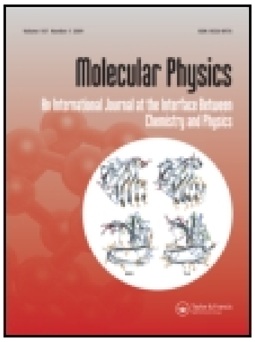

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A new electronic transition of CH^+ and CD^+

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The electronic transition $C^1\Sigma^+$–$A^1\Pi$ has been observed for the first time for CH^+ and CD^+. The n–4 and $(n+1)$–5 bands have been rotationally analysed for CH^+ and CD^+.

1. Introduction

Three electronic transitions are known for the CH^+ ion. The $A^1\Pi$–$X^1\Sigma^+$ was analysed for the first time by Douglas and Herzberg [1] as early as 1942, extended later by Douglas and Morton [2] and extended again in 1982 by Carrington and Ramsay [3]. The $B^1\Delta$–$A^1\Pi$ and $b^3\Sigma^-$–$a^3\Pi$ transitions of CH^+ were observed by Carré and Dufay [4] and analysed by Carré [5].

The $A^1\Pi$–$X^1\Sigma^+$ transition has been observed for CD^+ by Cisak and Rytel [6] and analysed by Antic-Jovanic and Bojovic [7] in 1979. More recently, electronic transitions have been reported in the 350 nm and 540 nm spectral regions.

Predissociated levels of CH^+ have been observed by Cosby *et al.* [8] near 350 nm. They attributed these levels to quasi-bound levels of the $A^1\Pi$ and $A^3\Pi$ states. Later on, Sarre *et al.* [9, 10] published two high-resolution laser photofragment spectroscopy studies for CH^+ between 535 nm and 620 nm, and Sarre and Whitham [11] discussed the nature of the observed transitions. Lines in the 540 nm region would be due to transitions from $d^3\Pi$ to $a^3\Pi$ or $c^3\Sigma^+$ states near the $C^+(^2P)+H(^2S)$ dissociation limit, while the lines in the 350 nm region are due to transitions from $C^1\Sigma^+$ to $A^1\Pi$ or $X^1\Sigma$ states near the $C^+(^2P)+H(^2S)$ dissociation limit.

Figure 1 shows the potential curves and the observed transitions. The curves of figure 1 have been drawn from the studies of Bruna and Peyerimhoff [12] and Sarre and Whitham [11].

Recently an interesting paper devoted to photoionization spectroscopy of CH^+ has been published by Hechtfischer *et al.* [13] giving new results and a complete view of the present knowledge of CH^+.

In the present paper, we report the observation of two unknown bands in the near-ultraviolet region which have been analysed as transitions from two successive vibrational levels of the $C^1\Sigma^+$ state to the $v''=4$ and $v''=5$ vibrational levels of the $A^1\Pi$ state for CH^+ and CD^+.

2. Experimental details

The new bands of CH^+ and CD^+ have been observed by emission spectroscopy. The light source was a quartz tube in which a gas flow composed of He

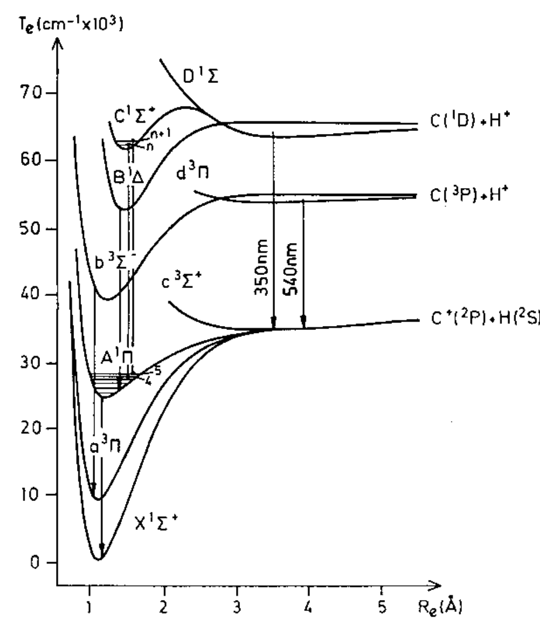

Figure 1. Potential curves for CH^+.

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(5×10^{-1} mbar) and traces CH_4 or CD_4 (5×10^{-3} mbar) was excited by a 200 W microwave generator (Microtron). The spectra were recorded on a 103 aO Kodak plate in the second order of a 21 feet Eagle spectrograph equipped with a 1200 lines mm^{-1} grating giving, in the second order, an inverse dispersion of 0.054 nm mm^{-1}. Exposure times as long as 30 hours were needed with a slit width of 20 µm. The new bands appear clearly above the hydrogen continuum as can be seen on figure 2. The plates have been measured on a Grant photoelectric comparator against Fe and Ne lines provided by a hollow cathode discharge with a precision better than 0.1 cm^{-1} for unblended lines.

