

Theoretical study of methane containing molecular pairs

Yulia Kalugina

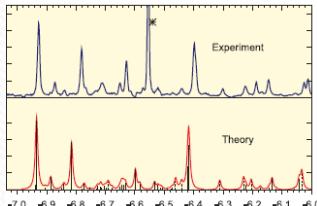
27 January 2017

Introduction

Weakly bound complexes can give an effect on the physical and chemical properties of gas media

- Line broadening
- Collisional (de-)excitation (**energy transfer**)
- Collision-induced absorption (**due to induced dipole moment**)

Spectroscopy, dynamics

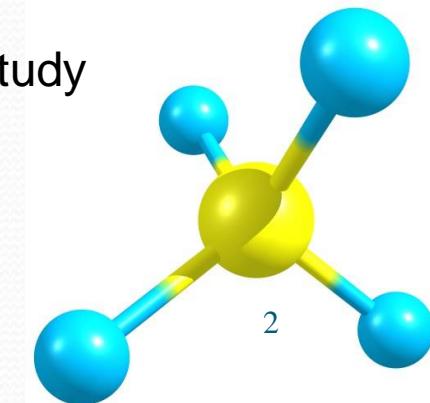
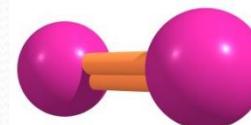


Almost free rotation of monomers;
Test for PESs, development of new theoretical models

Astrophysics



CH_4 , N_2 , Ar , CO_2 & CO are of great interest for study of interstellar medium. They are contained in atmospheres of planets and molecular clouds.



Introduction

TITAN

$\text{CH}_4\text{-N}_2$ and $\text{CH}_4\text{-Ar}$ complexes are of particular interest for the atmosphere of Titan

- low temperature (from 70 to 100 K)
- most abundant species of the atmosphere:
 N_2 (94%) and CH_4 (2-5 %), traces of Ar

$\text{CH}_4\text{-CO}_2$ complex is relevant to the early martian and terrestrial planet atmospheres

Methane – polluant of Earth's atmosphere

Introduction

In order to obtain physical properties of molecular complexes one needs to have a potential energy surface (PES) and for some applications also the dipole moment surfaces

Progress in computational quantum chemistry and in computational resources



tools to carry out accurate calculations

Introduction

Van-der-Waals systems

(R)CCSD(T) /AV5Z or (R)CCSD(T)/CBS

reference when system is monoconfigurational,
consisting of light atoms

problem: computational time

BSSE correction should be taken into account for
calculation of interaction energy and electric
properties

CH₄-Ar



Andrei Vigasin
Obukhov Institute of Atmospheric Physics
Moscow, Russia



Sergei Lokshtanov
Lomonosov Moscow State University
Department of Chemistry

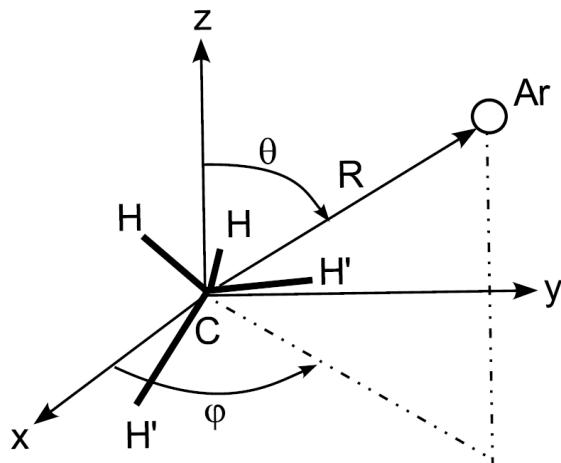
THE JOURNAL OF CHEMICAL PHYSICS 144, 054304 (2016)



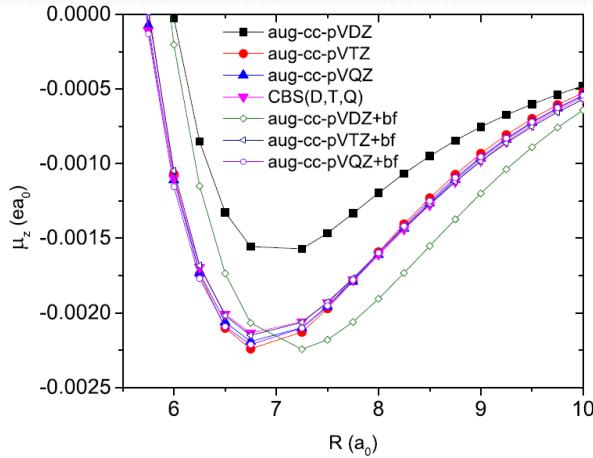
***Ab initio* 3D potential energy and dipole moment surfaces for the CH₄-Ar complex: Collision-induced intensity and dimer content**

Yulia N. Kalugina,^{1,a)} Sergei E. Lokshtanov,^{2,3} Victor N. Cherepanov,¹
and Andrey A. Vigasin^{3,b)}

Computational details

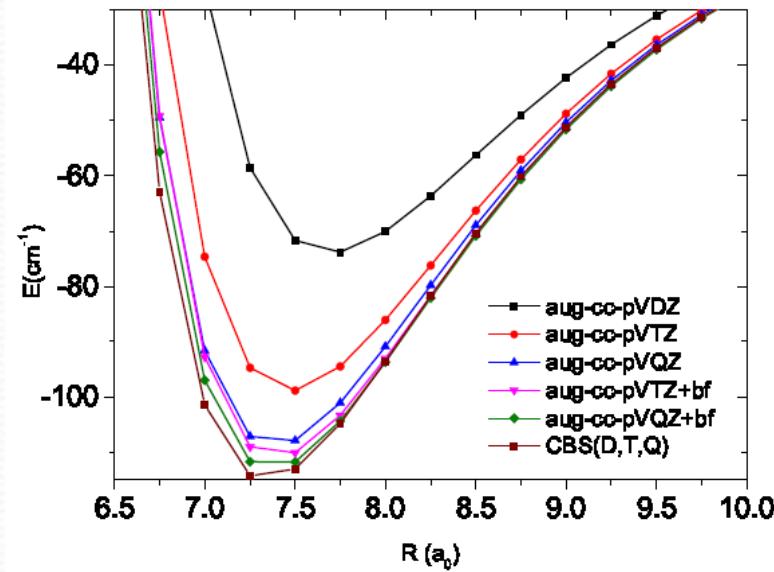


Molecule fixed frame
for $\text{CH}_4\text{-Ar}$



3D Potential energy and
dipole moment surfaces

$$\langle r_{\text{CH}} \rangle_0 = 2.0674 \text{ } a_0$$



Interaction energy for all angles = 0

Computational details

PES : CCSD(T)/CBS (X=D,T,Q) level

DMSs : CCSD(T)/aug-cc-pVTZ+bond functions

Angles θ and ϕ were chosen randomly in the intervals 0° - 180° and 0° - 360° .

