

NOTE

Rotationally Resolved $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ Electronic Transition of HC_4D^+

Key Words: diacetylene cation.

The diacetylene cation, HC_4H^+ , is considered to be a reactive intermediate in plasma, combustion, and astrochemical reaction schemes and has been the topic of several spectroscopic studies (1–4). The first assigned gas phase spectrum dates back to 1956 (1) when previously observed emission spectra (2) were identified as the origin band of the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ electronic transition. In subsequent emission studies the absolute rotational numbering was verified (3) and the bond lengths in the $\tilde{X}^2\Pi$ ground and $\tilde{A}^2\Pi$ electronically excited state were determined for the vibrational ground state upon isotopic substitution (4). The only main isotopic geometry not studied spectroscopically so far is the mixed diacetylene cation: $\text{H}^{12}\text{C}_4\text{D}^+$. In this note the line positions and a rotational analysis of the origin band of the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ electronic spectrum of this molecule are presented.

The HC_4D^+ cations were generated in a high pressure planar plasma expansion by discharging a gas pulse of a 0.25% HCCH and 0.25% DCCD mixture in

argon in the throat of a 3-cm \times 300- μm multilayer slit nozzle geometry (5). Cavity ring down spectroscopy was used to observe the species in direct absorption (6). An iodine spectrum was recorded simultaneously for absolute frequency calibration.

In the upper trace of Fig. 1 part of the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ electronic origin band transition of HC_4D^+ is shown, recorded under conditions that are optimized for strong rotational cooling ($T_{\text{rot}} = 15$ K). The lower trace shows the same spectral region for a higher rotational temperature of about 50 K. In the cold spectrum mainly the lower spin-orbit component ($\tilde{A}^2\Pi_{3/2} \leftarrow \tilde{X}^2\Pi_{3/2}$) is observed; the population of the other spin-orbit component is moderate for the low rotational temperatures in the jet and a ground state spin-orbit splitting that amounts to approximately $A'' = -31$ cm^{-1} (4). In the warmer spectrum transitions originating from the second spin-orbit component ($\tilde{A}^2\Pi_{1/2} \leftarrow \tilde{X}^2\Pi_{1/2}$) are visible as well. The higher temperature is reflected in the appearance of more pronounced

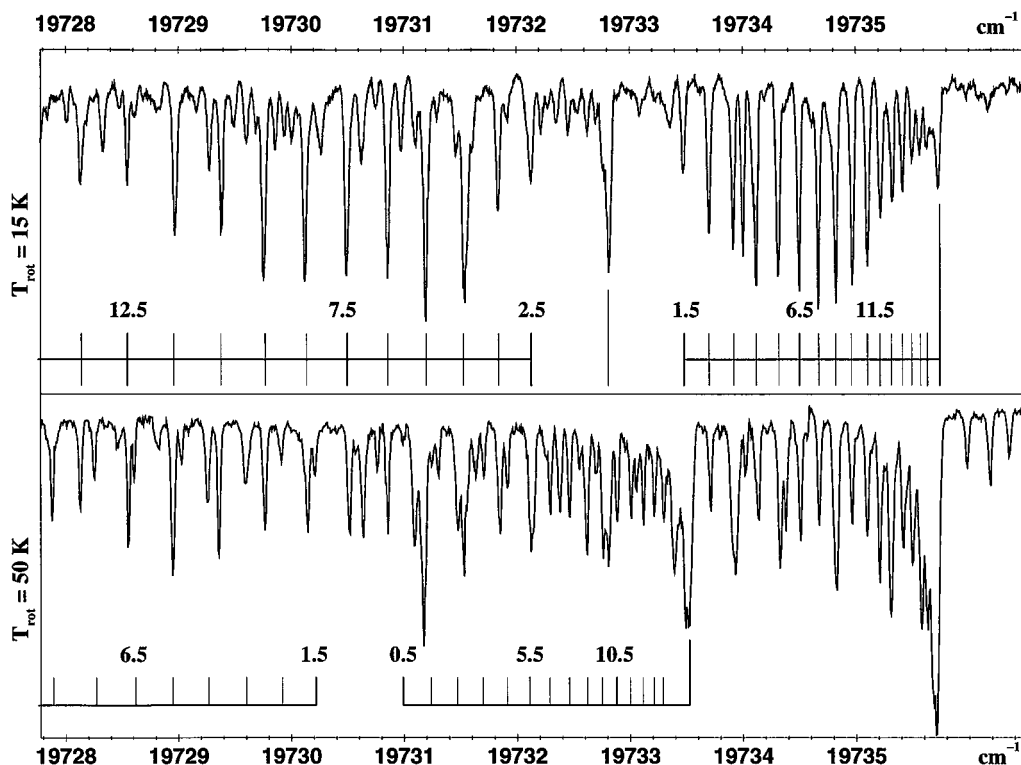


FIG. 1. The origin band in the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ electronic origin band transition of HC_4D^+ , measured by cavity ring down spectroscopy through a supersonic planar plasma. The upper trace is recorded for $T_{\text{rot}} \sim 15$ K, the lower trace for $T_{\text{rot}} \sim 50$ K. In the cold spectrum mainly transitions of the $\tilde{A}^2\Pi_{3/2} \leftarrow \tilde{X}^2\Pi_{3/2}$ component are seen. In the warmer spectrum transitions belonging to the upper spin-orbit system, $\tilde{A}^2\Pi_{1/2} \leftarrow \tilde{X}^2\Pi_{1/2}$, become visible.

