Svatopluk Civi-



š asov rozli-ená infra ervená emisní spektroskopie s Fourierovou transformací a její aplikace v pulzních výbojích a laserové ablaci kov õ.











Výboj v čistém vodíku



Helium discharge



Chemical Physics Letters 383 (2004) 256–260

He discharge plasma



Fig. 1. A portion of the time-resolved spectrum observed by a pulsed discharge in He with a pressure of 1.33 kPa (10 Torr). The discharge was applied in the interval of $0-20 \ \mu$ s with a peak current of 0.5 A. The strongest peak belongs to the atomic He line (4d–3p). Other lines pertain to 4f–3d transitions of He₂.

$He^m + He^m \rightarrow He^+ + He + e$	(1)
$\mathrm{He^+} + \mathrm{He} + \mathrm{M} \to \mathrm{He_2^+} + \mathrm{M}$	(2)
$\mathrm{He}_{2}^{+} + \mathrm{e} \rightarrow \mathrm{He}_{2}^{*} + \mathrm{h}\nu,$	(3)



Fig. 3. Observed time profiles of emission intensities of He₂. Abscissa values show normalized intensities of the emission lines. The discharge conditions are as given in the caption of Fig. 1.



Fig. 4. Energy level diagram of He₂. The transitions observed in the present study are shown by arrows. The energy values are represented relative to the $a^{3}\Sigma_{u}^{+}v = 0$ state. n(>1) is the principal quantum number in a united atom molecular orbital designation. The ionization limit to He₂⁺ is 34316 cm⁻¹.

He₂

Observed transitions of He ₂ (cm ⁻¹) ^a					Molecular constants of He ₂ in the $h^{3}\Sigma_{u}^{+}$, $g^{3}\Sigma_{g}^{+}$, and $d^{3}\Sigma_{u}^{+}$ states ^a		
Ν	P(N)	oc.	R(N)	oc.		Present	Previous
$h^3\Sigma_n^+$ - $g^3\Sigma_a^+$					$(h^3\Sigma_n^+)$		b
0 0	3177.5569	0.0006			В	7.148 49(24)	7.149
2	3134.9969	-0.0005	3206.4133	0.0018	$D \times 10^3$	0.505 3(24)	0.524
4	3107.2556	-0.0001	3235.5447	0.0000	Ε	6368.1202(30)	
6	3080.1473	-0.0010	3264.8626	-0.0064	(_3 v +)		c
8	3053.7916	0.0000	3294.3028	0.0089	$(g^{2}\Sigma_{g})$	5 007 400/0 D	5 007 0/1)
10	3028.3000	0.0012	3323.7108	-0.0054	B	7.096 423(94)	7.096 8(1)
12	3003.7698	-0.0002	3353.0067	0.0013	$D \times 10^{\circ}$	0.530 70(44)	0.538(7)
14	2980.2783	-0.0002			E	3204.8589(11)	
a ³ 5+ d ³ 5+					$(d^3\Sigma_n^+)$		d
$g^{*}L_{g}^{*}=d^{*}L_{u}^{*}$	2100 4064	0.001.0	2727 0664	0.0012	B	7.226 329(88)	7.228 6(15)
1	3150.4004	-0.0019	3232.9004	-0.0015	$D \times 10^3$	0.519 91(37)	0.532(3)
3	3100.7770	-0.0003	3239.9343	0.0005	Ε	0.0	0.0
5	3130.2548	0.0017	3285.6522	0.0016			
7	3098.9306	0.0021	3310.0069	0.0006	"cm"' unit. Nu	mbers in parentheses denc	ote one standard deviatio
9	3066.8917	-0.0002	3332.8839	-0.0017	and apply to the last significant digits.		
11	3034.2243	-0.0031	3354.1697	0.0005	^b Ref. [1].		

^a N denotes the rotational quantum number neglecting spin in lower electronic states.

0.0015

3001.0169

13

[°]Ref. [12]. ^dRef. [13].

