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Note

Revised molecular constants and term values for the $X^2\Pi$ state of CH

Reginald Colin [a], Peter F. Bernath [b,*]

[a] Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), 50, av. F.D. Roosevelt, 1050 Brussels, Belgium
[b] Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

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ABSTRACT

An improved set of molecular constants and term values are given for the $X^2\Pi$ (v = 0–5) state of the CH radical. They are derived from a fit of previously published data and additional lines taken from infrared solar spectra recorded on orbit and from new laboratory IR emission data.

1. Introduction

Satellite Fourier transform spectrometers (FTSs) which use the solar absorption ("solar occultation") technique to measure the composition of the Earth's atmosphere record spectra twice per orbit during sunrise and sunset. These atmospheric spectra are divided by "high sun" reference spectra in order to compute the atmospheric transmission. The numerous high sun reference spectra can be added together to produce a very high quality pure solar spectrum free from the absorption features of atmospheric species inevitably present in ground-based spectra. The solar spectra are also a source of spectroscopic information on small molecules present in the Sun's photosphere.

The first high resolution infrared solar spectra acquired from orbit were recorded on the Space Shuttle by the ATMOS 1985 experiment [1] on Spacelab and led to the observation of more extensive spectra of molecules such as OH [2] and CH [3] than could be obtained at that time in the laboratory. A second solar atlas was prepared using the high sun spectra recorded during the ATMOS 1994 flight for the Atlas 3 mission [4]. More recently the SCISAT satellite which has the ACE (Atmospheric Chemical Experiment) [5] FTS on board has yielded a new solar spectrum [6] from which additional information on the OH [7] and NH [8] free radicals were extracted. In this paper we will examine the ACE spectrum and some earlier laboratory data [9] in the IR region in order to improve the spectroscopic knowledge of the ground $X^2\Pi$ state of CH.

The CH radical is important because of the role it plays in many fields such as combustion, interstellar and stellar chemistry, and has been extensively studied in the past by a wide variety of spectroscopic techniques. Concerning the IR spectrum, the most important contributions are those of Mélen et al. [3], Bernath [9] and Bernath et al. [10]. In the previous work [10], four rotation-vibration bands (1-0, 2-1, 3-2, and 4-3) have been observed in the 3050–2150 cm^{-1} region and yield molecular constants for the five first levels of the $X^2\Pi$ state.

2. Data and analysis

The solar absorption spectrum used in this work [6] is the result of the co-addition of 224 782 individual spectra taken by the ACE-FTS on board the SCISAT satellite launched in August 2003. The resolution of this spectrum is 0.02 cm^{-1} and extends from 700 to 4430 cm^{-1}. The laboratory spectrum of CH was produced in a microwave discharge of helium, methane and white phosphorous as described in more detail by Bernath [9].

The analysis used the PGopher program [11] and was conducted in the following way: Using the molecular constants of the v = 0–4 levels of the $X^2\Pi$ state given in Bernath et al. [10], the wavenumbers for the lines of the P_{1ee}, P_{1ff}, P_{2ee}, P_{2ff}, Q_{1ef}, Q_{1fe}, Q_{2ef}, Q_{1fe}, R_{1ee}, R_{1ff}, R_{2ee}, and R_{2ff} branches of the 1-0, 2-1, 3-2, and 4-3 bands were calculated at a temperature of 3000 K for J values up to 49.5. Extrapolated values for the constants of the v = 5 level were used to calculate the corresponding wavenumbers for the 5-4 band. This synthetic spectrum, which extended from 1400 to 3050 cm^{-1}, was compared to the ACE solar spectrum and the laboratory spectrum. The 558 CH lines identified by Mélen et al. [3], which include those measured earlier by Bernath [9,10], were easily identified. In addition 171 previously unidentified lines were found for the known bands; they are mostly lines of the weaker P and Q

* Corresponding author. Fax: +44 (0) 1904 432516.
E-mail address: pfb500@york.ac.uk (P.F. Bernath).

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Table 1
Rotational lines of the 5-4 band of CH $X^2\Pi$ (cm^{-1}).

J	R_{1ee}	R_{1ff}	R_{2ee}	R_{2ff}
4.5			2357.9740	
5.5	2357.8560	2357.5280	2374.1329	2374.5040
6.5	2374.1329	2373.7650	2389.0290	2389.4490
7.5	2389.1430	2388.7680	2402.6930	2403.1040
8.5	2402.8640	2402.4230	2414.9770	2415.4650
9.5	2415.2690	2414.7780	2425.9530	2426.4400
10.5	2560.6850	2425.7820	2435.5570	2436.0510
11.5	2435.8930	2435.4160		

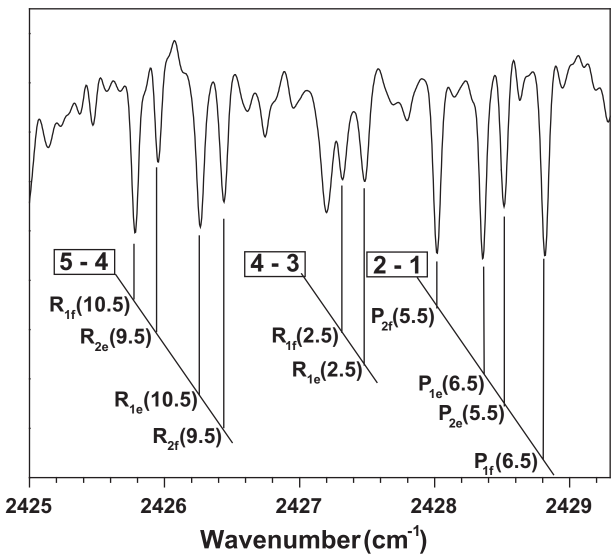

Fig. 1. A portion of the solar infrared spectrum recorded by ACE-FTS [6] showing lines of the 2-1, 4-3, and 5-4 bands of CH.

