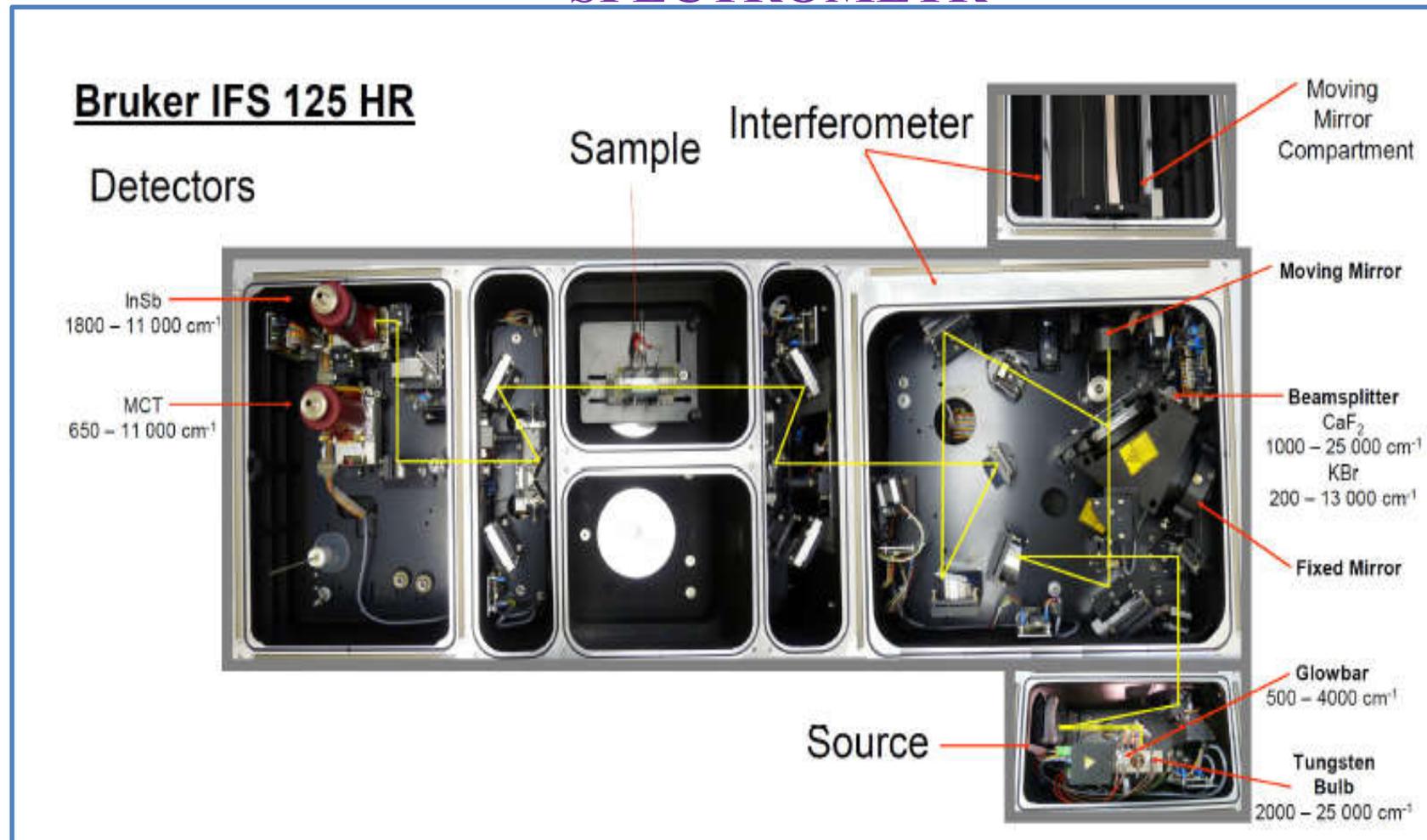


- **Range 400 - 12000 cm^{-1}**
- **Resolution 0.002 cm^{-1}**
- **T = 6 – 20 K**
- **OPUS software**