H₃⁺ FUNDAMENTAL BAND IN JUPITER'S AURORAL ZONES AT HIGH RESOLUTION FROM 2400 TO 2900 INVERSE CENTIMETERS

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ABSTRACT

Following our previous detection of H_3^+ in the southern auroral zone of Jupiter from its $2\nu_2$ band, we searched for the fundamental at 4 μ m. We detected up to 42 lines of this band in emission, at high resolution, on the auroral spot of each hemisphere. A rotational temperature was derived for the southern and northern zones, respectively, of 1000 ± 40 K and 835 ± 50 K. The intensity of the lines was on the average 2 times stronger in the south than in the north. The $2\nu_2$ band, which was sought in the north only on this occasion, was not detectable. A purely thermal mechanism for the H_3^+ production is implied. Spatial extension and temporal variability of the excitation is discussed.



 H_3^+ is extremely important to the chemistry of interstellar clouds. This is because H_3^+ willingly donates its extra proton to a variety of collision partners, thus laying the foundation for a large network of ion-molecule reactions.



Spectra of three interstellar clouds showing absorption lines due to the R(1,1)u and R(1,0) transitions of H_3^+ . Arrows indicate the expected positions of the absorption features from previous measurements of the interstellar gas velocity.



Why Molecular Ions?

As illustrated in the reaction chart to the left, molecular ions are responsible for driving the chemistry resulting in the formation of complex organic/prebiotic molecules. Detecting these ions in the ISM will lead to a better understanding of chemical evolution in space.

Why High-Resolution Spectroscopy?

High-resolution spectra serve as molecular fingerprints, enabling astronomical searches for these species $C_{2H_5CNH} \xrightarrow{+} C_{2H_5CN}$ in the ISM, planetary atmospheres, and circumstellar $\rightarrow CH_3CNH \xrightarrow{+} CH_3CN$ environments.

^{13 NH2} Why Infrared Spectroscopy?

Infrared frequencies can be used to search for molecules without a permanent dipole (precluding microwave spectroscopy/radio astronomy), and can also be used to derive pure rotational transition frequencies of species which do contain a permanent dipole.

He + H₂ discharge plasma





S. Civis, P. Kubat, S. Nishida, K. Kawaguchi, Chemical Physics Letters, 418 (2006) 448-453

Ar + H₂ discharge plasma



ArH radical



Fig. 5. Approximate potential curves for some states of ArH. The consequence of an avoided crossing between the A and X states has not been included in this figure.



Emission spectrum of the 4p-5s band of ArH. Sharp lines belong to the 4f-3d band and probably to other unnassigned bands of ArH. To calculate the spectrum a T=2500 K,and a halfwidth of 0.7 cm⁻¹ were assumed.

Investigated bands of ArH and ArD

	ArH	ArD		
Transition	Band cn	Origin Դ ¹	Resolution cm ⁻¹	Reference
$3d\pi \rightarrow 5s$	13024	13040	0.1	2
$4d\pi \rightarrow 5s$	19520	19570		3
$\pi \rightarrow 5s$?	-	22575		3
$5p \rightarrow 5s$	-	17487	0.13	5
$5p \rightarrow 6s$	-	3681	0.20	5
$6p \rightarrow 5s$	-	21676	0.20	5
$4p \rightarrow 5s$	-	6120	0.05; 0.2	4
$3d\sigma \rightarrow 4p$	-	10200	0.05; 0.2	4
$3d\pi \rightarrow 4p$	6934	6900	0.05; 0.2	4,6
$3d\delta \rightarrow 4p$	8534	8524	0.05	6
$4d\sigma \rightarrow 4p$	15097	15075	0.3	6
$6s \rightarrow 4p$	7703	7685	0.02	6
$8s \rightarrow 4p$	-	16749	0.20	6
$4f \rightarrow 5s$	20641	20682	0.20	7
$4f \rightarrow 3d\pi$	7627	7649	0.05	7
$4f \rightarrow 3d\delta$	6027	6038	0.05	7
$4f \rightarrow 3d\sigma$	~4400	4351	0.10; 0.20	7,8

Baskakov O.I., Civiš S., and Kawaguchi K, J. Chem. Phys., 2005, 122 (11) 114302



The time-resolved emission FT spectrum from a pulsed discharge in a $(CN)_2$ and He mixture. The discharge pulse duration was 20 s. The 30 time-resolved spectra were collected from t = 0–90 µs with a step of 3 µs. The spectra of C_2H_2 and C_2 were observed at 3300 and 3600 cm⁻¹.

