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New analysis of the Douglas-Herzberg system ($\mathbf{A^1\Pi - X^1\Sigma^+}$) in the $\mathbf{CH^+}$ ion radical

The $\mathbf{A^1\Pi - X^1\Sigma^+}$ system in the $\mathbf{CH^+}$

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Abstract. Three bands of the $A^1\Pi - X^1\Sigma^+$ system in the ^{12}CH$^+$ ion radical have been rephotographed under high resolution as an emission spectra using a Geissler-type discharge tube. The conventional technique of spectroscopy has been implemented. Using the Th lines as a standards, as well as an interferometric comparator equipped with a photoelectric scanning device, the $0{-}0, 0{-}1$ and $2{-}1$ bands have been reanalyzed. By means of much longer bands ($J_{max} = 17$ in the $Q(J)$ branch of the 0–0 band; $J_{max} = 16$ in the $R(J)$ branch of the 0–1 band; $J_{max} = 14$ in the $P(J)$ and $Q(J)$ branches of the 2–1 band), than have been observed so far, as well as the merged calculations, using another five bands given by Carrington et al. [A. Carrington, D.A. Ramsay, Phys. Scripta **25**, 272 (1982)] additionally, more accurate molecular constants for the $X^1\Sigma^+$ state, the improved reduced band system origin $T_e = 24118.726$ (14) cm^{-1} as well as for the first time the equilibrium molecular constants with their one standard deviation for the $A^1\Pi$ state in the CH$^+$ molecule have been computed: $\omega_e' = 1864.402(22)$, $\omega_e x_e' = 115.832(14)$, $\omega_e y_e' = 2.6301(24)$, $B_e' = 11.88677(72)$, $\alpha_e' = 0.9163(18)$, $\gamma_e' = -2.29(12) \times 10^{-2}$, $\varepsilon_e' = 4.95(20) \times 10^{-3}$, $D_e' = 1.92960(31) \times 10^{-3}$, $\beta_e' = 1.0733(50) \times 10^{-4}$, $\delta_e' = -1.312(16) \times 10^{-5}$, $q_e' = 4.102(23) \times 10^{-2}$, $\alpha_{qe}' = -3.14(16) \times 10^{-3}$, and $q_{D_e}' = -2.20(14) \times 10^{-5}$ cm^{-1}. Only in our research the addition to the zero-point energy $Y_{00}' = -1.9430$ cm^{-1} and $Y_{00}'' = 1.8953$ cm^{-1} have been calculated. The equilibrium bond lengths of $r_e' = 1.235053(37)$ Å and $r_e'' = 1.1308843(30)$ Å for the $A^1\Pi$ and $X^1\Sigma^+$ states, respectively have been computed. Full quantum-mechanics characteristic of the $A{-}X$ bands system in the ^{12}CH$^+$ molecule, i.e. RKR turning points, the Franck-Condon factors and r-centroids have been obtained. Dissociation energies $D_e^{X^1\Sigma^+} = (38470 \pm 3503)$ cm^{-1} and $D_e^{A^1\Pi} = (14415 \pm 3509)$ cm^{-1} for the molecule under consideration have been estimated.

PACS. 33.20.Kf Visible spectra

1 Introduction

The CH$^+$ ion radical has been the subject of both experimental and theoretical research for over 60 years. A large amount of information relating to its creation, destruction and abundance in interstellar space has become an inspiration for investigating the structure of this molecule, and for determining its molecular constants. The first spectroscopic investigation of the ^{12}CH$^+$ radical in a laboratory conditions was carried out by Douglas and Herzberg in 1941 and 1942 [1,2]. They studied four emission bands ($0{-}0, 1{-}0, 2{-}0,$ and $0{-}1$) of the $A^1\Pi{-}X^1\Sigma^+$ ($A{-}X$) system in the ^{12}CH$^+$ molecule and showed that the wavelengths of the $R(0)$ lines for the first three bands agree closely with the wavelengths of the interstellar absorption lines at 4232.58, 3957.72 and 3745.33 Å. Therefore they concluded that the CH$^+$ is presented in interstellar space. Their analysis allowed the identification of certain interstellar absorption lines observed by Adams [3], confirming that the CH$^+$ radical was a major constituent of the interstellar gas clouds. Douglas and Morton [4] have extended the study of $A{-}X$ system to the $v' - 1$ progression for the $v' = 0, 1, 2, 3,$ and 4 levels and they showed that the calculated wavelength for the $R(0)$ line of the 3–0 band agrees with that of the interstellar absorption line at 3579.04 Å. Carré, and Doufnay [5] and Carré [6] who were examining the emission spectra of CH$_4$ and C$_2$H$_2$ excited by proton impact, observed 3–0 and 4–0 bands for the $A{-}X$ band system and reported two new band systems $B^1\Delta - A^1\Pi$ (0–0, 1–1, and 2–2 bands) and $b^3\Sigma - a^3\Pi$ (0–0, 1–0, and 2–1 bands) in the CH$^+$ radical. By making use of previous experimental data, Botterud et al. [7] derived some of the molecular parameters for both states of this system. Kusonoki and Ottinger [8] have observed nine bands of the $b^3\Sigma - a^3\Pi$ transition for the CH$^+$. Carrington and Ramsay [9] have analyzed eight bands (0–0, 0–1, 1–0,

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1−1, 1−2, 1−3, 2−1, and 3−1) of the $A^1\Pi - X^1\Sigma^+$ system in the ^{12}CH$^+$. Bands involving the $v'' = 2$ and $v'' = 3$ levels of the ground state have been observed for the first time. This allowed them to obtain improved bands origins and rotational constants for both combining states and for the first time vibrational constants with a standard deviations for the $X^1\Sigma^+$ ground state. Succeeding new electronic transition $C^1\Sigma^+ - A^1\Pi$ (0−1 and 1−2 bands) was observed by Macau-Hercol et al. [10]. The formation, destruction, and abundance of the CH$^+$ radical in the interstellar space have been studied intensively in the last years by many authors [11–22]. The research on identification of the CH$^+$ spectra in the interstellar space have been also very intense [23–34]. The CH$^+$ is believed to be very important in formation of CH, C$_2$, CO, CN, and many other molecular species.