branches, but a few R lines with higher J values than known earlier were identified. The latter are mainly present in the laboratory spectrum [9] which appears therefore to be at a slightly higher effective rotational temperature than the solar spectrum. In the 2350–2440 cm^{-1} region of the solar ACE spectrum, 27 R lines belonging to a new 5-4 band were also found and are presented in Table 1. A small portion of the solar spectrum showing four lines of the 5-4 band is shown in Fig. 1. All the new line measurements are available on Science-Direct (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jma_hp.htm).

The lines of the five observed bands were fitted simultaneously to the $^2\Pi$ Hamiltonian of Brown et al. [12] using the PGopher program [8]. As no satellite lines, which would provide a link between the two spin components F_1 and F_2 of the $^2\Pi$ state were observed, it was necessary to fix the spin–orbit constant A_v for at least one vibrational level. Previous studies of the ground state of CH using microwave and laser magnetic resonance techniques provide precise values for the A constants [13] of $v = 0$ and $v = 1$ which were used in the present fit. For the $v = 5$ level several higher order constants, extrapolated from the five lower levels were also fixed.

3. Results and discussion

In all, 768 lines were fitted yielding 68 constants for the 6 observed vibrational levels of the $X^2\Pi$ state. They are presented in Table 2. Compared to the constants presented in earlier analyses of the infrared bands [3,10] the obtained constants present some differences which are larger than the experimental uncertainties, mainly for the higher order constants. In addition, we found that the resulting constants for all the levels are very sensitive to small changes of the input data in any one given level. We believe that this is due to the particular intensity distribution within the bands: The R branches are much more intense than the P or Q branches. For example, in the earlier work of Mélen et al. [3] the R branches of the 1-0 band reaches $N = 34$ whereas the P branches end at $N = 8$ and only two values of N are recorded for the Q branches. The majority of the levels of the four independent stacks (F_{1e}, F_{2e}, F_{1f} and F_{2f}) arising from $v = 0$ to $v = 5$ are therefore linked to each other by only one transition. In the present work the newly identified lines are mainly P and Q lines, which add some "stability" to the fitting process.

The principal equilibrium constants of the $X^2\Pi$ state were calculated to be (in cm^{-1}): $\omega_e = 2860.88(5)$, $\omega_e x_e = 64.55(5)$, $\omega_e y_e = 0.40(1)$, $\omega_e z_e = -0.019(1)$, $B_e = 14.45004(4)$, $D_e = 0.0014759(4)$, $A_e = 28.02(3)$, $\gamma_e = -0.0294(7)$, $p_e = 0.0352(3)$, and $q_e = 0.03935(3)$.

Term values for the $v = 0$ to 5 levels of the $X^2\Pi$ state of CH are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm). A list giving all the spectroscopic measurements used in this work along with the observed-calculated values obtained is also available on this site.

Table 2
Molecular constants for the $X^2\Pi$ state of CH (cm^{-1}).

v	0	1	2	3	4	5
T	0	2732.978138(940)	5339.90364(145)	7822.21844(182)	10 180.99960(217)	12 416.7867(102)
A	28.14675[a]	28.33833[a]	28.616(51)	28.765(48)	28.968(45)	29.17[b]
B	14.1923933(611)	13.66178964(525)	13.1358097(500)	12.6134415(495)	12.0929931(541)	11.573004(227)
$D \times 10^3$	1.461129(367)	1.437420(307)	1.415538(307)	1.396120(320)	1.379116(350)	1.36927(110)
$H \times 10^7$	1.10648(746)	1.06257(849)	1.02124(972)	0.9799(101)	0.9173(101)	0.88[b]
$L \times 10^{12}$	−3.42(177)	−4.34(162)	−5.69(147)	−7.55(129)	−9.27(111)	−11.6[b]
$\gamma \times 10^2$	−2.8538(860)	−2.6549(852)	−2.4629(832)	−2.3236(812)	−2.1388(800)	−1.933(70)
$\gamma_D \times 10^5$	1.785(239)	1.645(222)	1.538(206)	1.503(190)	1.331(175)	1.29[b]
$q \times 10^2$	3.86600(314)	3.72853(294)	3.59195(323)	3.45416(361)	3.31791(425)	3.17762(320)
$q_D \times 10^5$	−1.5901(202)	−1.5506(221)	−1.5094(239)	−1.4610(244)	−1.4099(245)	−1.35[b]
$q_H \times 10^9$	4.062(574)	3.798(526)	3.560(478)	3.304(424)	2.904(371)	2.52[b]
$p \times 10^2$	3.4645(360)	3.2607(344)	3.1191(364)	2.9673(415)	2.8360(520)	2.6739(620)
$p_D \times 10^5$	−1.011(369)	−0.849(342)	−0.735(316)	−0.632(293)	−0.604(272)	−0.55[b]

[a] Taken from Ref. [13].
[b] Kept fixed in the fit.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (http://www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm) Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2010.06.013.

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