He + CH₄ discharge plasma







Astronularilis of lite Manth

Vis lines at 3878.8, 3886.4, 3890.2, 4300.3, UV lines near 1271, 1368, 1369, 1370, 1549, & 1694

 $J = 1/2, v_{01} (3263.794 \text{ MHz})$ $J = 1/2, v_{11} (3335.481 \text{ MHz})$ $J = 1/2, v_{10} (3349.193 \text{ MHz})$

Large Magellanic Cloud

P. Swings and L. Rosenfeld, ApJ 86:483-486 (1937)
A. McKellar, Publ Astron Soc Pac 52:187-192 (1940)
W. S. Adams, ApJ 93:11-23 (1941)
O. E. H. Rydbeck, J. Elldér, and W. M. Irvine, Nature 246:246-248 (1973)
Y. Sheffer and S. R. Federman, ApJ 659:1353-1359 (2007)





CH vibrational temperature





vzájemné reakce

Vibrational temperature5000 ó 6000 KRotational temperature550 ó 700 KExcitation temperature2500 ó 3000 K

HNC/HCN emission



















Moflné cesty vzniku HNC ve výboji:

M25 - M27



Výboj - hasivo FM 200



Result - information about reaction

dynamics

Decomposition of extinguish agents CF₃Br and (CF₃)₂CH









Time resolved FTIR measurement in the laser spark



The emission arises in ablation of metal target by laser radiation of a pulsed nanosecond ArF (λ = 193 nm) laser 1 kHz repetition, at fluences around 15 mJ

1/n system







Comparison of Arcturus spectrum with FTIR emission spectrum



The observed IR emission spectrum of Au



Some parts of the observed IR emission spectra of Au



Spectral resolution 0.05 cm⁻¹



Part of the FTIR spectrum of the emission from Cu target





Conclusions

Several systems inside of discharge plasma has been studied by High resolution FT spectroscopy

New systems such extinguishing agents will be studied (C

Laboratory chemistry of HCN and HNC isomerisation

Many High resolution atomic spectra has been measured by High resolution FT spectroscopy (better understanding of the stellar spectra)

New detection technique was developed which can be applied for a study of the relaxation profiles of the individual atomic or molecular levels

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Thanks

http://www.jh-inst.cas.cz/~ftirlab/

(Spectral library)



From the left: M. Ferus, M. Kamas, J. Cihelka, P. Kubelík, S. Civiš, K. Sovová, I. Matulková.





Letter to the Editor

Radio Astronomical Determination of Ground State Transition Frequencies of CH

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Summary. From a comparison of the spectra of CH and other molecules towards Cas A and dark clouds, we have determined the rest frequencies of the three allowed transitions of the ${}^{2}\Pi_{1/2}$, J = 1/2, ground state Λ -doublet of CH to be $v_{01} = 3263.794 \pm 0.003$, $v_{11} = 3335.481 \pm 0.002$ and $v_{10} = 3349.193 \pm 0.003$ MHz. These frequencies cannot be checked by the sum rule, $v_{11} + v_{00} = v_{10} + v_{01}$, since the v_{00} -transition is forbidden in this particular case. The relative errors in

these frequencies are about twice as small as those obtained earlier by radio astronomical methods for the two main lines of ground state OH. Further refinements in the determination of the CH frequencies are desirable, since these transitions have not yet been directly measured in the laboratory.

Key words: CH — Cas A — dark clouds — transition frequencies — interstellar molecules

Radio astronomical detection of the ground state ${}^{2}\Pi_{1/2}$, J = 1/2, A-doublet of CH has recently been announced by Rydbeck *et al.* (1973). The upper satellite line was detected independently by Turner and Zuckerman (1974). The CH-lines were observed in southern galactic sources by Robinson *et al.* (1974). Measurements of satellite and main line intensity ratios of CH have recently been reported by Rydbeck *et al.* (1974a). The subject of the present Letter is a more accurate determination of the CH frequencies.

The equipment and observing procedure were the same as described by Rydbeck *et al.* (1974a), except that filters of bandwidth and spacing 1 kHz were also used for the present observations. Most of the integrations were done with left circular polarization, there being no evidence for polarization in any of the sources observed.