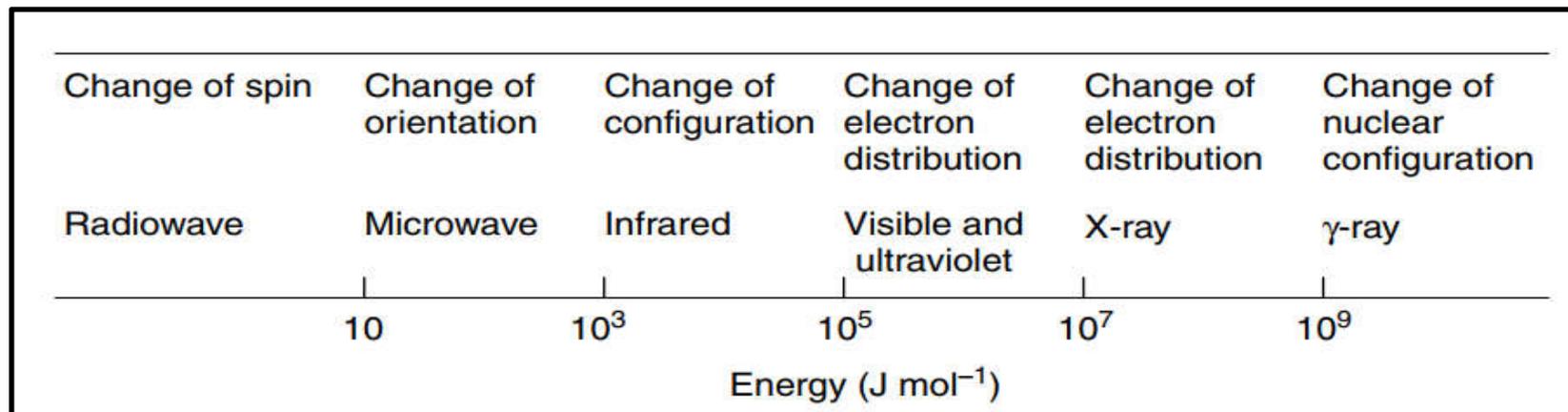


Temperature and pressure control

DIAGRAM SCHEME OF THE BRUKER IFS 125 HR SPECTROMETER



- **FTIR spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data**
- **With constant improvements to computers, infrared spectroscopy has made further great strides**
- **IR spectroscopy is a technique based on the vibrations of the atoms of a molecule**
- **FTIR 200 times larger than grating spectrometers(S/N; where S = signal and N = noise)**