So far values of the equilibrium constants,both vibrational as well as rotational,of the $A^1\Pi$ exciting state in the ^{12}CH$^+$ ion molecule have been only estimated, both in experimental [2,4] and theoretical research [36–45]. Due to the fundamental importance of the CH$^+$ ion molecule to recognize the characteristics of the interstellar space, we decided to reinvestigate the emission spectra emploing $A^1\Pi$ state. With this end in view,we received high resolution spectra of the three bands (0−0, 0−1, and 2−1) of the $A^1\Pi - X^1\Sigma^+$ system again.

2 Experimental details

The emission spectrum of the $A^1\Pi - X^1\Sigma^+$ system of the CH$^+$ radicals has been obtained from a Geissler-type tube filled with a mixture of acetylene (90%) and helium at a total pressure of about 8 Torr. The tube was operated at about 5 kV and 100 mA ac. Spectra were obtained by using a 2-m Ebert plane grating PGS-2 spectrograph equipped with a 651 grooves/mm grating with a total number of 45600 grooves, blazed at 1.0 μm. The observations were made in the fifth and sixth orders, which permitted us to obtain a spectrum with a linear reciprocal dispersion in the range 0.067–0.091 nm/mm. The exposure times on the ORWO UV-1 plates varied from 1 to 6 h.

As a calibration spectrum the Th standard lines [46] obtained from several overlapped orders of the spectrum from a water-cooled hollow-cathode tube have been used. The measurements were carried out carefully using an automatic interferometric comparator assembled in our laboratory. The positions of the line centers were calculated by means of an interactive graphic computer program using the least-squares procedure and assuming Gaussian profiles for the lines. Repeatability of the measurements was tested to be 0.25–0.5 μm according to the grain of the plates. For the wavenumbers calculations seventh-order interpolation polynomials were used. The typical standard deviation of the least-squares fit for the 30–90 calibration lines was about $(1.4–1.9) \times 10^{-3}$ cm^{-1}.

The calibration procedure of each of the plates was tested and very slow varying disagreement of the Th and molecular line positions (−1.5, 0, +1.5 μm at the left border, middle, and right border of the plate, respectively) has been detected and readily removed. The final calculations of the positions of the molecular linecenters were supported by (from preliminary measurements) an earlier set of sorted wavenumbers of the CH$^+$ lines in measured regions.

Table 1. Summary of observations and analyses of the Douglas-Herzberg ($A^1\Pi - X^1\Sigma^+$) system of the CH$^+$ ion molecule.

Band	Number of lines included in the fit	J_{max}	f^a	$\sigma^b \times 10^3$ (cm^{-1})
0–0	36	17 (14^c)	27	3.86
0–1	32	16 (14^c)	23	3.98
2–1	30	14 (10^c)	21	5.34

^{a} Number of degrees of freedom of the fit for the individual band analysis. ^{b} Standard deviation of the fit for the individual band analysis. ^{c} The previously obtained data [9] concerning the bands under consideration.

Consequent1y, the precision of the single lines with a good line background ratio was about 0.0025 cm^{-1}. However, many lines were blended or faint, with a typical accuracy of 0.003−0.01 cm^{-1}. Remaining lines of less than 0.01 cm^{-1} precision are asterisked in the tables and have not been used to calculate molecular constants. In Table 1 we collected general information about presently recorded and analyzed spectra. Observed wavenumbers of lines of the 0−0, 0−1, and 2−1 bands of the A−X system and their rotational assignments are highlighted in Table 2.

3 Analysis and calculations

Each band of the CH$^+$ radical originating as a result of the $A^1\Pi - X^1\Sigma^+$ transition has a simple and regular structure consisting of single $P_{11ee}(J)$, Q_{11fe}(J) and $R_{11ee}(J)$ branches. A preliminary rotational assignments of the band lines and J numbering have been performed on the basis of the characteristic spectrum of this bands system (from Ref. [9]) and traditional methods described in the monograph of Herzberg [47]. The reduction of the wavenumbers of lines to rovibronic parameters was performed in an individual band-by-band analysis via a nonlinear least-squares fitting for the 0−0, 0−1, and 2−1 bands reanalyzed in this paper, as well as for the 1−0, 1−1, 1−2, 1−3, and 3−1 bands given by Carrington and Ramsay [9] using our program. In this program both analyzed states are represented by effective Hamiltonians from Brown et al. [48]. Direct matrix elements of this Hamiltonian for the $^1\Pi$ and $^1\Sigma^+$ states are well-known. The rotational levels have been described by the formulae:

$$\begin{aligned} F_v(J) &= B_v[J(J+1)-1] - D_v[J(J+1)-1]^2 \\ &\quad + H_v[J(J+1)-1]^3 + \ldots \\ &\quad \pm \tfrac{1}{2}[q_v J(J+1) + q_{Dv} J^2(J+1)^2 + \ldots] \end{aligned} \quad (1)$$

Table 2. Wavenumbers (in cm^{-1}) and rotational assignments for the 0−0, 0−1, and 2−1 bands of the $A^1\Pi - X^1\Sigma^+$ system of the CH$^+$ ion radical[a].

