

## The v1 fundamental band of HCO+ by difference frequency laser spectroscopy

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<sup>12</sup>The dissociation constant for Al<sub>2</sub>Me<sub>6</sub> → 2 AlMe<sub>3</sub> in the gas phase is 3.07×10<sup>-6</sup> at 25 °C representing a 5.7×10<sup>-4</sup>% degree of dissociation (Ref. 10).

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## The $v_1$ fundamental band of HCO<sup>+</sup> by difference frequency laser spectroscopy

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Recently Gudeman  $et\ al.$  detected the  $\nu_1$  fundamental band of HCO $^+$  using a color center laser. Because of the limited tuning range of the laser, they could observe only the R-branch lines. Therefore, the assignment of J values was not unique, and was made to get a reasonable agreement of the rotational constants with those from microwave spectroscopy.  $^{2-4}$ 

We have observed the P-branch lines as well as the R-branch lines with a difference frequency laser spectrometer by employing a discharge modulation at 18.2 kHz. Almost the same multiple reflection cell as in our previous works<sup>5,6</sup> was used. The cell was cooled by allowing liquid nitrogen to pass through Tygon tubing wound around the cell, though the cell temperature was considerably higher than the liquid nitrogen temperature. The HCO<sup>+</sup> ions were generated in a modulated dc glow discharge of 150 mA in a mixture of CO (about 80 mTorr) and  $H_2$  (about 700 mTorr). The transition wave numbers were calibrated against  $C_2H_4^{-7}$  or  $H_2O.8$  The accuracy of our measurement was about  $\pm 0.001$  cm<sup>-1</sup>.

Table I lists the observed wave numbers. The P-branch transitions observed here confirm the assignment of J values made by Gudeman  $et\ al.^1$  The least-squares analysis was made by fixing the rotational and centrifugal distortion constants for the ground state at their microwave values,  $^3$  and varying the band origin, the rotational and centrifugal distortion constants in the excited state. The parameters determined are  $\nu_0=3088.739\,51(31),\ B_1=1.475\,699(11),\ and\ D_1=2.68(11)\times 10^{-6}\ cm^{-1},$  where one standard error is in parentheses. The rotational constant  $B_1$  (44 240.34 MHz) is in excellent agreement with that by microwave spectroscopy (44 240.538 MHz). The band origin is 0.012 cm<sup>-1</sup> higher than that estimated by Gudeman  $et\ al.$  and about five times more precise.

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TABLE I. The  $\nu_i$  fundamental band of HCO<sup>\*</sup> (in cm<sup>-1</sup>).

	$\nu_{0}$	$(O-C) \times 10^4$		$\nu_0$	$(O-C)\times 10^4$
P(1)	3085.7646	1	R(0)	3091.6919	10
P(2)	3082.7662	3	R(1)	3094, 6181	<b>-</b> 5
P(3)	3079.7437	-2	R(2)	3097.5223	- 3
P(4)	3076.6977	-7	R(3)	3100.4034	7
P(5)	3073.6291	<del></del> 5	R(4)	3103.2586	-4
P(6)	3070.5377	2	R(5)	3106,0909	-4
P(7)	3067.4224	2	R(6)	3108,9002	5
P(8)	3064. 2834	-4	R(7)	3111.6841	1
P(9)	3061, 1226	3	R(8)	3114. 4445	2
P(10)	3057.9380	1	R(9)	3117. 1800	-4

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<sup>&</sup>lt;sup>8</sup>The methyl radical exhibits a strong MPI resonance (Ref. 9) at 450.8 nm assigned to the  $\gamma(0,0)$  Rydberg level. Mass selective MPI has been observed using a pulse energy of 12 mJ focused with a 50 mm fl lens. The detected methyl radical concentration was estimated in Ref. 9 to be  $10^{10}-10^{11}$  cm<sup>-3</sup>. Absolute ion current measurements in the present study indicated a methyl radical concentration of an order of magnitude less in the confocal volume at a pulse energy of  $\sim 350~\mu J$ .

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