CAVITIES FOR A GAS PHASE

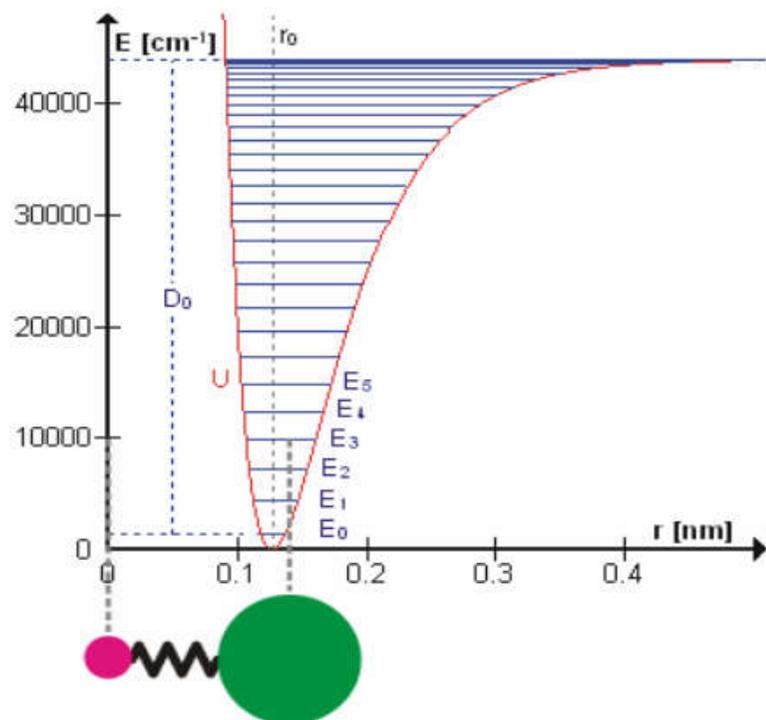


$10^{-5} - 10^{-7}$ MM Hg

Indium for a window,
Teflon



ANHARMONIC CALCULATIONS



Only $\Delta V=+1$

No selection rules

Fundamental transitions

Overtone

Hot transitions

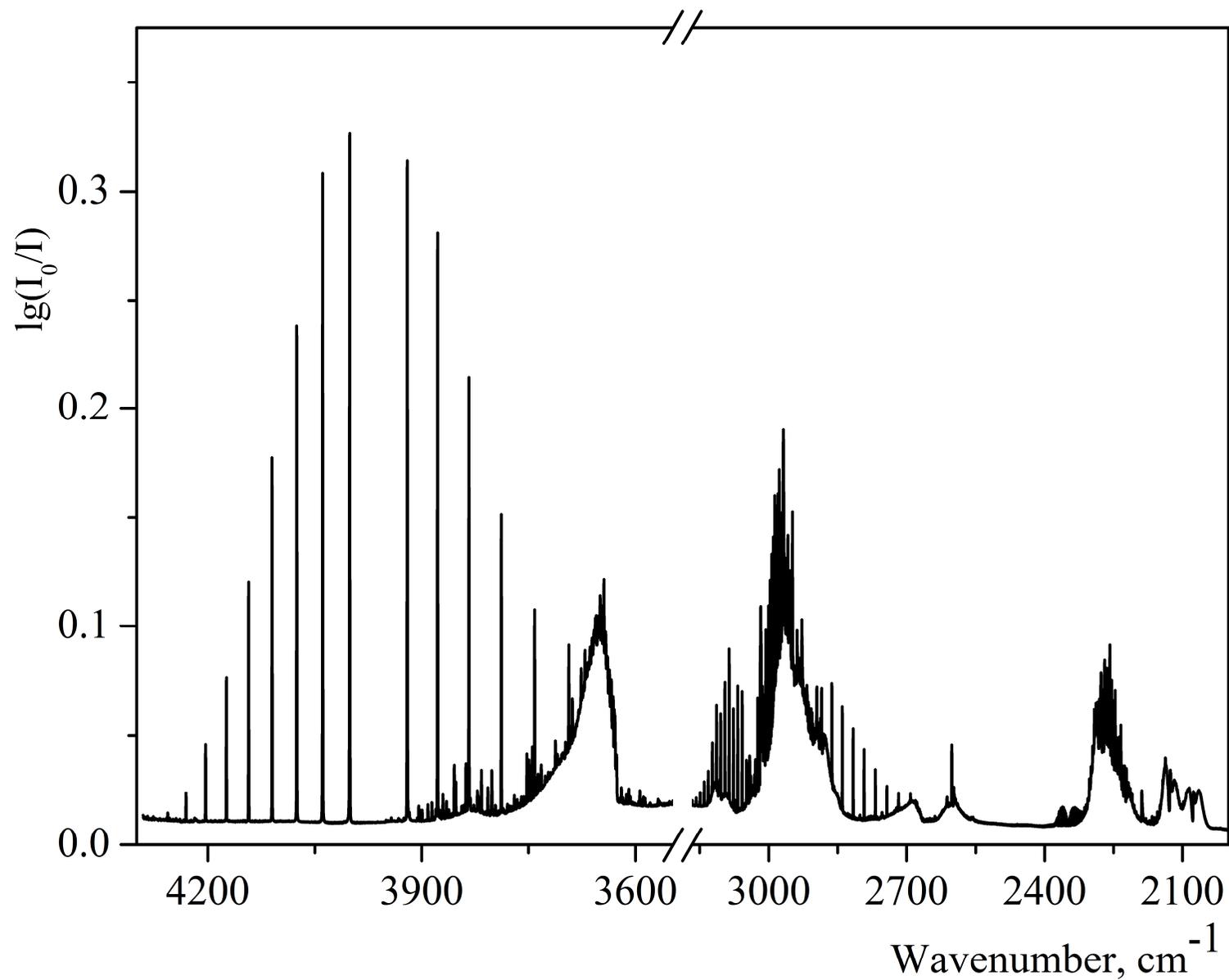
Combination transitions

$$H = -\frac{\hbar^2}{2m} \sum_k \frac{d^2}{dq_{1k}^2} + \sum_j \frac{M_j^2}{2I_j} + V(q_1, q_3, \theta_1, \theta_2, \theta_3, \theta_4)$$