J	$P_{11ee}(J)$		$Q_{11fe}(J)$		$R_{11ee}(J)$	
			0−0 band			
0.0					23619.7802	(−6)
1.0			23591.8430	(−30)	23637.6543	(42)
2.0	23536.2547	(86)	23581.7303	(−47)	23650.4424	(28)
3.0	23498.5334	(−21)	23566.5329	(1)	23658.0711	(−6)
4.0	23455.9082	(−15)	23546.1988	(27)	23660.4538	(2)
5.0	23408.3579	(14)	23520.6772	*	23657.4751	(−18)
6.0	23355.8567	(89)	23489.8711	(4)	23649.0126	(−43)
7.0	23298.3357	(−35)	23453.7199	(12)	23634.9423	*
8.0	23235.7727	(36)	23412.1027	(−13)	23615.0369	*
9.0	23168.0699	*	23364.8944	(−84)	23589.2110	*
10.0	23095.1284	*	23311.9693	(−31)	23557.2308	*
11.0	23016.7987	(−46)	23253.1557	(49)	23518.8674	*
12.0	22933.0012	(−15)	23188.2578	(27)	23473.9113	(−13)
13.0			23117.0820	(15)	23422.0651	(25)
14.0			23039.3995	(9)	23363.0454	(−57)
15.0			22954.9563	(3)	23296.5678	(22)
16.0			22863.4598	*	23222.2642	(−19)
17.0			22764.6413	(6)	23222.2642	(−19)
			0−1 band			
0.0					20880.1219	(6)
1.0			20853.1643	(−15)	20898.9750	(51)
2.0	20799.5245	(5)	20845.0128	(−1)	20913.7132	(−43)
3.0	20764.7507	(18)	20832.7382	(−80)	20924.2797	(−54)
4.0	20726.0345	(4)	20816.3131	(−74)	20930.5911	*
5.0	20683.3678	(29)	20795.6874	*	20932.4873	(21)
6.0	20636.7069	(−33)	20770.7358	(27)	20929.8759	(−34)
7.0	20586.0354	*	20741.4020	(3)	20922.6110	(−43)
8.0	20531.2357	(0)	20707.5757	(50)	20910.5300	(−7)
9.0	20472.2770	(95)	20669.1190	(71)	20893.4486	(45)
10.0	20409.0058	*	20625.8656	*	20871.0742	*
11.0			20577.7047	(−8)	20843.4395	(−24)
12.0			20524.3713	*	20810.0641	(17)
13.0			20465.7634	(−57)	20770.7361	*
14.0			20401.5642	(−23)	20725.2226	(36)
15.0					20673.1539	(25)
16.0					20614.2061	(−8)
			2−1 band			
0.0					23952.7997	(−36)
1.0			23925.8667	(68)	23964.0614	(−19)
2.0	23872.2126	(66)	23910.1464	(38)	23967.4108	(−86)
3.0	23829.8352	(−70)	23886.5282	(71)	23962.7898	*
4.0	23779.7278	(−82)	23854.9537	*	23950.0464	(24)
5.0	23721.8464	*	23815.3268	(3)	23929.0879	*
6.0	23656.1645	*	23767.5923	(69)	23899.7229	(−32)
7.0	23582.5989	*	23711.5992	(−36)	23861.8187	(−71)
8.0	23501.0840	(14)	23647.2398	(−29)	23815.1762	(−38)
9.0	23411.4850	(70)	23574.3527	(58)	23759.5679	(−26)
10.0	23313.6730	(82)	23492.7252	(−77)	23694.7455	*
11.0	23207.4718	*	23402.1947	(15)		
12.0	23092.7513	(−3)	23302.4935	(2)		
13.0	22969.2609	(79)	23193.3678	(−22)		
14.0	22836.7397	(−55)	23074.5321	(22)		

[a] Figures in parentheses denote observed minus calculated values in units of 10^{-3} cm^{-1}. * The lines marked by asterisk are less accurate and not used in the evaluation of molecular constants.

Table 3. Merged molecular constants (in cm^{-1}) of the $A^1\Pi$ state of the CH$^+$ ion molecule[a].

Constant	$v = 0$	$v = 1$	$v = 2$	$v = 3$
B_v	$\mathbf{11.42351_{56}(18)}$ $11.4227_{29}(4)^{b}$	$\mathbf{10.47749_{30}(21)}$ $10.4776_{26}(4)^{b}$	$\mathbf{9.53019_{26}(30)}$ $9.5305_{22}(6)^{b}$	$\mathbf{8.61132_{72}(51)}$ $8.6107_{93}(6)^{b}$
$D_v \times 10^3$	$\mathbf{1.9800_{40}(19)}$ $1.966_{52}(6)^{b}$	$\mathbf{2.0610_{48}(23)}$ $2.060_{65}(6)^{b}$	$\mathbf{2.1161_{48}(38)}$ $2.118_{94}(8)^{b}$	$\mathbf{2.143_{83}(11)}$ $2.130_{05}(8)^{b}$
$H_v \times 10^8$	$\mathbf{-5.34_{94}(68)}$ $-12_{.01}(3)^{b*}$	$\mathbf{-9.92_{86}(80)}$ $-12_{.01}(3)^{b*}$	$\mathbf{-13.2_{26}(15)}$ $-12_{.01}(3)^{b*}$	$\mathbf{-3.2_{79}(63)}$ $-12_{.01}(3)^{b*}$
$q_v \times 10^2$	$\mathbf{3.9504_{90}(82)}$ $3.92_{21}(2)^{b}$	$\mathbf{3.6123_{31}(99)}$ $3.60_{89}(2)^{b}$	$\mathbf{3.348_{02}(15)}$ $3.30_{11}(6)^{b}$	$\mathbf{2.959_{86}(38)}$ $2.94_{55}(6)^{b}$
$q_{Dv} \times 10^5$	$\mathbf{-2.139_{39}(61)}$ $-1.7_{95}(3)^{b}$	$\mathbf{-2.011_{91}(91)}$ $-1.9_{40}(2)^{b}$	$\mathbf{-2.67_{51}(11)}$ $-2.1_{50}(9)^{b}$	$\mathbf{-1.65_{96}(51)}$ $-1.3_{74}(7)^{b}$