30 values of R : 4.5 - 30 a_0

$$V(R, \theta, \varphi) = \sum_{l,m} v_{lm}(R) P_{lm}(\cos(\theta)) \cos(m\varphi) (-1)^m$$

$$\mu_{x,z}(R, \theta, \varphi) = \sum_{l,m} \alpha_{lm}(R) P_{lm}(\cos(\theta)) \cos(m\varphi) (-1)^m$$

$$\mu_y(R, \theta, \varphi) = \sum_{l,m} \alpha_{lm}(R) P_{lm}(\cos(\theta)) \sin(m\varphi) (-1)^m$$

Finite-Field method:

$$E(F_\alpha) = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\alpha} F_\alpha^2 - \frac{1}{6} \beta_{\alpha\alpha\alpha} F_\alpha^3 - \frac{1}{24} \gamma_{\alpha\alpha\alpha\alpha} F_\alpha^4 + \dots$$

$$\mu_\alpha = -\frac{E(F_\alpha) - E(-F_\alpha)}{2F_\alpha}, \quad \mu_\alpha = \frac{256D_\alpha(F_\alpha) - 40D_\alpha(2F_\alpha) + D_\alpha(4F_\alpha)}{180F_\alpha},$$

$$D_\alpha = \frac{E(F_\alpha) - E(-F_\alpha)}{2}$$

Basis functions

Energy		μ_x, μ_y		μ_z	
l	m	l	m	l	m
0	0	1	1	1	0
3	2	2	1	2	2
4	0	3	1	3	0
4	4	3	3	3	2
6	0	4	1	4	2
6	4	4	3	4	4
7	2	5	1	5	0
7	6	5	3	5	2
8	0	5	5	5	4
8	4	6	1	6	2
8	8	6	3	6	4
9	2	6	5	6	6
9	6	7	1	7	0
10	0	7	3	7	2
10	4	7	5	7	4
10	8	7	7	7	6
		8	1	8	2
		8	3	8	4
		8	5	8	6
		8	7	8	8

Computational details

PES : CCSD(T)/CBS (X=D,T,Q) level

DMSs : CCSD(T)/aug-cc-pVTZ+bond functions

Angles θ and ϕ were chosen randomly in the intervals 0° - 180° and 0° - 360° .

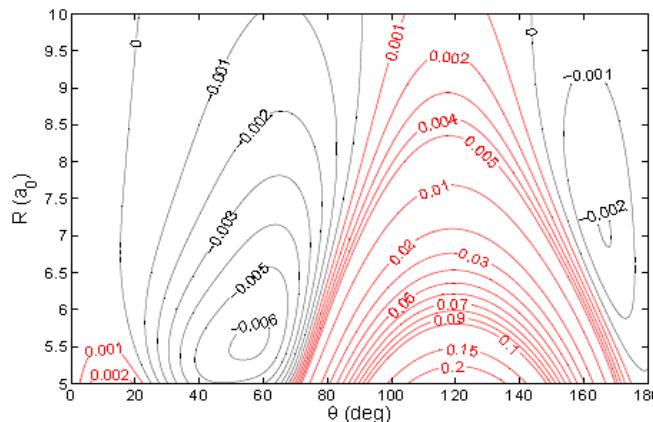
30 values of R : 4.5 - 30 a_0

$$V(R, \theta, \varphi) = \sum_{l,m} v_{lm}(R) P_{lm}(\cos(\theta)) \cos(m\varphi) (-1)^m$$

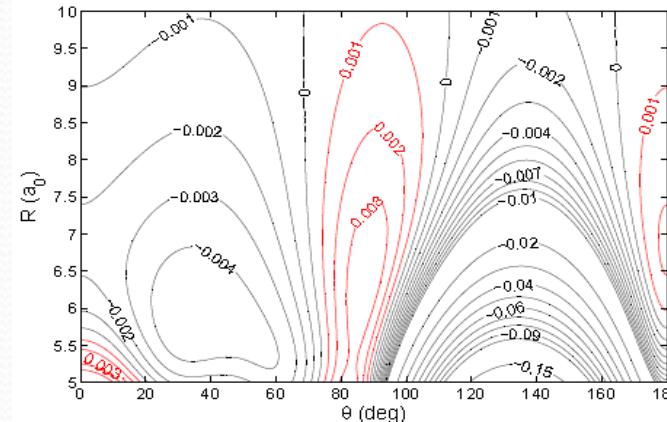
$$\mu_{x,z}(R, \theta, \varphi) = \sum_{l,m} \alpha_{lm}(R) P_{lm}(\cos(\theta)) \cos(m\varphi) (-1)^m$$

$$\mu_y(R, \theta, \varphi) = \sum_{l,m} \alpha_{lm}(R) P_{lm}(\cos(\theta)) \sin(m\varphi) (-1)^m$$

μ_x



μ_z



2D cuts of the DMSs for $\phi=0^\circ$

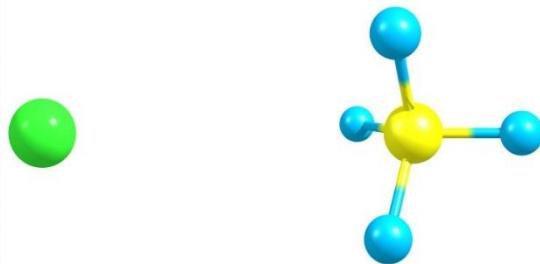
Basis functions

Energy		μ_x, μ_y		μ_z	
1	m	1	m	1	m
0	0	1	1	1	0
3	2	2	1	2	2
4	0	3	1	3	0
4	4	3	3	3	2
6	0	4	1	4	2
6	4	4	3	4	4
7	2	5	1	5	0
7	6	5	3	5	2
8	0	5	5	5	4
8	4	6	1	6	2
8	8	6	3	6	4
9	2	6	5	6	6
9	6	7	1	7	0
10	0	7	3	7	2
10	4	7	5	7	4
10	8	7	7	7	6
		8	1	8	2
		8	3	8	4
		8	5	8	6
		8	7	8	8