SPECTROSCOPIC MEASUREMENTS

The IR spectra of gas mixtures $\text{CH}_3\text{CN}\bullet\bullet\bullet\text{HF}$ were recorded at room temperature in the absorption region $4200\text{--}2100\text{ cm}^{-1}$ by using of Bruker IFS125HR spectrometer. The resolutions were varying from 0.1 to 0.005 cm^{-1} at total pressures between 20 and 100 Torr of mixtures $\text{CH}_3\text{CN}\bullet\bullet\bullet\text{HF}$.

**FTIR SPECTRUM OF THE CH₃CN + HF COMPLEX IN GAS PHASE
P=110 TORR AND RESOLUTION 0.01 CM⁻¹.**



SPECTRAL MOMENTS OF CH₃CN +HF COMPLEX

$$M_1^* = M_0^{-1} \int_{\nu_1}^{\nu_2} \nu \cdot D(\nu) d\nu = \nu_0$$

$$M_2^* = M_0^{-1} \int_{\nu_1}^{\nu_2} (\nu - \nu_0)^2 \cdot D(\nu) d\nu$$

$$D(\nu) = \lg\left(\frac{I_0}{I}\right) \rightarrow \text{Optical density,}$$

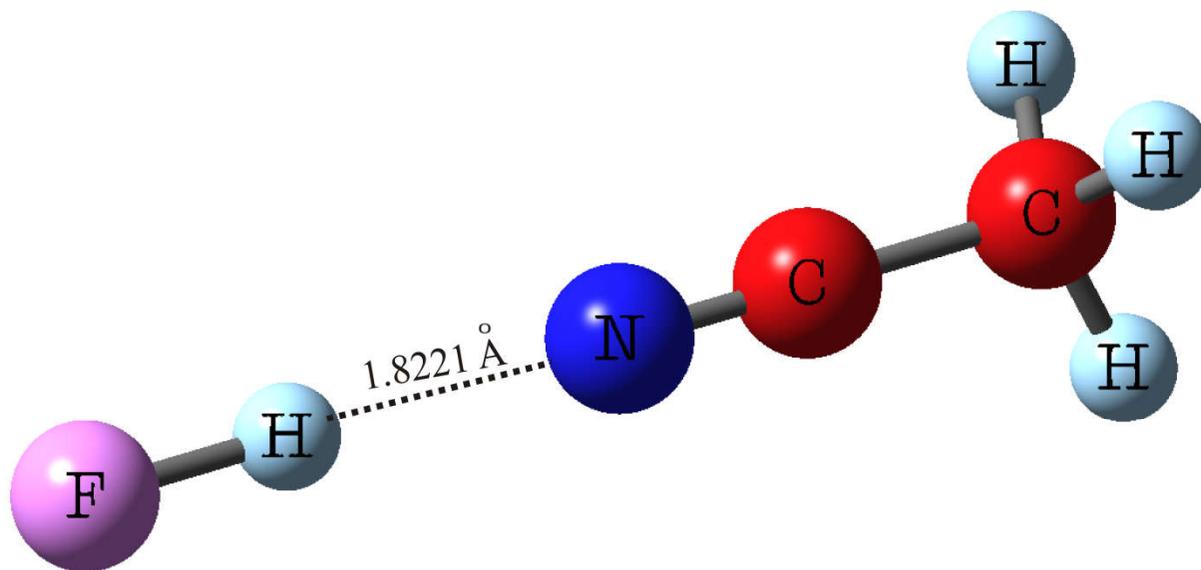
$$M_0 = \int_{\nu_1}^{\nu_2} D(\nu) d\nu$$

T(K)	M* ₁ sm ⁻¹		M* ₂ sm ⁻²	
	EXPERIMENT	THEORY	EXPERIMENT	THEORY
190	3470	3478	4400	6685
230	3480	3481	5900	7200
285	3490	3485	8700	7694

COMPUTATIONAL METHODS

The electronic structure of the CH₃CN•••HF complex was calculated using the Gaussian 09 and Gaussian 16 package of programs in the second order mp2 set of the atomic functions 6-311++G(3df,3pd) and with the basis set superposition error taken into account.