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit; sufficient additional digits are quoted below the line to reproduce the original data with full accuracy. [b] After Carrington and Ramsay [9]; the error limits are 3σ and are right justified to the last digit on the line (* denotes constrained values in their work).

Table 4. Merged molecular constants (in cm^{-1}) of the $X^1\Sigma^+$ state of the CH$^+$ ion molecule[a].

Constant	$v = 0$	$v = 1$	$v = 2$	$v = 3$
B_v	$\mathbf{13.93070_{78}(19)}$ $13.9302_{16}(5)^{b}$	$\mathbf{13.44096_{94}(20)}$ $13.4407_{58}(5)^{b}$	$\mathbf{12.95612_{14}(41)}$ $12.9562_{72}(6)^{b}$	$\mathbf{12.47646_{54}(87)}$ $12.4759_{91}(8)^{b}$
$D_v \times 10^3$	$\mathbf{1.3761_{54}(21)}$ $1.365_{80}(7)^{b}$	$\mathbf{1.3485_{63}(23)}$ $1.342_{67}(8)^{b}$	$\mathbf{1.3224_{09}(79)}$ $1.322_{54}(8)^{b}$	$\mathbf{1.334_{74}(30)}$ $1.308_{32}(12)^{b}$
$H_v \times 10^8$	$\mathbf{11.02_{40}(78)}$ $4.62(4)^{b*}$	$\mathbf{8.87_{37}(86)}$ $4.62(4)^{b*}$	$\mathbf{6.5_{07}(42)}$ $4.62(4)^{b*}$	$\mathbf{31_{.48}(29)}$ $4.62(4)^{b*}$

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit; sufficient additional digits are quoted below the line to reproduce the original data with full accuracy. [b] After Carrington and Ramsay [9]; the error limits are 3σ and are right justified to the last digit on the line (* denotes constrained values in their work).

Table 5. Merged band origins (in cm^{-1}) for the Douglas-Herzberg band system ($A^1\Pi - X^1\Sigma^+$) of the CH$^+$ ion radical[a].

Band	This work	Carrington et al. [9]
0–0	23608.3198(25)	23608.324
0–1	20868.6603(26)	20868.666
2–1	23943.2418(39)	23943.229
1–0	25249.6033(37)	25249.596
1–1	22509.9497(36)	22509.946
1–2	19886.8978(43)	19886.898
1–3	17379.1033(60)	17379.101
3–1	25184.3240(51)	25184.326

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

for the $A^1\Pi$ state, and

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \ldots \tag{2}$$

for the $X^1\Sigma^+$ state, where + and − signs refer to the e or f sublevels respectively, according to Brown et al. [49]. Symbols used are the traditional ones; their physical meaning is well-known and therefore will not be discussed here. The calculation of the final molecular parameters using values of our reanalyzed individual molecular constants for the $v = 0, 2$ levels of the $A^1\Pi$ state and for $v = 0, 1$ levels of the $X^1\Sigma^+$ state and the values given by Carrington et al. [9] for the $v = 1, 3$ levels of the $A^1\Pi$ state and for $v = 2, 3$ levels of the $X^1\Sigma^+$ state have been performed by the least-squares merge fit described by Albritton et al. [50] and by Coxon [51]. The estimated variance of the merging was $\sigma_M^2 = 3.36$ and the number of degrees of freedom was $f_M = 32$. The output final molecular constants as a result of the merge fit are compared with earlier results and highlighted in Tables 3 and 4 for the $A^1\Pi$ and $X^1\Sigma^+$ state, respectively. This merge fit let us obtain improved merged bands origins and vibrational term differences for both states under consideration, whose results are shown in Tables 5 and 6, respectively. On the basis of obtained values of rovibronic constants, and assuming their

Table 6. Merged vibrational term differences (in cm^{-1}) of the $A^1\Pi$ and $X^1\Sigma^+$ states for the CH$^+$ ion molecule^a.

$A^1\Pi$ State		$X^1\Sigma^+$ State	
Difference	Value	Difference	Value
$G(1) - G(0)$	**1641.2863(36)**	$G(1) - G(0)$	**2739.6582(33)** 2739.70(3)^b *2743*^{c} *2740*^{d}
$G(2) - G(0)$	**3074.5807(47)**	$G(2) - G(0)$	**5362.7078(56)**
$G(3) - G(0)$	**4315.6629(58)**	$G(3) - G(0)$	**7870.5024(71)**
		T_{00}	**23608.3193(25)**

^{a} Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. ^{b} After Douglas and Morton [4]. ^{c} Ab initio calculation after Saxon et al. [39]. ^{d} Ab initio calculation after Follmeg et al. [41].

traditionally recognized polynomial dependence on the vibrational quantum number, by means of calculations based on the weighted least-squares method, the improved equilibrium molecular constants for the ground state $X^1\Sigma^+$ and for the excited state $A^1\Pi$ of the CH$^+$ ion radical were calculated and are given in Table 7. These equilibrium constants were then used to determine the RKR turning points, the Franck-Condon factors and r-centroids for the $A{-}X$ system, which are presented in Tables 8 and 9, respectively.