3. Rotational analysis

Two red degraded bands have been observed at 35 558 and 35 000 cm^{-1} for CH^+ and 34 811 and 34 285 cm^{-1} for CD^+. Figure 2 shows the rotational structure of the 34 811 cm^{-1} band of CD^+. Aside from the presence of a clear R head and some regular segments of branches, the rotational analysis was not obvious at all. From the spacing of successive lines within branches and from the second differences (ΔB), it appears that CH^+ and CD^+ are the best candidates for the emitter.

A great deal of effort was necessary to obtain an acceptable solution, because, as can be seen in figure 2, many extra lines do appear. No common combination differences have been found with any known vibrational state of CH^+ [2, 3] or CD^+ [7]. The only possible agreement was found with the $\upsilon=4$ vibrational level of the $A^1\Pi$ state. The (4–1) band of the $A^1\Pi$–$X^1\Sigma^+$ transition of CH^+ was analysed by Douglas and Morton [2], but very partially; only thirteen lines have been identified because of a strong overlapping by the $\Delta\upsilon=0$ sequence of the $C^1\Pi_g$–$A^1\Pi_u$ of C_2. Nevertheless, the B value given by Douglas and Morton [2] agrees reasonably well with our value obtained for the 35 558 cm^{-1}

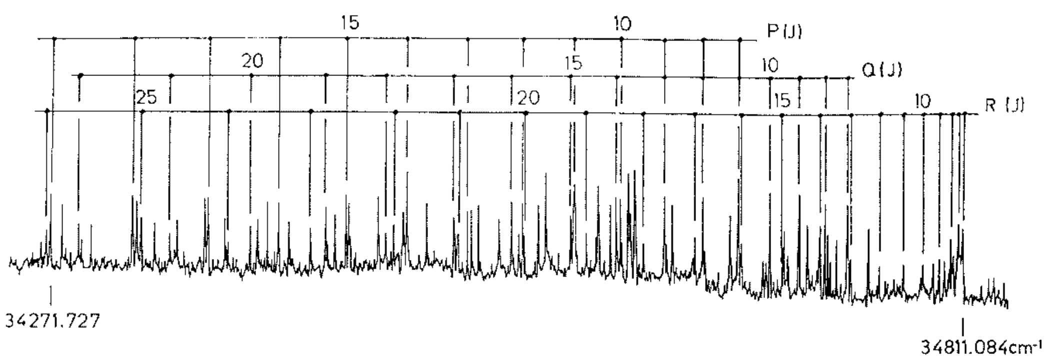

Figure 2. Rotational analysis of the n–4 band of CD^+.

Table 1. Vacuum wavenumbers (in cm^{-1}) and rotational assignments for n–4 and $(n+1)$–5 bands of CH^+.

	n–4				$(n+1)$–5		
J	R(J)	Q(J)	P(J)	J	R(J)	Q(J)	P(J)
5	35529.563	—	—	1	34997.387	—	—
6	35544.459	35449.167	—	2	35000.561	34968.506	—
7	35544.472	35442.187	35349.165	3	35000.561	34959.667	34927.985
8	35559.855	35433.742	35324.754	4	34997.387	34946.313	34904.641
9	35560.437	35427.787	35303.128	5	34989.822	34928.738	34877.824
10	35557.138	35407.987	35278.165	6	34979.011	34907.787	34845.842
11	35549.897	35398.977	35247.350	7	34964.952	34883.759	34813.251
12	35538.735	35366.395	35211.087	8	34950.417	34856.803	—
13	35517.245	35337.470	35168.649	9	34930.943	34827.184	—
14	35490.239	35303.128	35121.535	10	34909.728	34794.108	—
15	35457.288	35255.204	35068.936	11	—	34759.083	—
16	35419.009	35214.276	35018.945				
17	35375.347	35157.758	34946.313				
18	—	35092.240	34876.721				
19	—	—	348001.257				

Table 2. Vacuum wavenumbers (in cm^{-1}) and rotational assignments for n–4 and $(n+1)$–5 and bands of CD^+.