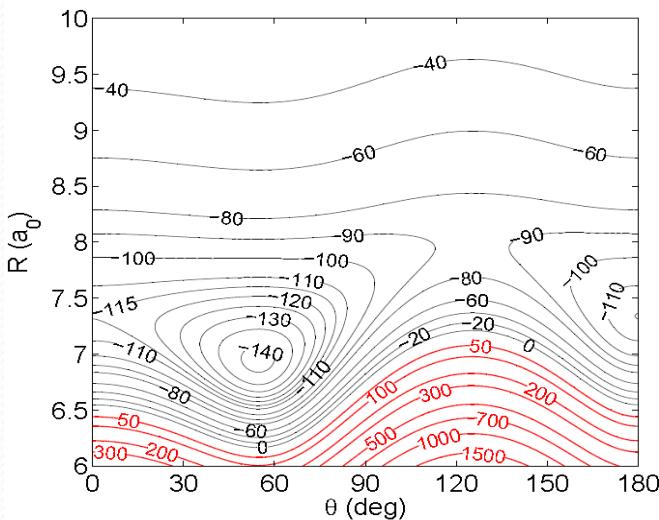
Potential energy

Table. Present and literature values of D_e and equilibrium geometry

[Alex2006] fp-CCSD(T)/CBS
 [Heijmen1997] SAPT



Equilibrium structure of $\text{CH}_4\text{-Ar}$



2D cut of the PES for $\phi=0^\circ$

	This work	Literature
D_e	-141.47 cm^{-1}	-140.6 cm^{-1} [Alex2006] -143.4 cm^{-1} [Heijmen1997]
R_e	6.95 a_0	7.00 a_0 [Alex2006] 7.00 a_0 [Heijmen1997]

There are two non-equivalent minima on the interaction surface :

Global minimum
 $-141.47 \text{ cm}^{-1} R=6.95 a_0 \theta=54.7^\circ \phi=0^\circ$
 Local minimum
 $-115.06 \text{ cm}^{-1} R=7.34 a_0 \theta=180^\circ \phi=0^\circ$

Temperature dependence of physical properties

Mixed part of Second Virial Coefficient (Classical)

$$B_{12}(T) = \frac{N_0}{2} \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(1 - e^{-\frac{V(R,\theta,\phi)}{kT}} \right) R^2 dR \sin \theta d\theta d\phi$$

No is the Avogadro number

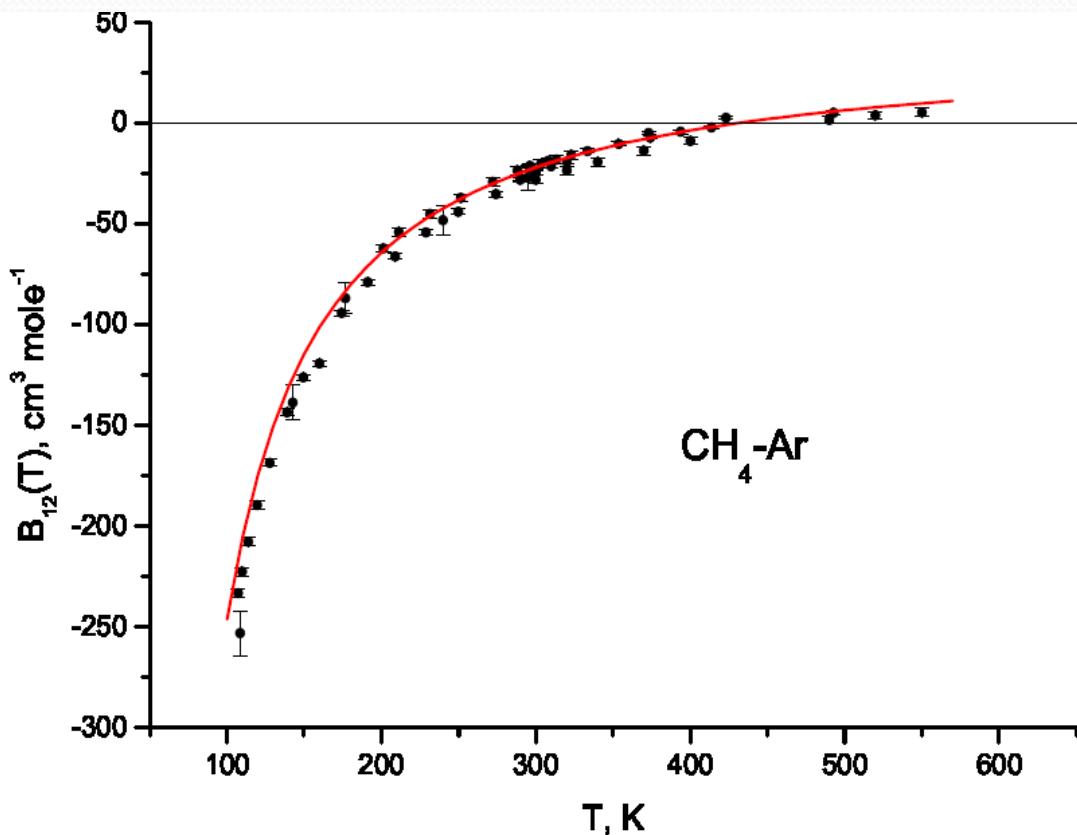
Total second virial coefficient (SVC)

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}$$

x_i stands for the molar fraction

Red line – present work;

Symbols - J. D. Dymond, K. N. Marsh, R. C. Wilhoit,
Virial Coefficients of Pure Gases and Mixtures, M.
Fenkel and K. N. Marsh, editors, (Series: Physical
Chemistry, Subvolume 21B, Springer, 2003).



Temperature dependence of physical properties

Equilibrium constant for true bound $\text{CH}_4\text{-Ar}$ dimer formation

$$K_P^{\text{bound}} = \frac{N_0}{\mathfrak{R}T} \int_{V(R,\theta,\varphi) \leq 0} \dots \int \frac{\gamma\left(3, -\frac{V(R,\theta,\varphi)}{kT}\right)}{\Gamma(3)} e^{-\frac{V(R,\theta,\varphi)}{kT}} R^2 dR \sin \theta d\theta d\varphi$$

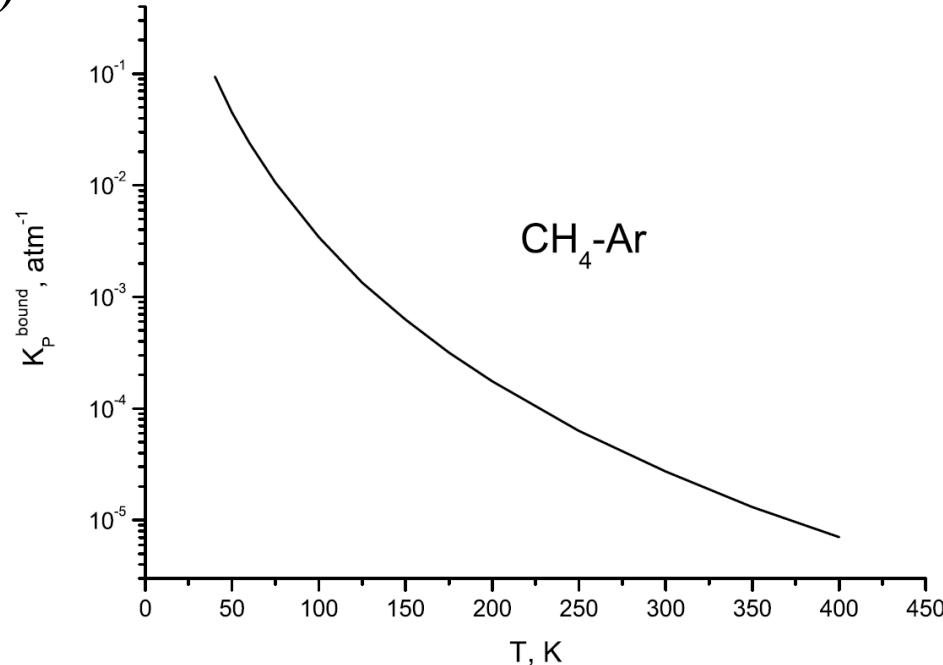
$\Gamma(3)=2$; \mathfrak{R} is a gas constant and incomplete gamma-function:

$$\gamma(a, b) = \int_0^b \varpi^{a-1} e^{-\varpi} d\varpi$$

To obtain the dimer mole fraction at relatively low density it is sufficient to use approximation

$$x_{12} = K_P(T)P$$

where P is the pressure in atm.



