

# A Combined Dunham Analysis of the Rotational and Electronic Transitions of $\text{CH}^+$ : Revisiting the $\Lambda$ -doubling in the $A^1\Pi$ State

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## Introduction

The  $J = 1 - 0$  lines of  $^{12}\text{CH}^+$  and  $^{13}\text{CH}^+$  and the  $J = 1 - 0$  and  $J = 2 - 1$  lines of  $^{12}\text{CD}^+$  were observed in the laboratory [1, 2]. More recently several THz transitions were detected with a JPL THz spectrometer based on frequency multiplication technique [3]. Still number of lines available from pure rotational transitions is limited, so the conventional analysis to determine the spectroscopic parameters has not been quite successful. One way of alleviating this difficulty is employing a Dunham analysis of all the available data.

Before the successful laboratory detection of the  $J = 1 - 0$  transition of  $\text{CH}^+$ , a Dunham analysis of the  $A^1\Pi - X^1\Sigma^+$  band was carried out by Müller, and astronomically important predictions of the pure rotational transition frequencies were made [4]. See references concerning some historical development of both astronomical and laboratory measurements of  $\text{CH}^+$  cited in Ref. [2]. In this investigation, the newly obtained rotational lines are incorporated in addition to the electronic data in the Dunham analysis.

## Observation of THz lines

The experiment was performed at Jet Propulsion Laboratory (JPL) by using the JPL THz spectrometer. THz radiation sources are frequency multiplier chains developed at JPL or purchased from Virginia Diodes. For production of  $\text{CH}^+$ , an extended negative glow discharge in a gas mixture of  $\text{CH}_4$  ( $\sim 0.5$  mTorr) diluted in He ( $\sim 60$  mTorr) was used. The optimum discharge current was about 15 mA and the axial magnetic field of 160 Gauss was applied. The discharge cell was cooled down to liquid nitrogen temperature.

## Analysis

The vibration-rotation energy of diatomic molecules is expressed as

$$E(v, J) = hY_{kl}(v + 1/2)^k [J(J + 1) - \Lambda^2]^l, \quad (1)$$

where  $Y_{kl}$  are the Dunham coefficients that depend on the masses. Watson formulated the mass dependences of

the Dunham coefficients [5].

$$Y_{kl} = \mu_C^{-(k+2l)/2} U_{kl} \{1 + m_e \Delta_{kl}^a / M_a + m_e \Delta_{kl}^b / M_b\}, \quad (2)$$

where  $m_e$  is the mass of electron,  $M_a$  and  $M_b$  are the masses of atoms  $a$  and  $b$ , respectively.  $\mu_C$  is the charge modified reduced mass defined

$$\mu_C = M_a M_b / (M_a + M_b - C m_e), \quad (3)$$

where  $C$  is the charge number, for  $\text{CH}^+$   $C = 1$ .

In the analysis, the pure rotational transitions in the ground state and the  $A^1\Pi - X^1\Sigma^+$  band lines [6–11] were subject to the least squares fitting to determine the mass independent Dunham coefficients.

In the fitting, how to treat the  $\Lambda$ -doubling needs an additional consideration. The  $\Lambda$ -doubling splittings in  $^1\Pi$  electronic states have been expressed as  $\pm(1/2)qJ(J + 1)$  in most investigations. However, it should be noted that the  $e$ -levels of  $^1\Pi$  state interact with  $^1\Sigma^+$  states, while the  $f$ -levels with  $^1\Sigma^-$  states. For  $\text{CH}^+$ , the  $e$ -levels of  $A^1\Pi$  are pushed upward largely from the interaction with the ground  $X^1\Sigma^+$  state. The  $^1\Sigma^-$  states are not known experimentally, and they, if any, should lie high over the  $A^1\Pi$  state.

In general, there may be several  $^1\Sigma$  states to interact with the  $A^1\Pi$  states, and the “ $\Lambda$ -doubling” energy term is given,

$$E_\Lambda = +(1/2)qJ(J + 1) \text{ for } e \text{ levels} \quad (4)$$

$$E_\Lambda = -(1/2)q'J(J + 1) \text{ for } f \text{ levels}, \quad (5)$$

where  $q$  and  $q'$  are defined as

$$q = 4B^2 \sum_i \frac{|\langle \Lambda = 1 | L_+ | \Lambda = 0; ^1\Sigma^+(i) \rangle|^2}{E(A^1\Pi) - E(^1\Sigma^+(i))} \quad (6)$$

$$q' = 4B^2 \sum_i \frac{|\langle \Lambda = 1 | L_+ | \Lambda = 0; ^1\Sigma^-(i) \rangle|^2}{E(^1\Sigma^-(i)) - E(A^1\Pi)}. \quad (7)$$

The electric dipole transitions are allowed between the levels of opposite parity. The  $P$ - and  $R$ -branches occur between the  $e$ -levels and between the  $f$ -levels, and the  $Q$ -branch transitions are allowed between  $e$ - and  $f$ -levels. Therefore, in principle,  $B$ ,  $q$ , and  $q'$  in the excited state cannot be determined independently. If no low-lying  $^1\Sigma^-$  electronic states exist, as ab initio calculations suggest, the  $q'$  term could be negligible. If the rotational constant obtained from the  $A - X$  band by neglecting

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TABLE I: Mass independent Dunham parameters determined by a least-squares fit of the pure rotational and electronic  $A^1\Pi - X^1\Sigma^+$  transitions (in MHz).