	n–4				$(n+1)$–5		
J	R(J)	Q(J)	P(J)	J	R(J)	Q(J)	P(J)
5	34811.084	—	—	2	34282.817	—	—
6	34811.084	—	—	3	34284.934	—	—
7	34808.923	34745.770	34688.550	4	34282.817	34249.252	—
8	34804.823	34734.255	34669.849	5	34280.421	34239.951	34209.170
9	34798.589	34720.320	34649.615	6	34277.074	34228.431	34189.540
10	34790.222	34704.511	34626.383	7	34270.470	34215.510	34170.582
11	34779.622	34686.388	34601.456	8	34262.274	34200.938	34148.993
12	34766.618	34665.449	34573.798	9	34251.730	34184.659	34124.564
13	34751.366	34642.811	34545.438	10	34239.951	34166.599	34101.169
14	34733.701	34619.989	34513.380	11	34224.990	34146.592	34076.289
15	34713.434	34591.968	34479.085	12	34209.170	34124.564	—
16	34690.709	34561.835	34441.832	13	34191.365	34100.425	—
17	34665.459	34530.344	34402.117	14	34170.582	34074.157	—
18	34637.538	34496.591	34361.042	15	34147.610	34045.655	—
19	34606.997	34458.865	34317.645	16	—	34014.930	—
20	34573.798	34418.550	34270.470	17	34016.547	—	—
21	34537.876	34377.194	34220.812				
22	34499.109	—	—				
23	34457.778	—	—				
24	34413.166	—	—				
25	34365.872	—	—				
26	34315.549	—	—				
27	34262.274	—	—				
28	34200.938	—	—				

band. Therefore, the four bands we have observed would correspond to the n–4 and (n + 1)–5 transitions of the $C^1\Sigma^+$–$A^1\Pi$ transition of CH^+ and CD^+.

The rotational analyses are given in table 1 for the two analysed bands of CH^+ (35 558 and 35 000 cm^{-1}) and in table 2 for the two analysed bands of CD^+ (34 811 and 34 285 cm^{-1}).

The lines have been submitted to a least squares calculation using for the two states the following formulas:

$$C^1\Sigma^+\colon F_\upsilon(J) = B_\upsilon J(J+1) - D_\upsilon J^2(J+1)^2, \quad (1)$$

$$A^1\Pi^+\colon F_\upsilon(J) = B_\upsilon[J(J+1)-1] - D_\upsilon[J(J+1)-1]^2 \pm \frac{1}{2} q_\upsilon J(J+1), \quad (2)$$

where the + and − signs refer to the e and f levels respectively [14]. The results of such a fitting are rather poor ($\sigma = 1.6$, 0.52, 1.77 and 0.73 for n–4, $(n+1)$–5 of CH^+ and n–4, $(n+1)$–5 of CD^+ respectively) because, very likely, of perturbations of the $A^1\Pi$ state by the $a^3\Pi$ state, as already mentioned by Douglas and Morton [2] and by Carrington and Ramsay [3]. It must be noted that the high vibrational levels of the ground $X^1\Sigma^+$ state could also perturb some levels of the $A^1\Pi$ state.

Table 3. Rotational B values (in cm^{-1}) for the n–4 and $(n+1)$–5 bands of CH^+ and CD^+.

	$B_\upsilon(CH^+)$		$B_\upsilon(CD^+)$	
$A^1\Pi$				
$\upsilon=4$	7.74(2)	7.746[a]	4.70(4)	
$\upsilon=5$	6.84(4)		4.23(4)	
$C^1\Sigma^+$				
$\upsilon=n$	6.5(3)		3.8(1)	
		$\alpha=1.37$		$\alpha=0.50$
$\upsilon=n+1$	5.13(7)		3.30(5)	

[a]Reference [2].

The rotational constants B_v given in table 3 have been obtained from Δ_2F(J) combination differences. In the present case, the Δ_2F(J) results are more credible. Among others the combination defect [R(J)–Q($J+1$) − [Q(J)–P($J+1$)] is clearly observed when Δ_1F are compared and the Λ doubling is shown to be comparable with those observed for the other states of the $A^1\Pi$ state [2, 3], while the q_υ is not defined in the whole fitting of all the lines (R, Q, P).

A last argument in favour of the proposed identification of the new band is the fact that the B_υ values obtained are perfectly represented by the expression

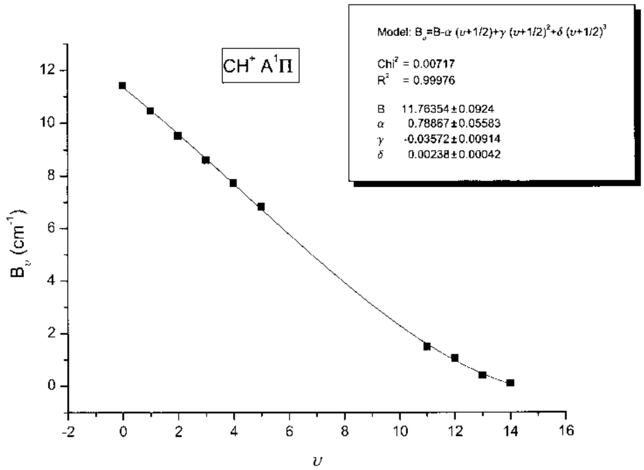

Figure 3. Variation of B_{υ} as a function of υ for CH^+.