Temperature dependence of physical properties

0th spectral moment of the rototranslational collision-induced band

Γ_0 has the meaning of the total intensity of an absorption band

There are 2 ways of getting this property :

1. From experimentally measured absorption coefficient

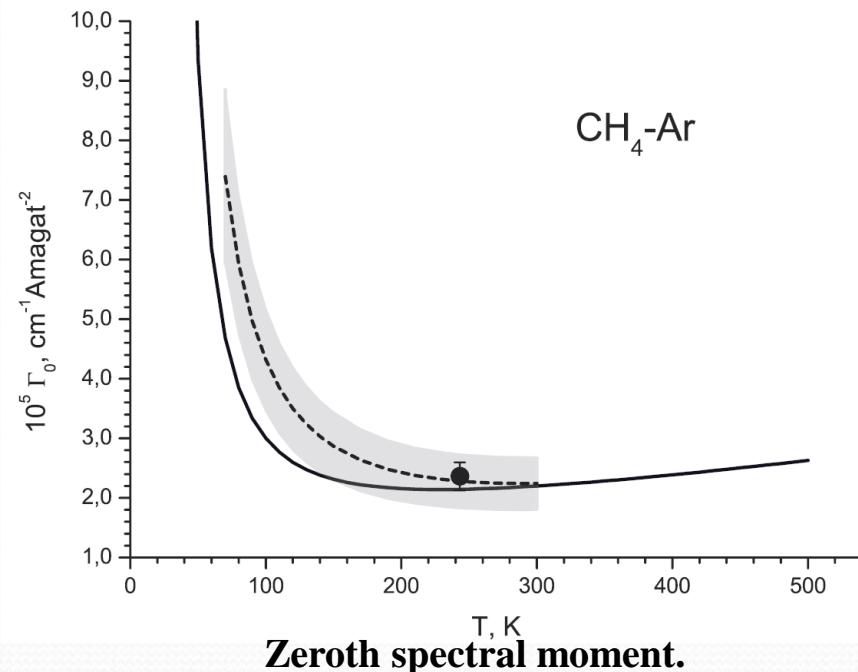
$$\Gamma_0 = \int_0^{\infty} \frac{\alpha(\nu) d\nu}{\nu \tanh\left(\frac{hc\nu}{2kT}\right)}$$

ν is a frequency in cm^{-1} ; $\alpha(\nu)$ is a binary absorption coefficient in $\text{Amagat}^{-2} \text{ cm}^{-1}$;

Amagat is a number density of an ideal gas at normal conditions ($2.7 \cdot 10^{19}$ molecules cm^{-3})

2. From theory

$$\tilde{\Gamma}_0 = \frac{32\pi^4}{3hc} \int_0^{\infty} \int_{\Omega} \mu^2(R, \Omega) e^{-\frac{V(R, \Omega)}{kT}} R^2 dR d\Omega$$



Line – this work, symbols – Borysow,
cross- integration of spectra Dore and
Filabozzi. Uncertainty 15-20%.

$\text{CH}_4\text{-CO}$

Experiment



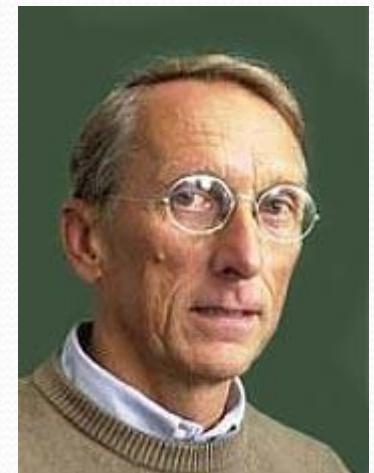
L. Surin



A. Potapov



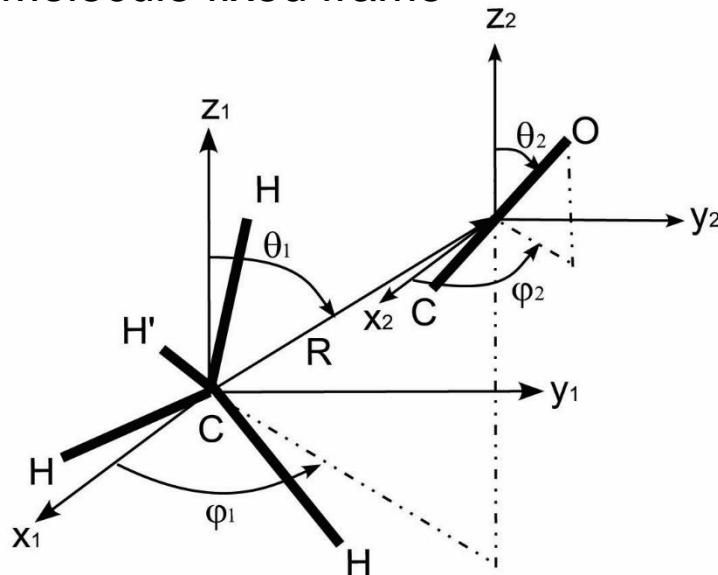
A. Faure



A. van der
Avoird

CH₄-CO

Molecule fixed frame



Experiment was done at the
Cologne University by
L. Surin and A. Potapov
using
OROTRON jet spectrometer

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Rotational study of the CH₄-CO complex: Millimeter-wave measurements and *ab initio* calculations

L. A. Surin,^{1,2,a)} I. V. Tarabukin,² V. A. Panfilov,² S. Schlemmer,¹ Y. N. Kalugina,³ A. Faure,^{4,5} C. Rist,^{4,5} and A. van der Avoird^{6,b)}

¹*I. Physikalisches Institut, University of Cologne, Zülpicher St. 77, 50937 Cologne, Germany*

²*Institute of Spectroscopy, Russian Academy of Sciences, Fizicheskaya St. 5, 142190 Troitsk, Moscow, Russia*