EQUILIBRIUM CONFIGURATION OF THE TITLE COMPLEX



Calculated in Gaussian 16 package of program with the mp2//6-311++G(3df,3pd) approximation

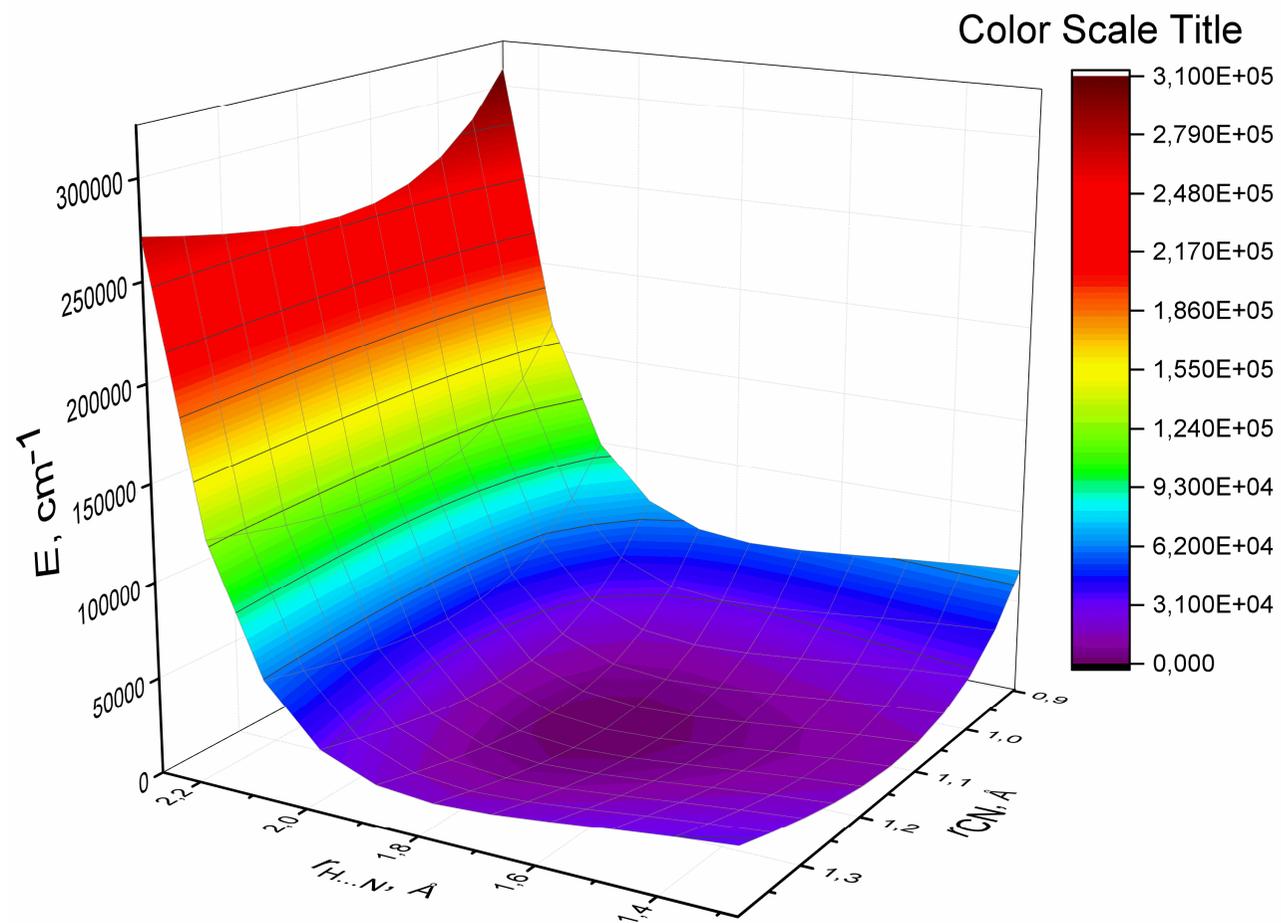
GEOMETRICAL PARAMETERS OF THE TITLE COMPLEX IN EQUILIBRIUM CONFIGURATION

Monomer	Upon complex formation
$r(\text{H-F})=0.9317 \text{ \AA}$, $r(\text{C}\equiv\text{N})=1.1647 \text{ (The all)}$ $r(\text{C-C})=1.4552 \text{ \AA}$ $r(\text{H-C})=1.0865 \text{ \AA}$ $r(\text{N}\dots\text{H}) = 1.8220 \text{ \AA}$ $\angle\text{HCH}=109.20^\circ\text{(The