On the basis of very far extrapolation using the Birge-Sponer method [52], the dissociation energy $D_e^{X^1\Sigma^+} = (38470 \pm 3503)$ cm^{-1} i.e. (4.77 ± 0.43) eV of the $X^1\Sigma^+$ ground state have been also estimated. Uncertainty of this parameter has been calculated by means of comparison the extrapolated values of the dissociation energies evaluated with the Birge-Sponer method [52] on the basis of the equilibrium vibrational constants obtained in this work for three ($v'' = 0, 1, 2$) and four ($v'' = 0, 1, 2, 3$) observed levels of the ground state. The ab initio calculations of the dissociation energy for this state give 33842 cm^{-1} (4.196 eV) [13], 4.140 eV [39], and 4.66 eV [42].

4 Discussion

Registration and interpretation of the line with higher J-values than observed so far in the $A{-}X$ system of the CH$^+$ molecule for the 0–0 band [$R(15)$, $R(16)$, $Q(12)$, $Q(13)$, $Q(14)$, $Q(15)$, $Q(16)$, $Q(17)$, $P(10)$, $P(11)$, and $P(12)$] and for the 0–1 band [$R(13)$, $R(14)$, $R(15)$, $R(16)$] as well as for the 2–1 band [$R(8)$, $R(9)$, $R(10)$, $Q(11)$, $Q(12)$, $Q(13)$, $Q(14)$, $P(10)$, $P(11)$, $P(12)$, $P(13)$, $P(14)$] allowed the merged molecular constant H_v to become statistically significant and well determined both for the $v = 0, 1$ and for the $v = 0, 2$ levels of the $A^1\Pi$ and $X^1\Sigma^+$ state, respectively for the first time. All other constants, except centrifugal distortion D_v for $v = 3$ level (unobserved in this work), for both states as well as merged band origins are more accurate than obtained earlier in reference [9] (see Tabs. 3, 4, and 5, respectively). Only in our research (except $\Delta G_{1/2}$ for the $X^1\Sigma^+$) the merged vibrational term differences for both combining states of the $A{-}X$ band system have been calculated and highlighted in Table 6. Equilibrium molecular constants together with their uncertainties for the $A^1\Pi$ upper state of the $A{-}X$ system have also been calculated for the first time. The most important ones are: $\omega'_e = 1864.402(22)$ cm^{-1}, $\omega_e x'_e = 115.832(14)$ cm^{-1}, $\omega_e y'_e = 2.6301(24)$ cm^{-1}, as well as $B'_e = 11.88677(72)$ cm^{-1}, $\alpha'_e = 0.9163(18)$ cm^{-1}, $D'_e = 1.92960(31) \times 10^{-3}$ cm^{-1}. The improved reduced band system origin $T_e = 24118.726(14)$ cm^{-1} for the $A^1\Pi$ state has been computed. The value estimated by Bembenek [53] for the ^{12}CH$^+$ molecule (in research concerning ^{13}CH$^+$ isotopomer) was $T_e = 24122.595(146)$ cm^{-1}. The other constants are presented in Table 7. Equlibrium constants for lower $X^1\Sigma^+$ state, except B_e and $\omega_e x_e$, are more accurate than those given by Carrington et al. [9], especially $B''_e = 14.177461_2(75)$ cm^{-1} (see Tab. 7). Relatively high, positive value of the vibrational anharmonicity constant $\omega_e x'_e = 2.6301(24)$ cm^{-1} for the $A^1\Pi$ state makes fitting of the higher vibrational levels of this state impossible. We assume that this is caused by irregularities which occur in the $A^1\Pi$ upper state of the CH$^+$ molecule, mentioned earlier by Douglas and Morton [4], and also by Carrington and Ramsay [9]. Therefore, it is obvious that there is no foundation to determine value of the dissociation energy of this state on the basis of Birge-Sponer method [52]. However, the $A{-}X$ band origin (calculated within the framework of this project) and the dissociation energy for the ground state (estimated in this paper) as well as taking into account the fine-structure splitting of the lowest dissociation limit [43] (63.4 cm^{-1} [36]), allowed us to estimate the dissociation energy $D_e^{A^1\Pi} = (14415 \pm 3509)$ cm^{-1} i.e. (1.79 ± 0.44) eV for the $A^1\Pi$ state. The ab initio calculations of the dissociation energy for this state give 0.936 eV [39] and 1.53 eV [42].

The equilibrium rotational constants have been used to evaluate the equilibrium bond lengths of $r'_e = 1.235053(37)$ Å and $r''_e = 1.1308843(30)$ Å for the $A^1\Pi$ and $X^1\Sigma^+$ states, respectively. To compare, in Table 8 suitable estimated both experimental by Douglas and Herzberg [2] and Douglas and Morton [4] as well as theoretical values have been placed.

For the first time the addition to the zero-point energy $Y'_{00} = -1.9430$ cm^{-1} for the $A^1\Pi$ state and $Y''_{00} = 1.8953$ cm^{-1} for the $X^1\Sigma^+$ state have been calculated. Due to relatively high value of this Dunham's factor, characteristic for the light molecules, it has a significant influence on the structure of this molecule spectra, and it can't be omitted in correct quantum-mechanical analysis of the

Table 7. Equilibrium molecular constants (in cm^{-1}) for the $A^1\Pi$ and $X^1\Sigma^+$ states of the CH$^+$ ion radical[a].