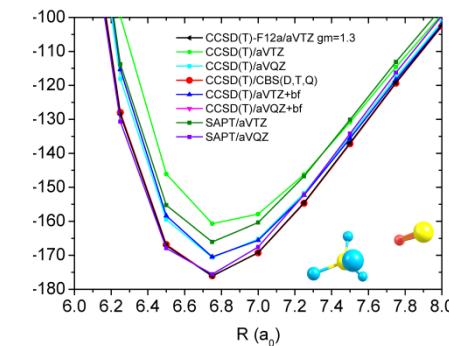
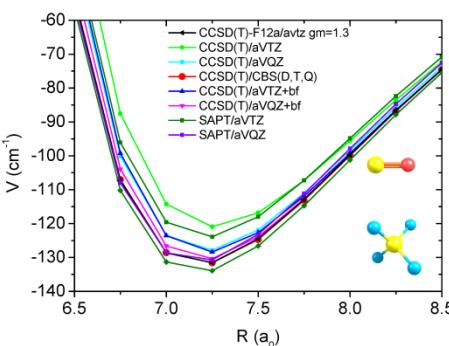
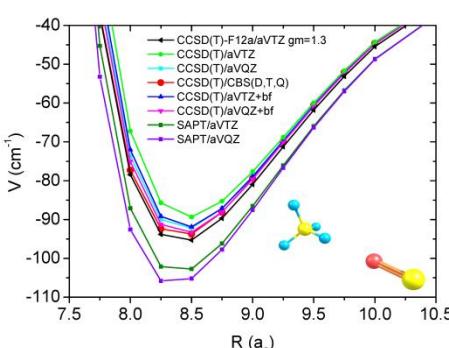
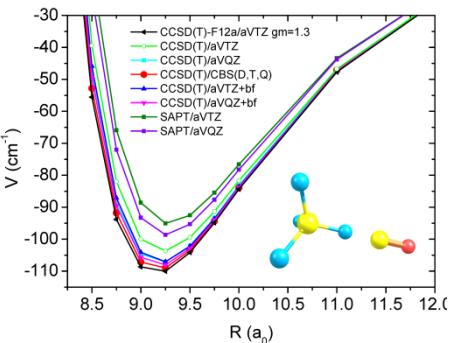
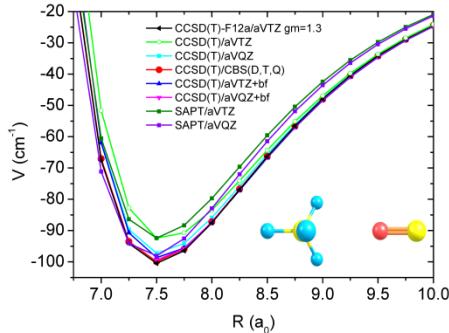
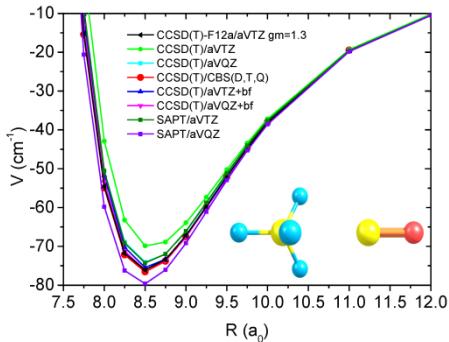
³*Department of Optics and Spectroscopy, Tomsk State University, 36 Lenin Ave., 634050 Tomsk, Russia*

⁴*University Grenoble Alpes, IPAG, F-38000 Grenoble, France*

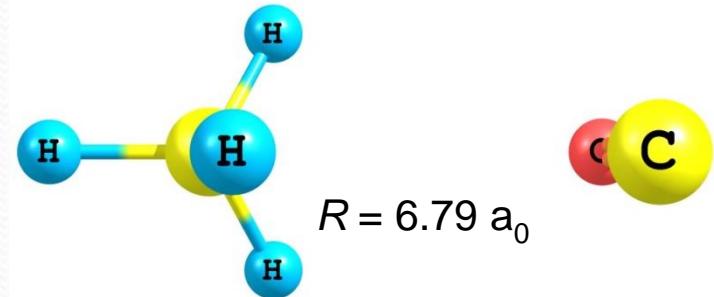
⁵*CNRS, IPAG, F-38000 Grenoble, France*

⁶*Theoretical Chemistry, Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands*

Computational details



CCSD(T)-F12a/aVTZ BSSE
90 000 geometries in total



$D_e = 177.82 \text{ cm}^{-1}$ binding energy

$D_0 = 91.32, 104.21, 94.46 \text{ cm}^{-1}$
for A, E, F modifications

Method	Basis set	Real time
CCSD(T)	aVDZ	1 m
CCSD(T)	aVTZ	28 m
CCSD(T)	aVQZ	14 h
CCSD(T)-F12	aVTZ	30 m

Theoretical and experimental energy levels of CH₄-CO

CH₄-CO, jCH4 = 0

State	<i>J</i>	Calculation (cm ⁻¹)	Observation (cm ⁻¹)	O-C (cm ⁻¹)
<i>K</i> = 0 (<i>e</i>)	0	0.000 00	0.000 00	0.000
	1	0.207 75	0.207 34	0.000
	2	0.623 13	0.621 91	-0.001
	3	1.245 88	1.243 44	-0.002
	4	2.075 65	2.071 58	-0.004
	5	3.111 92	3.105 81	-0.006
	6	4.354 08	4.345 50	-0.009
<i>K</i> = 1 (<i>e</i>)	1	2.289 34	2.280 78	-0.009
	2	2.695 08	2.686 12	-0.009
	3	3.303 42	3.293 87	-0.010
	4	4.114 05	4.103 71	-0.010
	5	5.126 54	5.115 23	-0.011
	6	6.340 34	6.327 88	-0.012
<i>K</i> = 1 (<i>f</i>)	1	2.297 48	2.288 71	-0.009
	2	2.719 48	2.709 91	-0.010
	3	3.352 20	3.341 49	-0.011
	4	4.195 28	4.183 16	-0.012
	5	5.248 26	5.234 54	-0.014
	6	6.510 56	6.495 15	-0.015

(e) → ε=+1

(f) → ε=-1

K is the projection of total angular momentum *J* on intermolecular axis.