The CH transition frequencies were determined by Rydbeck et al. (1973) to be $v_{10}(F = 1 \rightarrow 0) = 3349.185 \pm 0.010$ MHz, $v_{11}(F = 1 \rightarrow 1) = 3335.475 \pm 0.010$ MHz, $v_{01}(F = 0 \rightarrow 1) = 3263.788 \pm 0.010$ MHz. Those values have now been refined, with the following assumptions: (1) in the sources observed, CH, OH, H₂CO and NH₃ are well mixed, and have the same radial velocity; (2) the correct frequencies for the main lines of OH at 18 cm are those given by ter Meulen and Dymanus

* On leave from the Department of Physics and Astronomy, University of Massachusetts, Amherst. (1972); (3) the frequency for the $F = 2 \rightarrow 2$ component of H₂CO at 6 cm is that given by Tucker *et al.* (1971).

For the comparison of OH and CH spectra, we observed towards Cas A and four dark clouds which, according to Turner (1973), have either a single velocity component or at least one narrow, well-defined component.

The profile for the main $F = 1 \rightarrow 1$ line of CH, in the direction of Cas A, was compared with the OH profiles taken by Davies and Matthews (1972) and with unpublished OH data taken at Onsala. The presence of two components in the Orion arm feature at $v \approx -1 \text{ km s}^{-1}$ (Fig. 1) and the characteristic structure of the Perseus arm feature allows the CH and OH spectra to be compared with an accuracy of about $\pm 1 \text{ kHz}$. We estimate a correction, δv_{11} , of $6 \pm 1 \text{ kHz}$ to our previously published value of v_{11} (Rydbeck *et al.*, 1973).

Another estimate of $\delta v_{11} = 5.5 \pm 2 \text{ kHz}$ was obtained by comparing the main line spectrum of CH with that of H₂CO (Davies, 1973; Davies, 1974; Zuckerman *et al.*, 1970) in the direction of Cas A.

A third, independent, estimate of δv_{11} was obtained from a comparison of our CH spectra with those of other molecules towards four dark clouds. Table 1 gives a compilation of the radial velocities for CH and other molecules observed at approximately the same positions. The OH values are averages of the data of

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Title: Les bandes de CH et la présence de l'hydrogène dans les Comètes. **Authors:** Nicolet, M. **Journal:** Zeitschrift für Astrophysik, Vol. 15, p.154

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Les bandes de CH et la présence de l'hydrogène dans les Comètes.

Par M. Nicolet, D. Sc.

(Reçu janvier 12, 1938.)

Il est montré que l'étude de la structure de rotation est nécessaire pour l'identification des bandes cométaires et que le groupe de raies cométaires vers λ 4300 Å doit probablement être attribué à la molécule CH.

Les raies de la série de Balmer n'apparaissent certainement pas dans les spectres des comètes et les bandes de résonance de H_2 , étant en dehors de la région spectrale astronomique, ne peuvent être observées. Quant à la présence des bandes cométaires attribuées au système de Raffety, elle ne peut être envisagée. Rien ne permet donc d'établir jusqu'ici la présence de l'hydrogène dans les Comètes. Cependant, si l'identification de la molécule CH était assurée, la présence d'hydrogène dans les Comètes serait du même coup démontrée.

F. BALDET ¹), R. C. JOHNSON ²) et N. T. BOBROVNIKOFF ³) ont examiné la possibilité de l'identification de CH par la comparaison du maximum d'intensité de la bande λ 4300 Å de CH avee λ 4313 Å. F. BALDET avait considéré la coïncidence avec la radiation cométaire à λ 4314 Å comme fortuite (Comète Brooks) parce que la comète ne montre pas une bande dégradée vers le violet, mais bien une ligne piquée. Cependant, N. T. BOB-ROVNIKOFF avait indiqué (Comète Halley) que cette circonstance rendait l'identification quelque peu incertaine, mais que la faible dispersion employée et les transitions restreintes aux faibles nombres quantiques de rotation pourraient donner une bande aigue de forme analogue à celle d'une raie. Bref, l'identification était extrèmement douteuse et n'était généralement pas acceptée⁴).

Le but de cette note est d'indiquer que le spectre de la molécule CH est très probablement présent dans les spectres cométaires. Le composé CH

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⁽¹⁾ Thèse, Paris 1926. — ²) M. N. 87, 625, 1927. — ³) Public. Lick Obs. 17, 443, 1931. — ⁴) Voir K. WURM, Handb. d. Astrophys. 7, 305, 1936 et R. MIN-KOWSKI, P. A. S. P. 49, 276, 1937.