	$A^1\Pi$ state	$X^1\Sigma^+$ state
$U_{01}$	331611.5(173)	397355.0(28)
$U_{02}$	-50.005(185)	-36.758(42)
$U_{03}$	-0.00169(40)	0.00228(50)
$U_{04}$	0.00014(24)	0.00014(24)
$U_{10}$	$5.380881 \times 10^7$ (121)	$8.268447 \times 10^7$ (157)
$U_{11}$	-24597.9(116)	-13387.3(119)
$U_{12}$	-3.126(169)	0.987(122)
$U_{13}$	0.000284(76)	-0.00154(58)
$U_{20}$	$-3.04946 \times 10^6$ (107)	$-1.65652 \times 10^6$ (131)
$U_{21}$	-617.3(49)	83.0(65)
$U_{22}$	0.473(53)	-0.128(52)
$U_{23}$	-0.000389(24)	0.00048(27)
$U_{30}$	$4.80 \times 10^3$ (40)	$7.60 \times 10^3$ (50)
$U_{31}$	126.84(63)	-3.09(105)
$U_{40}$	7951.(48)	-191.(61)
$U_{01}\Delta_{01}^H$	$-1.4867 \times 10^6$ (189)	$-3.6697 \times 10^6$ (42)
$U_{02}\Delta_{02}^H$	$5.4 \times 10^2$ (31)	$8.73 \times 10^2$ (39)
$U_{10}\Delta_{10}^H$	$-2.0466 \times 10^8$ (83)	$-1.3155 \times 10^8$ (93)
$U_{11}\Delta_{11}^H$	$1.012 \times 10^5$ (55)	$1.093 \times 10^5$ (57)
$U_{20}\Delta_{20}^H$	$7.53 \times 10^6$ (27)	$-2.01 \times 10^6$ (30)
$U_{01}\Delta_{01}^C$	$-8.1 \times 10^5$ (29)	$-3.1616 \times 10^6$ (62)
$U_{10}\Delta_{10}^C$	$8.46 \times 10^7$ (133)	$-7.6 \times 10^7$ (21)
$U_{00}$	$7.2353307 \times 10^8$ (147)	
$U_{00}\Delta_{00}^H$	$7.4063 \times 10^8$ (85)	
$U_{00}\Delta_{00}^C$	$-1.77 \times 10^8$ (31)	

<sup>a</sup>The numbers in parentheses indicate the standard deviation from the fits in the last digits shown.

the contributions from the interaction with  $1\Sigma^-$  states agrees with the one determined from the pure rotational spectra in the ground state, the assumption that the  $q'$  term was negligible could be verified. In this analysis, only the  $Q$ -branch transitions of the  $A - X$  band system are included in the least-squares analysis by neglecting the  $\Lambda$ -doubling.

## Results and Discussion

The mass independent parameters have been obtained as listed in Table I. It is somewhat difficult to grasp the

meaning of these mass independent Dunham parameters. It is more intuitive to convert back to the  $Y_{kl}$  coefficients for each isotopologue, and further to the conventional spectroscopic parameters. From these parameters, as shown in Table II, the conventional spectroscopic parameters are derived for each isotopologue. The molecular constants obtained from the conventional fits are listed in Table III for comparison. From the Dunham fit, the higher-order centrifugal distortion constant,  $H$ , was not determined very well, and the accuracy of  $B$  and  $D$  is not as good as the one obtained from the conventional individual fit. The Dunham fit is sometimes difficult, and the Dunham coefficients determined need careful scrutiny. In this analysis of  $\text{CH}^+$ , the agreement between the two sets of constants is reasonable.

TABLE II: Derived spectroscopic constants for  $^{12}\text{CH}^+$  and its isotopologues (in MHz).

	$^{12}\text{CH}^+$	$^{13}\text{CH}^+$	$^{12}\text{CD}^+$
$B_0$	417652.0(28)	415190.3(28)	226785.35(110)
$D_0$	41.417(42)	40.925(42)	12.157(10)
$H_0$	0.0018(31)	0.0018(31)	0.00033(49)

TABLE III: Molecular constants for  $\text{CH}^+$  and its isotopologues determined with the conventional energy expression<sup>a</sup> (in MHz).

	$^{12}\text{CH}^+$	$^{13}\text{CH}^+$	$^{12}\text{CD}^+$
$B_0$	417651.536(23)	415189.9201(199)	226785.2370(85)
$D_0$	41.4062(27)	40.9521(62)	12.15398(128)
$H_0$	0.003699(55)	0.00589(39)	0.000561(47)

<sup>a</sup>The fits were carried out with the 0-0 band of the  $A - X$  system in addition to the rotational lines.

With these Dunham coefficients, the transition frequencies for the vibration-rotation band can be calculated with improved accuracy. These results should be useful for determining the potential energy curves of this fundamental ion [12].

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