Calculations of the bound states were performed using DVR method
 Basis: *j*CH4 ≤ 9, *j*CO ≤ 12
J ≤ 6

CH₄-CO, jCH4 = 1

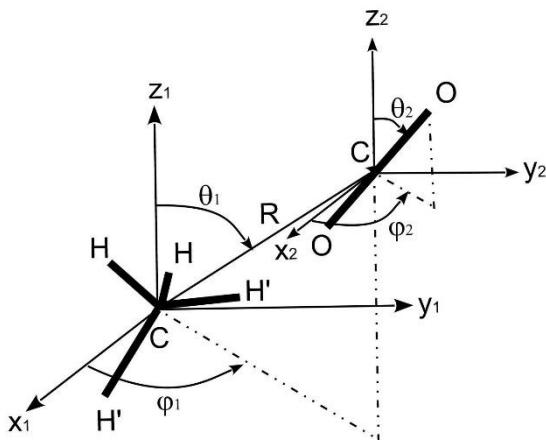
State	<i>J</i>	Calculation (cm ⁻¹)	Observation ^a (cm ⁻¹)	O-C (cm ⁻¹)
<i>K</i> = 0 (<i>e</i>)	0	0.000 00	0.000 00	0.000
	1	0.190 05	0.192 16	0.002
	2	0.571 17	0.577 10	0.006
	3	1.145 06	1.156 06	0.011
	4	1.913 67	1.930 87	0.017
	5	2.878 77	2.904 01	0.025
	6	4.041 73	4.078 56	0.037

Ground state

	1	2	3	4
1	002	002	002	002
2	051	051	051	051
3	112	112	112	112
4	193	193	193	193
5	293	293	293	293
6	481	481	481	481

CH₄-CO₂ and CH₄-N₂

The *ab initio* calculations of the PES were carried out at the CCSD(T)-F12a/aVTZ level of theory

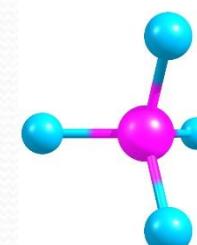


Equilibrium geometry:
 $R_e = 6.38 \text{ a}_\text{o}$, $D_e = 338 \text{ cm}^{-1}$

60 000 energies
213 basis functions

Equilibrium geometry:
 $R_e = 6.80 \text{ a}_\text{o}$, $D_e = 166 \text{ cm}^{-1}$

90 000 energies
103 basis functions



Difference between CO₂ and N₂:

Θ	-3.16 a.u.	-1.11 a.u.
α	17.44 a.u.	11.76 a.u.

PESs for CH₄-CO₂ and CH₄-N₂

The PES was represented in form

$$V(R, \theta_1, \varphi_1, \theta_2, \varphi_2) = \sum_{l_1, l_2, m_1, l} v_{l_1 l_2 m_1 l}(R) t_{l_1 l_2 m_1 l}(\theta_1, \varphi_1, \theta_2, \varphi_2)$$
$$t_{l_1 l_2 m_1 l}(\theta_1, \varphi_1, \theta_2, \varphi_2) = \alpha_{l_1 l_2 m_1 l} (1 + \delta_{m_1 0})^{-1} \sum \binom{l_1}{r_1} \binom{l_2}{r_2} \binom{l}{r} Y_{l_2 r_2}(\theta_2, \varphi_2) Y_{l r}(\theta_1, \varphi_1)$$
$$\times [\delta_{m_1 r_1} + (-1)^{l_1 + m_1 + l_2 + l} \delta_{-m_1 r_1}]$$

with normalization factor

$$\alpha_{l_1 l_2 m_1 l} = [2(1 + \delta_{m_1 0})^{-1} (2l_1 + 1)^{-1}]^{-1/2}$$

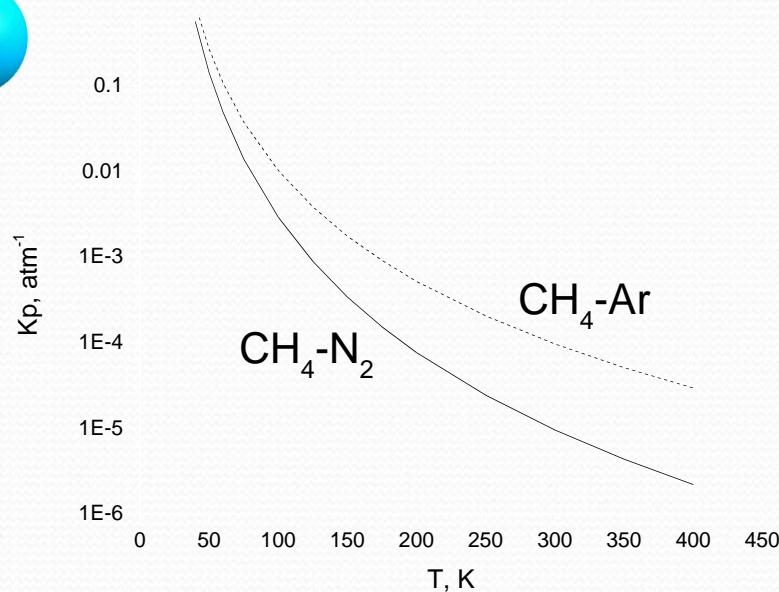
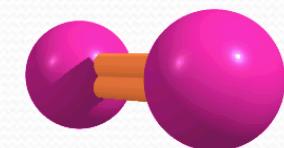
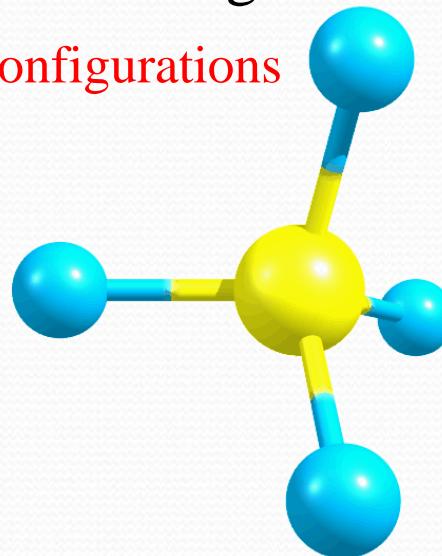
Indices l_1, m_1, l_2, l refer to the CH₄ orientation, the N₂/CO₂ orientation and the collision vector orientation (R), respectively.

Most stable configuration

For $\text{CH}_4\text{-N}_2$ complex barrier height is only $\sim 0.001 \text{ cm}^{-1}$

Family of the most stable configurations

φ , deg	Energy, cm^{-1}
0	-165.59905
10	-165.59937
20	-165.59978
30	-165.59982
40	-165.59978
50	-165.59937
60	-165.59905

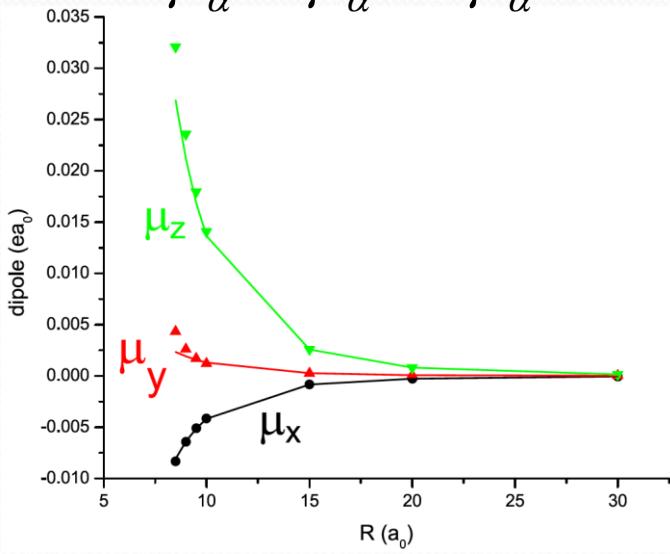


Equilibrium constant for true
bound $\text{CH}_4\text{-N}_2$ dimer formation

Dipole moment

The Dipole Moment surface was obtained the long-range approximation

$$\mu_\alpha = \mu_\alpha^{ind} + \mu_\alpha^{disp}$$



Induced Dipole moment components for CH₄-CO₂ pair. Symbols: *ab initio* CCSD(T)/aVTZ+BSSE correction; Lines: long-range approximation.