	Experimental results		Ab initio calculations	
Constant	$A^1\Pi$	$X^1\Sigma^+$	$A^1\Pi$	$X^1\Sigma^+$
T_e	$\mathbf{24118.726_2(14)}$			
	24111^{b*}		*24970*^{d}	
			25690^{f}	
			23366^{g}	
			24934^{k}	
ω_e	$\mathbf{1864.402(22)}$	$\mathbf{2857.560_9(22)}$		
	1865.35^{b}	2857.558^{c}	*1865.4*^{e}	*2864.2*^{e}
			1526^{f}	*2445.6*^{g}
			1619^{g}	*2856*^{h}
			2111.3^{i}	*3111.0*^{i}
			1827^{k}	*2622–3201*^{j**}
$\omega_e x_e$	$\mathbf{115.831_7(14)}$	$\mathbf{59.317_9(15)}$		
	115.85^{b}	59.3192^{c}	*115.85*^{e}	*62.13*^{e}
			81.59^{g}	*4.328*^{g}
			104.39^{i}	*58*^{h}
				38.44^{i}
				53.4–81.2^{j**}
$\omega_e y_e$	$\mathbf{2.6301(24)}$	$\mathbf{0.2253_4(26)}$		
	2.64^{b}	0.2258^{c}		
B_e	$\mathbf{11.88677_4(72)}$	$\mathbf{14.177461_2(75)}$		
	11.898_8^{b}	$14.1766(3)^{c}$	*10.73*^{g}	*13.508*^{g}
				14.146^{h}
				13.116–14.861^{j**}
α_e	$\mathbf{0.9162_9(18)}$	$\mathbf{0.49473_9(12)}$		
	0.9414^{b}	$0.4939(4)^{c}$	*0.916*^{g}	*0.601*^{g}
			1.210^{i}	*0.429*^{h}
				0.621^{i}
				0.433–0.551^{j**}
$\gamma_e \times 10^2$	$\mathbf{-2.29_2(12)}$	$\mathbf{0.2490_4(36)}$		
	-0.19^{b}	$0.229(9)^{c}$		
$\varepsilon_e \times 10^3$	$\mathbf{4.95_2(20)}$			
$D_e \times 10^3$	$\mathbf{1.92960_6(31)}$	$\mathbf{1.3891_4(29)}$		
	1.9^{b}	$1.373(3)^{c}$		*1.25–1.44*^{j**}
$\beta_e \times 10^4$	$\mathbf{1.0733_1(50)}$	$\mathbf{-0.266(25)}$		
		$-0.193(14)^{c}$		
$\delta_e \times 10^5$	$\mathbf{-1.312_3(16)}$			
$H_e \times 10^7$		$\mathbf{1.203_6(79)}$		
$\alpha_{H_e} \times 10^8$		$\mathbf{2.07_9(71)}$		
$q_e \times 10^2$	$\mathbf{4.101_8(23)}$			
$\alpha_{q_e} \times 10^3$	$\mathbf{-3.13_5(16)}$			
$q_{D_e} \times 10^5$	$\mathbf{-2.20(14)}$			

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit; sufficient additional digits are quoted below the line to reproduce the original data with full accuracy. [b] After Huber and Herzberg [35] (* Douglas and Morton [4]). [c] After Carrington and Ramsay [9]; the error limits in brackets are 1σ. [d] Ab initio calculation after Green et al. [37]. [e] Ab initio calculation after Smith et al. [38]. [f] Ab initio calculation after Saxon et al. [39]. [g] Ab initio calculation after Sun et al. [40]. [h] Ab initio calculation after Follmeg et al. [41]. [i] Ab initio calculation after Kanzler et al. [42]. [j] Ab initio calculation after Sinnokrot et al. [44] (** depending on which theoretical method was used). [k] Ab initio calculation after Sattelmeyer et al. [45].

Table 8. Vibrational levels and RKR turning points for the $A^1\Pi$ and $X^1\Sigma^+$ states for the CH$^+$ ion molecule^a.

		$A^1\Pi$	$X^1\Sigma^+$
	Y_{00}	−1.9430	1.8953
	r_e	1.235053(37)	1.1308843 (30)
		1.2345^b	1.1310^b
		1.2345^c	1.1309^c
		1.234^{d*}	*1.130*^{d*}
		1.2345^e	*1.1309*^{e}
		1.260^{f*}	*1.129*^{f*}
		1.312^{g*}	*1.140*^{g*}
		1.205^{i*}	*1.132*^{h}
		1.2633^k	*1.125*^{i*}
			1.1046-1.1758^{j**}
$v = 0$	$G(v) + Y_{00}$	901.6288	1415.8744
	r_{min}	1.11656	1.02946
	r_{max}	1.40260	1.25689
$v = 1$	$G(v) + Y_{00}$	2542.9153	4155.5319
	r_{min}	1.05174	0.96798
	r_{max}	1.57525	1.36877
$v = 2$	$G(v) + Y_{00}$	3976.2092	6778.5816
	r_{min}	1.01631	0.93100
	r_{max}	1.73211	1.45791
$v = 3$	$G(v) + Y_{00}$	5217.2912	9286.3756
	r_{min}	0.99224	0.90386
	r_{max}	1.89201	1.53912
$v = 4^m$	$G(v) + Y_{00}$	6281.9420	11680.2660
	r_{min}	0.97382	0.88236
	r_{max}	2.06140	1.61674