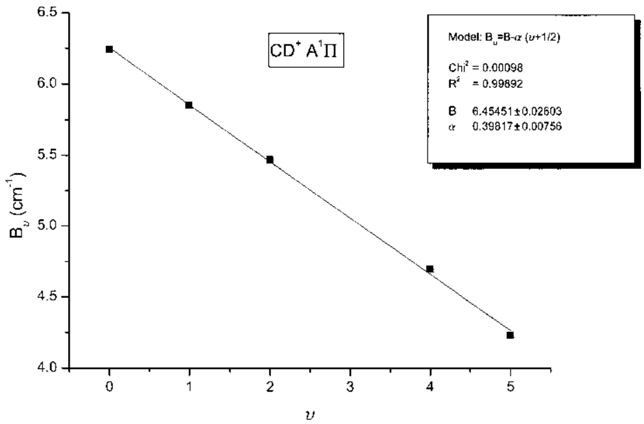

Figure 4. Variation of B_{υ} as a function of υ for CD^+.

Table 4. Equilibrium constants (cm^{-1}) of the $A^1\Pi$ state.

CH^+	Ref. [2][a]	CD^+	Ref. [7][b]
$B_e = 11.763 \pm 0.092$	11.898	$B_e = 6.4545 \pm 0.026$	6.428
$\alpha_e = 0.789 \pm 0.056$	0.9114	$\alpha_e = 0.3982 \pm 0.0076$	0.388
$\gamma = 0.0357 \pm 0.0091$	-0.0019		
$\delta = 0.00238 \pm 0.00042$			

[a] These constants do not fit the vibrational levels higher than $\upsilon = 2$.
[b] Limited to $\upsilon = 0$, 1 and 2.

$$B_{\upsilon} = B_e - \alpha_e\left(\upsilon + \frac{1}{2}\right) + \gamma\left(\upsilon + \frac{1}{2}\right)^2 + \delta\left(\upsilon + \frac{1}{2}\right)^3, \quad (3)$$

as can be seen in figure 3 for CH^+. The results and the uncertainties are given in this figure. For CD^+, the coefficients γ and δ have been kept equal to zero and the fitting is quite acceptable as can be seen in figure 4. The equilibrium constants obtained are summarized in table 4 and compared with the known constants. The value of the rotation–vibration constant α_e for the $C^1\Sigma^+$ electronic state is greater than for the other electronic states, meaning that the ω value must be smaller. Indeed, the T_e values of the n and $n+1$ vibrational levels of $C^1\Sigma^+$, calculated from the vibrational constants of the $A^1\Pi$ state given by Carrington and Ramsay [3] for CH^+ and by Antic-Jovanic and Bojovic [7] for CD^+ are 64 464 cm^{-1} and 64 879 cm^{-1} for $\upsilon = n$ and $\upsilon = n+1$ levels of CH^+ and 62 867 cm^{-1} and 63 149 cm^{-1} for $\upsilon = n$ and $\upsilon = n+1$ levels of CD^+. Therefore, $\Delta G = 415\,cm^{-1}$ and $\Delta G = 282\,cm^{-1}$ for CH^+ and CD^+ respectively. The ratio $\Delta G(CH^+)$ to $\Delta G(CD^+)$ is 1.47, that is a reasonable value for the isotope substitution $H \rightarrow D$ in CH.

4. Conclusion

The analysis of the four new bands gives strong arguments for their identification as the n–4 and $(n+1)$–5 bands of the electronic $C^1\Sigma^+$–$A^1\Pi$ transition of CH^+ and CD^+. The variation of B_{υ} as a function of v is quite convincing even when the $v = 11$ to 14 levels are considered [13].

Some doubt could remain and we plan to observe the bands analysed in the present paper at high resolution with the Bruker IFS120HR Fourier transform spectrometer in a microwave and in a hollow cathode discharge. With the Fourier transform spectrometer resolution, we hope to be able to deperturb the spectra and to find other new bands giving more data on the $C^1\Sigma^+$ electronic state, observed for the first time.

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