$$T_{\gamma\delta\dots\varphi} = \nabla_\gamma \nabla_\delta \dots \nabla_\varphi (R^{-1})$$

$$\mu_\alpha^{disp(CRA)} = -\frac{5\beta_{\alpha\beta\gamma}^A \alpha_{\delta\varepsilon}^B}{36\alpha^A \alpha^B} T_{\beta\delta} T_{\gamma\varepsilon} C_6 - \left(B_{\alpha\beta,\gamma\delta}^A \alpha_{\varepsilon\varphi}^B - B_{\alpha\beta,\gamma\delta}^B \alpha_{\varepsilon\varphi}^A \right) \frac{5T_{\beta\varepsilon} T_{\varphi\gamma\delta} C_6}{54\alpha^A \alpha^B}.$$

Induction contribution:

$$\begin{aligned} \mu_\alpha^{ind} = & \frac{1}{3} \alpha_{\alpha\beta}^A \Theta_{\gamma\delta}^B T_{\beta\gamma\delta} - \frac{1}{9} A_{\alpha,\beta\gamma}^A \Theta_{\delta\varepsilon}^B T_{\beta\gamma\delta\varepsilon} + \frac{1}{15} \alpha_{\alpha\beta}^B \Omega_{\gamma\delta\varepsilon}^A T_{\beta\gamma\delta\varepsilon} + \\ & + \frac{1}{105} \alpha_{\alpha\beta}^A \Phi_{\gamma\delta\varepsilon\varphi}^B T_{\beta\gamma\delta\varepsilon\varphi} - \frac{1}{105} \alpha_{\alpha\beta}^B \Phi_{\gamma\delta\varepsilon\varphi}^A T_{\beta\gamma\delta\varepsilon\varphi} + \frac{1}{45} E_{\alpha,\beta\gamma\delta}^A \Theta_{\varepsilon\varphi}^B T_{\beta\gamma\delta\varepsilon\varphi} - \\ & - \frac{1}{315} A_{\alpha,\beta\gamma}^A \Phi_{\delta\varepsilon\varphi\nu}^B T_{\beta\gamma\delta\varepsilon\varphi\nu} + \frac{1}{225} E_{\alpha,\beta\gamma\delta}^B \Omega_{\varepsilon\varphi\nu}^A T_{\beta\gamma\delta\varepsilon\varphi\nu} + \frac{1}{3} \alpha_{\alpha\beta}^B \Theta_{\gamma\delta}^B \alpha_{\varepsilon\varphi}^A T_{\beta\varepsilon} T_{\varphi\gamma\delta} + \\ & - \frac{1}{315} D_{\alpha,\beta\gamma\delta\varepsilon}^A \Theta_{\varphi\nu}^B T_{\beta\gamma\delta\varepsilon\varphi\nu}, \end{aligned}$$

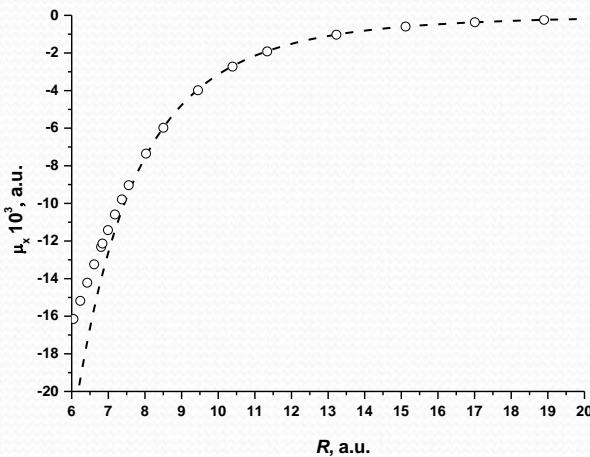
Dispersion contribution:

$$\begin{aligned} \mu_\alpha^{disp} = & -\frac{1}{2\pi} \int_0^\infty d\omega \beta_{\alpha\beta\gamma}^A(i\omega, 0) \alpha_{\delta\varepsilon}^B(i\omega) T_{\beta\delta} T_{\gamma\varepsilon} + \\ & + \frac{1}{3\pi} \int_0^\infty d\omega [B_{\alpha\beta,\gamma\delta}^B(0, i\omega) \alpha_{\varepsilon\varphi}^A(i\omega) - B_{\alpha\beta,\gamma\delta}^A(0, i\omega) \alpha_{\varepsilon\varphi}^B(i\omega)] T_{\beta\varepsilon} T_{\varphi\gamma\delta} \end{aligned}$$

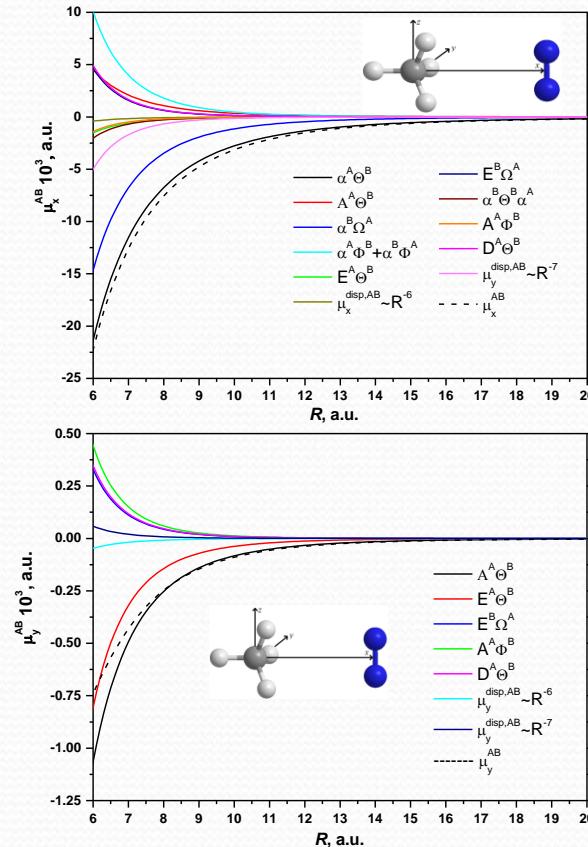


CH₄-N₂

DMS for CH₄-N₂ was constructed by analogy with CH₄-CO₂ pair



Induced Dipole moment components for CH₄-N₂ pair. Symbols: *ab initio* CCSD(T)/aVTZ+BSSE correction; Dash line: long-range approximation.