^{a} $G(v)$ values are in cm^{-1}; all r-values are in Å. ^{b} By Douglas and Herzberg [2]. ^{c} By Douglas and Morton [4]. ^{d} Ab initio calculation after Green et al. [37] (* obtained from the *au* unit). ^{e} Ab initio calculation after Smith et al. [38]. ^{f} Ab initio calculation after Saxon et al. [39] (* obtained from the *au* unit). ^{g} Ab initio calculation after Sun et al. [40]. ^{h} Ab initio calculation after Follmeg et al. [41]. ^{i} Ab initio calculation after Kanzler et al. [42]. ^{j} Ab initio calculation after Sinnokrot et al. [44] (** depending on which theoretical method was used). ^{k} Ab initio calculation after Sattelmeyer et al. [45]. ^{m} Determined for the $A^1\Pi(v = 4)$ and $X^1\Sigma^+(v = 4)$ levels unobserved in the present research.

Table 9. Franck-Condon factors, r-centroids and relative intensities for the Douglas-Herzberg band system ($A^1\Pi - X^1\Sigma^+$) of the CH$^+$ ion radical^a.

$v'' \setminus v'$	0	1	2	3	4^b
0	0.6343	0.2580	7.6941×10^{-2}	2.1727×10^{-2}	6.3356×10^{-3}
	1.1999	1.1021	1.0062	0.9108	0.8146
	10.0000	5.5940	1.7612	0.4922	0.1367
1	0.2788	0.1246	0.2589	0.1727	8.6618×10^{-2}
	1.3639	1.2398	1.1710	1.0983	1.0289
	6.0299	2.8593	4.4758	2.8698	1.3871
2	7.1995×10^{-2}	0.3256	7.1374×10^{-3}	6.9608×10^{-2}	0.1353
	1.4836	1.4087	1.4407	1.2227	1.1783
	2.0493	10.0000	0.1678	1.2272	1.7883
3	1.2906×10^{-2}	0.2033	0.1343	0.1187	6.5331×10^{-3}
	1.6024	1.5230	1.4591	1.4108	1.4550
	0.4674	8.0514	4.1252	2.7673	0.1155
4^b	1.8218×10^{-3}	6.9164×10^{-2}	0.2575	2.0091×10^{-4}	8.9111×10^{-2}
	1.7046	1.6368	1.5678	1.5855	1.4672
	8.1659×10^{-2}	3.4273	10.0000	5.9821×10^{-3}	2.0304

^{a} The values represented in sequence one under the other stand for the Franck-Condon factor, r-centroids (in Å), and relative intensities (in quantum/s scaled to ten) for each band. ^{b} Determined for the $A^1\Pi(v = 4)$ and $X^1\Sigma^+(v = 4)$ levels unobserved in the present research.

$A{-}X$ system. So real zero-point energy of the $A^1\Pi$ and $X^1\Sigma^+$ states amounts to $G'(0) + Y'_{00} = 901.6288$ cm^{-1} and $G''(0) + Y''_{00} = 1415.8744$ cm^{-1}, respectively. Remains values of the vibrational terms ($v = 1, 2, 3$, and 4) taking into consideration the additions to the zero-point energy are highlighted in Table 8.

In our research we have also calculated the values of the RKR turning points up to the $v = 4$ vibrational levels for the $A^1\Pi$ and $X^1\Sigma^+$ states as well as Franck-Condon factors, r-centroids and relative intensities for the $A{-}X$ system. The results are given in Tables 8 and 9, respectively.

5 Conclusions

The precision recording of the 0–0, 0–1, and 2–1 bands,under high resolution, using the Th standard lines as a calibration spectrum, and reinvestigating of the $A^1\Pi - X^1\Sigma^+$ electronic transition, being an important source of information about both of these states of the CH$^+$ molecule and its isotopic species, ameliorates the knowledge of the $A^1\Pi$ state of the ^{12}CH$^+$ ion radical. Due to the high resolution spectra of the longer bands than have been observed before,the high precision of the calculated wavenumbers of lines, and the special method of spectrum reduction, well determined molecular constants were derived. Subsequently, this made it possible to calculate improved equilibrium molecular constants for the $X^1\Sigma^+$ state, and for the first time with their standard deviation for the $A^1\Pi$ state in the CH$^+$ molecule. We have also obtained full quantum-mechanics characteristic for the A–X bands system of the CH$^+$ molecule, namely RKR potential curves and r-centroids for both, the $A^1\Pi$ and $X^1\Sigma^+$ states as well as the Franck-Condon factors for the system under consideration. Therefore, we conclude that the presented results widen and improve the spectroscopic and quantum-mechanical information about the spectrum and energetic structure of the CH$^+$ ion molecule.