TABLE 1
Line Positions (in cm^{-1}) for the Origin Band of the
 $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ Electronic Transition of HC_4D^+

J	$\Omega = 3/2$				$\Omega = 1/2$			
	P -branch	o - c^a	R -branch	o - c^a	P -branch	o - c^a	R -branch	o - c^a
0.5							19730.99	-14
1.5			19733.48	10	19730.20	1	19731.24	-7
2.5	19732.13	-11	19733.70	0	19729.92	13	19731.47	-9
3.5	19731.84	2	19733.92	3	19729.60	-2	19731.70	2
4.5	19731.53	7	19734.12	-2	19729.27	-14	19731.91	6
5.5	19731.20	4	19734.32	6	19728.95	-5	19732.11	11
6.5	19730.86	4	19734.50	6	19728.62	7	19732.29	9
7.5	19730.50	-5	19734.67	7	19728.27	11	19732.46	9
8.5	19730.14	-1	19734.82	2	19727.89	-2	19732.62	12
9.5	19729.77	5	19734.96	-2	19727.51	-4	19732.75	-4
10.5	19729.38	3	19735.10	7	19727.12	-3	19732.88	-7
11.5	19728.96	-16	19735.21	-3	19726.70	-19	19733.00	-7
12.5	19728.55	-13	19735.31	-9			19733.12	-6
13.5	19728.14	2	19735.41	-4			19733.21	-2
14.5	19727.70	-1	19735.49	-7	19725.44	4	19733.30	-6
15.5	19727.25	-2	19735.57	3	19724.98	-3		
16.5			19735.63	5	19724.52	1		
17.5					17924.05	8		
18.5					19723.56	7		
19.5					19723.06	9		

^a Observed minus calculated in units of 10^{-3} cm^{-1} .

bandheads and a weaker Q -branch for the $\Omega = \frac{3}{2}$ component. The cold spectrum allows an unambiguous rotational assignment of the $\tilde{A}^2\Pi_{3/2} \leftarrow \tilde{X}^2\Pi_{3/2}$ band system with a band gap of approximately 10 B. The warmer spectrum provides line positions for higher J -levels in the $\Omega = \frac{3}{2}$ component as well as transitions originating from the $\Omega = \frac{1}{2}$ component. The rotational assignment

TABLE 2
Rotational Constants (in cm^{-1}) for
the Origin Band of the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$
Electronic Transition of HC_4D^+

ν_{00}	19731.725(2)
B''_0	0.136 599(30)
$D''_0 (10^{-8})$	2.1(3)
B'_0	0.130 469(30)
$D'_0 (10^{-8})$	2.1(3)
ΔA	2.2(1)

is given for $\Omega = \frac{3}{2}$ in the upper trace and for $\Omega = \frac{1}{2}$ in the lower trace. Some remaining lines, particularly in the warmer spectrum, are due to transitions originating from HC_4H^+ and DC_4D^+ as can be concluded from the line positions given in Ref. (4).

A combined analysis of the two spectra with about 60 transitions (Table 1) allows an accurate determination of the rotational parameters. The rotational analysis of the data has been performed using the program PGopher (7). The line positions were fitted with an effective Hamiltonian where both spin-orbit components were considered simultaneously. The band origin and rotational B -constants were varied. The centrifugal distortion constants were fixed to the values found for HC_4H^+ and DC_4D^+ (4). As the spin-orbit splittings A'' and A' are highly correlated in the fit, ΔA has been determined instead. The fit has an rms of 0.007 cm^{-1} , significantly smaller than the observed linewidth of approximately 0.035 cm^{-1} (FWHM). The resulting constants are listed in Table 2. These values are in between the values found for the two other main isotopes, HC_4H^+ and DC_4D^+ (4), as may be expected.

The rotational constants found here allow an additional check of the change in overall length of the diacetylene cation upon electronic excitation, using Kraitchman's equations (8). This yields an H-H distance in the $\tilde{X}^2\Pi_g (\tilde{A}^2\Pi_u)$ state of 592 (600) pm, which is in perfect agreement with the values derived from the previous isotopic studies: 591 (599) pm (4).

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