all)}$ $\angle\text{HCC}=109.74^\circ\text{(The all)}$	$r(\text{H-C})= 0.0001 \text{ \AA}$ $r(\text{C-C})=0.0021 \text{ \AA}$ $r(\text{C}\equiv\text{N})=0.0036 \text{ \AA}$ } Become Shorter $\angle\text{HCH}=0.20^\circ \text{ increase}$ $\angle\text{HCC} =0.20 \text{ decrease}$ $r(\text{H-F}) \text{ increases by } 0.015 \text{ \AA}$

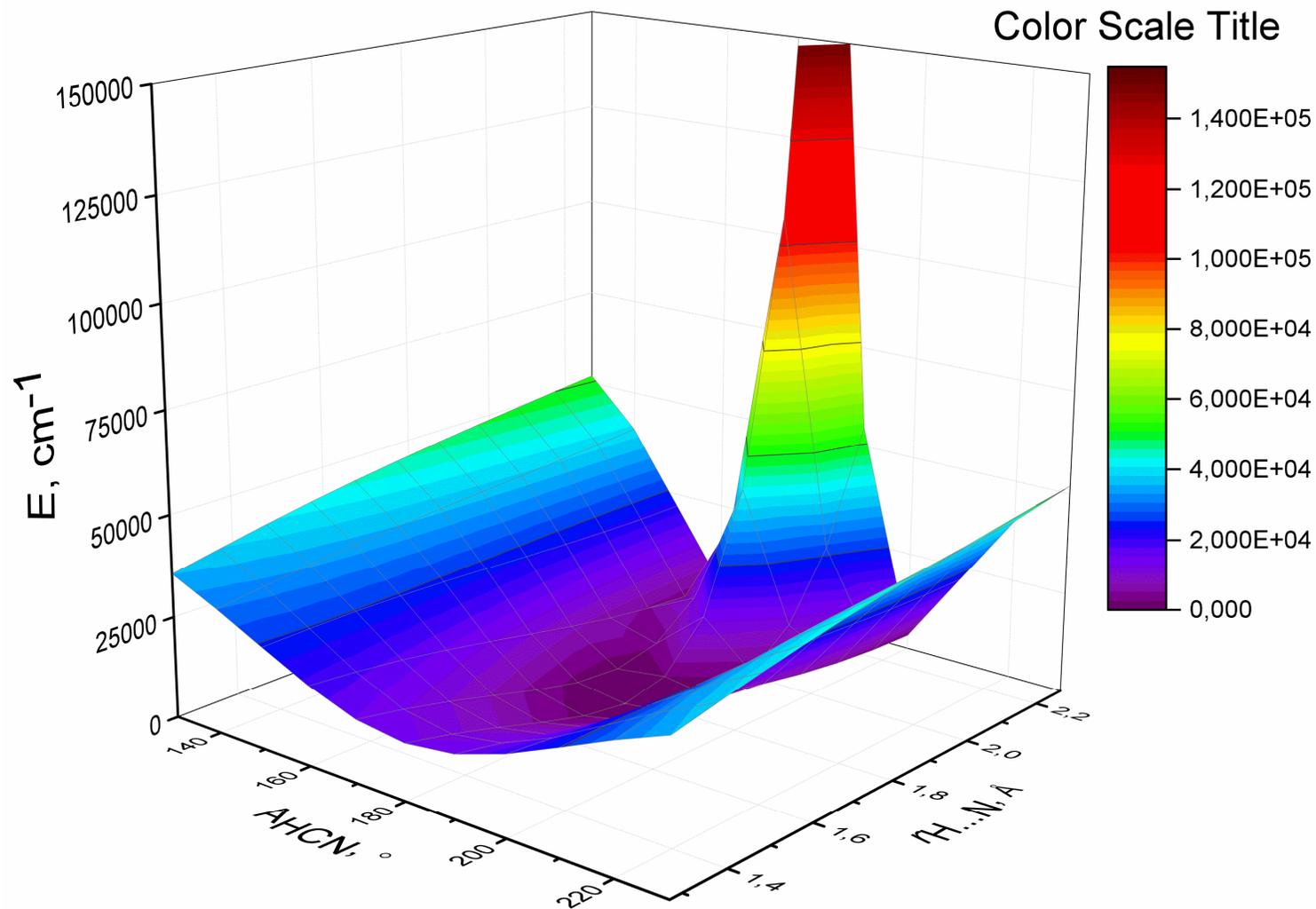
**CALCULATED HARMONIC VIBRATIONAL
FREQUENCIES BANDING ENERGY AND DIPOLE
MOMENTS OF THE COMPLEX IN EQUILIBRIUM
CONFIGURATION**