References

1. E.A. Douglas, G. Herzberg, Astrophys. J. **94**, 381 (1941)
2. E.A. Douglas, G. Herzberg, Canad. J. Res. A **20**, 71 (1942)
3. W.S. Adams, Astrophys. J. **93**, 11 (1941)
4. E.A. Douglas, J.R. Morton, Astrophys. J. **131**, 1 (1960)
5. M. Carré, M. Doufnay, C. R. Acad. Sci. Paris B **266**, 1367 (1968)
6. M. Carré, Physica **41**, 63 (1969)
7. I. Botterud, A. Lofthus, L. Veseth, Phys. Scripta **8**, 218 (1973)
8. I. Kusunoki, Ch. Ottinger, J. Chem. Phys. **73**, 2069 (1980)
9. A. Carrington, D.A. Ramsay, Phys. Scripta **25**, 272 (1982)
10. D. Macau-Hercol, F. Remy, I. Dubois, H. Bredohl, E. Somé, J. Breton, *Laboratory and astronomical High resolution spectra* (Brussels, Belgium, August 29–September 2, 1994)
11. D. Bates, L. Spitzer Jr, Astrophys. J. **113**, 441 (1951)
12. P.M. Solomon, W. Klemperer, Astrophys. J. **178**, 389 (1972)
13. Wm. H. Smith, H.S. Liszt, B.L. Lutz, Astrophys. J. **183**, 69 (1973)
14. J. Brzozowski, N. Elander, P. Erman, M. Lyra, Astrophys. J. **193**, 741 (1974)
15. A. Dalgarno, *Atomic Processes and Applications*, edited by P.G. Burke, B.L. Moiseiwitsch (North-Holland, New York, 1976)
16. K. Kieby, W.G. Roberge, R.P. Saxon, B. Liu, Astrophys. J. **239**, 855 (1980)
17. T.P. Snow, Astrophys. J. Lett. **402**, 73 (1993)
18. M. Elitzur, W.D. Watson, ApJ **222**, L141 (1978)
19. L. Spitzer, *Physical Processes in the Interstellar Medium* (J. Willey, New York 1978)
20. M. Elitzur, W.D. Watson, ApJ **236**, 172 (1980)
21. M.M. Graff, J.T. Moseley, E. Roueff, ApJ **269**, 796 (1983)
22. H. Helm, P.C. Cosby, M.M. Graff, J.T. Moseley, Phys. Rev. A **25**, 304 (1982)
23. P. Swings, Astrophys. J. **95**, 270 (1942)
24. J.L. Greenstein, ApJ **136**, 688 (1962)
25. D.M. Meyer, K.C. Roth, ApJ **349**, 91 (1990)
26. P.J. Sarre, Nature **351**, 356 (1991)
27. S.P. Balm, M. Jura, Astron. Astrophys. **261**, L25 (1992)
28. D.I. Hall, J.R. Miles, P.J. Sarre, S.J. Fossey, Nature **358**, 629 (1992)
29. C. Waelkens, H. Van Winckel, N.R. Trams, L.B.F.M. Waters, Astron. Astrophys. **256**, L15 (1992)
30. M. Centurión, C. Cássola, G. Vladilo, Astron. Astrophys. **302**, 243 (1995)
31. H. van Winckel, C. Waelkens, L.B.F.M. Waters, Astron. Astrophys. **293**, L25 (1995)
32. E.J. Bakker, E.F. Van Dishoeck, L.B.F.M. Waters, T. Schoenmaker, Astron. Astrophys. **323**, 469 (1997)
33. J. Cernicharo, X.-W. Liu, E. Gonzáles-Alfonso, P. Cox, M.J. Barlow, T. Lim, B.M. Swinyard, ApJ **483**, L65 (1997)
34. L.M. Hobbs, J.A. Thorburn, T. Oka, J. Barentine, T.P. Snow, D.G. York, ApJ **615**, 947 (2004)
35. K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979)
36. C.E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, National Standards Reference Data Series-34 (U.S. GPO, Washington, DC, 1970)
37. S. Green, P.S. Bagus, B. Liu, A.D. McLean, M. Yoshimine, Phys. Rev. A **5**, 1614 (1972)
38. Wm.H. Smith, H.S. Liszt, B.L. Lutz, Astrophys. J. **183**, 69 (1973)
39. R.P. Saxon, K. Kirby, B. Liu, J. Chem. Phys. **73**, 1873 (1980)
40. H. Sun, K.F. Freed, Chem. Phys. Lett. **78**, 531 (1981)
41. B. Follmeg, P. Rosmus, H.J. Werner, Chem. Phys. Lett. **136**, 562 (1987)
42. A.W. Kanzler, H. Sun, K.F. Freed, Int. J. Quant. Chem. **39**, 269 (1991)
43. U. Hechtfischer, Z. Amitay, P. Forck, M. Lange, J. Linkemann, M. Schmitt, U. Schramm, D. Schwalm, R. Wester, D. Zajfman, A. Wolf, Phys. Rev. Lett. **80**, 2809 (1998)
44. M.O. Sinnokrot, C.D. Sherrill, J. Chem. Phys. **115**, 2439 (2001)
45. K.W. Sattelmeyer, J.F. Stanton, J. Olsen, J. Gauss, Chem. Phys. Lett. **347**, 499 (2001)
46. B.A. Palmer, R. Engleman Jr, *Atlas of the Thorium Spectrum Los Alamos National Laboratory* (Los Alamos NM, 1983), unpublished
47. G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950)
48. J.M. Brown, E.A. Colbourn, J.K.G. Watson, F.D. Wayne, J. Mol. Spectrosc. **74**, 294 (1979)
49. J.M. Brown, J.T. Hougen, K.P. Huber, J.W.C. Johns, I. Kopp, H. Lefebvre-Brion, A.J. Merer, D.A. Ramsay, J. Rostas, R.N. Zare, J. Mol. Spectrosc. **55**, 500 (1975)
50. D.L. Albritton, A.L. Schmeltekopf, R.N. Zare, J. Mol. Spectrosc. **67**, 132 (1977)
51. J.A. Coxon, J. Mol. Spectrosc. **72**, 252 (1978)
52. R.T. Birge, H. Sponer, Phys. Rev. **28**, 259 (1926)
53. Z. Bembenek, J. Mol. Spectrosc. **181**, 136 (1997)