Contribution of different terms in the dipole moment of the most stable configuration of the CH₄-N₂ complex

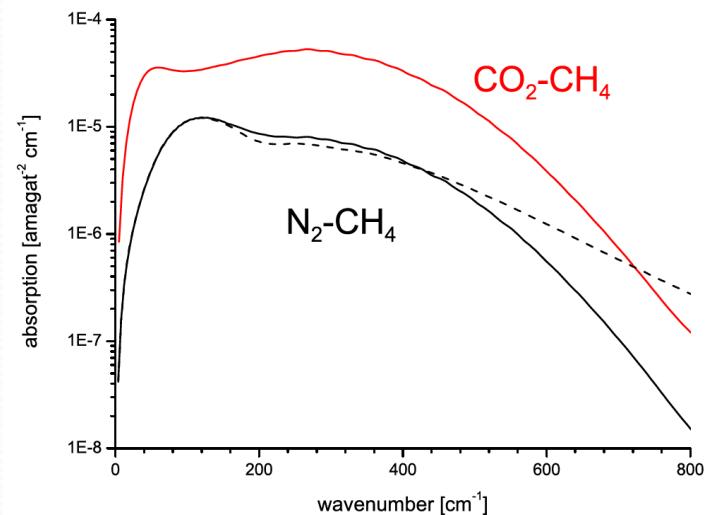
CIA for CH₄-CO₂ and CH₄-N₂

The work on these systems was initiated due to a high interest of researchers conducting the climate simulations of early Mars and exoplanets. The CIA is necessary for their radiative transfer models.

The CIA for CH₄-CO₂ is absent!

$$\Gamma_0 = \int_0^\infty \frac{\alpha(\nu) d\nu}{\nu \tanh\left(\frac{hc\nu}{2kT}\right)} \equiv \tilde{\Gamma}_0 = \frac{32\pi^4}{3hc} \int_0^\infty \int_\Omega \mu^2(R, \Omega) e^{-\frac{V(R, \Omega)}{kT}} R^2 dR d\Omega$$

Simulated (solid lines) and experimental (dash line, HITRAN) rototranslational band profiles at 300K



CIA for CH₄-CO₂ and CH₄-N₂

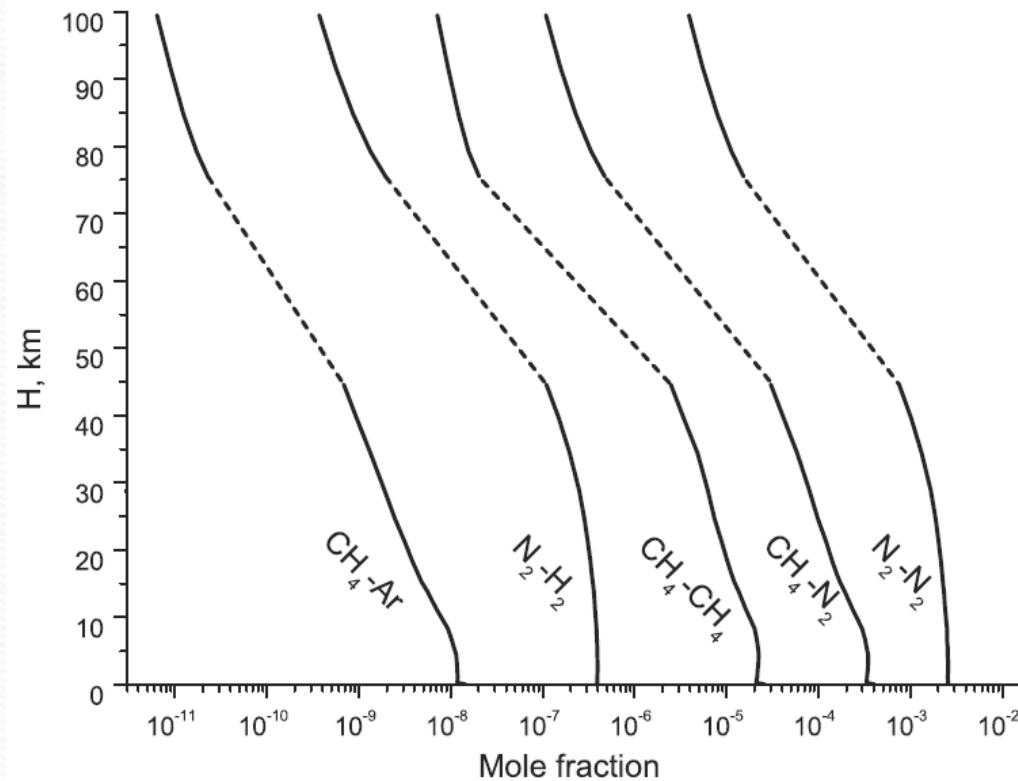
Our results on CIA allowed to carry out the first realistic calculations of greenhouse warming on early Mars.

Results: just 0.5 bar (or more) of atmospheric CO₂, a few percent of H₂ or CH₄ would have raised surface temperature by tens of degrees, with temperatures reaching 273K, leading to the geological observations that we can see now (evidence of abundant liquid water on early Mars: dendritic valley networks, fluvial conglomerates, open-basin lakes...)

It was shown that the strength of both CO₂-H₂ and CH₄-CO₂ CIA has previously been significantly underestimated. Because due to the lack of information, scientists used scaling of N₂-H₂ data to get CIA for CO₂-H₂ and didn't consider CH₄-CO₂ as an effective warming agent. But it turned out to be! due to the peak of CO₂-CH₄ CIA in a key spectral window region : 250-500 cm⁻¹

Height profiles for some dimers in atmosphere of Titan

Height profiles of some true bound dimers in Titan's atmosphere.
Dashed parts of the curves relate to the altitudes for which the data measured
on-board of Cassini-Huygens spacecraft are missed



Results

- 3D PES and DMSs of CH₄-Ar are obtained in analytical form based on coupled cluster calculations
- 5D PESSs for CH₄-CO, CH₄-CO₂ and CH₄-N₂ are calculated at the CCSD(T)-F12a/aVTZ level and represented in analytical form
- Equilibrium constant (T) of dimer formation is reported for CH₄-N₂ and CH₄-Ar
- CIA for CH₄-N₂ and CH₄-CO₂
- The rotational energy levels of CH₄-CO complex are calculated. New measured transitions assigned.

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- RFBR Grant 13-05-00751 “Theoretical modeling and laboratory study of collision-induced absorption in gas media containing methane”
- RFBRI Grant 15-05-00736 “Laboratory and theoretical studies of greenhouse effect related to dipole forbidden molecular absorption in planetary and paleo-atmospheres”
- Ab initio calculations were performed using HPC resources of SKIF-Cyberia (TSU) and Harvard Odyssey supercomputer

Thank you for
your attention!!!