- ❖ THE ν_4 STRETCHING H-BOND VIBRATION 177.5 cm^{-1}**
- ❖ THE ν_6 BENDING VIBRATION 681.2 cm^{-1}**
- ❖ THE ν_1 H-F STRETCHING VIBRATION 3837.0 cm^{-1} LOWERING OF
the H-F VIBRATION FREQUENCY BY 339.4 cm^{-1}**
- ❖ THE H-F STRETCHING INTENSITY OF THIS VIBRATION
INCREASES FROM 117 to 1104 KM/MOL UPON COMPLEX
FORMATION**
- ❖ THE BINDING ENERGY OF THE COMPLEX 35.97 KJ/MOL**
- ❖ DIPOLE MOMENT FOR THE EQUILIBRIUM NUCLEAR
CONFIGURATION OF THE COMPLEX $\mu_{\text{compl}} = 7.45 \text{ D}$**

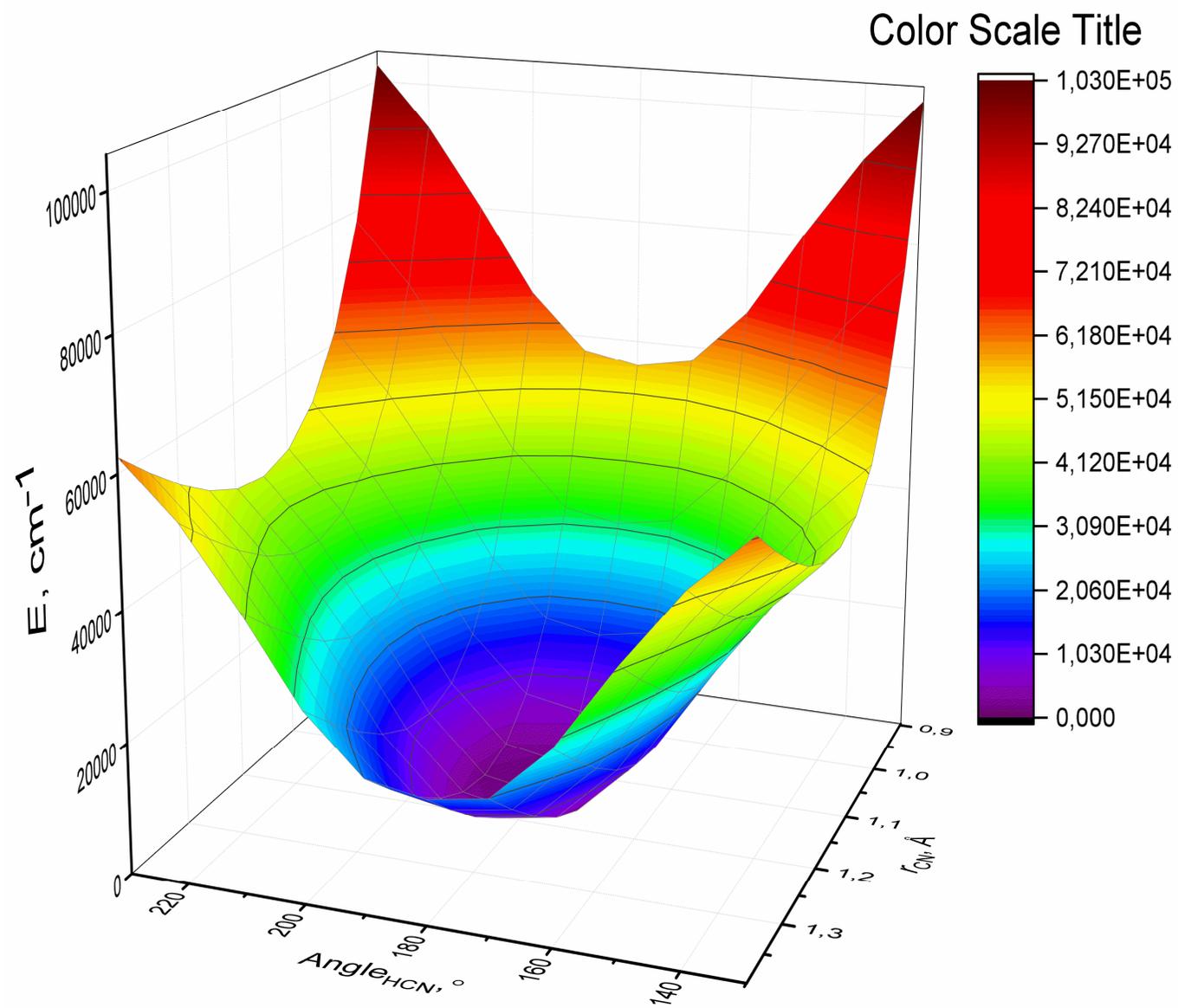
3D POTENTIAL ENERGY PLOT AS A FUNCTION OF $r(\text{HN})$ AND $r(\text{CN})$ DISTANCES IN THE TITLE COMPLEX



3D POTENTIAL ENERGY PLOT AS A FUNCTION OF $r(\text{H}\dots\text{N})$ DISTANCE AND $\angle(\text{H}\dots\text{N})$ ANGLE IN THE TITLE COMPLEX



3D POTENTIAL ENERGY PLOT AS A FUNCTION OF $\angle\text{HCN}$ ANGLE AND $r(\text{CN})$ DISTANCE IN THE TITLE COMPLEX



CONCLUSIONS

- ❖ The fine structure of the absorption spectrum of the CH₃CN...HF hydrogen-bonded complex in the region of the $\nu_1(\text{HF})$ band studied (4000–3000 cm⁻¹) in the gas phase
- ❖ The main spectral characteristics of the CH₃CN...HF complex were determined from a model calculation carried out in this paper
- ❖ The frequency of the $\nu_1(\text{HF})$ stretching vibration in the CH₃CN...HF complex (3628.5 cm⁻¹) obtained with allowance for the anharmonic coupling of this vibration to librations of two monomers in the same plane is in good agreement with the experimental value 3627 cm⁻¹
- ❖ These results, as well as the performed analysis of the influence of intermode anharmonic interaction on the vibrational energy levels and the spectral transition frequencies and intensities of the CH₃CN...HF complex studied in detail
- ❖ Several 3D potential energies obtained which is important to analyses structure of the complex and determined dipole moment of the title complex
- ❖ Calculated parameters of the complex can be used to link between internal dynamics and IR absorption spectra of the complex in gas phase

THANK YOU FOR YOUR ATTENTION!