

Theoretical determination of the spectroscopic constants of CaH^+

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Fourth-order many-body perturbation-theory calculations of the spectroscopic constants of CaH^+ are presented as an attempt to help identify possible astronomical or laboratory observations. The results for the rotational and vibrational constants are, respectively, 4.61 and 1511 cm^{-1} . Similar calculations are made on MgH^+ , where comparison with experimental values shows excellent agreement, indicating reliable results for CaH^+ .

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Experimental observations of new molecular species either in laboratory or in space are usually guided by the knowledge of the spectroscopic constants. In recent years [1] *ab initio* calculations have greatly aided in the search and identification of new molecules.

Diatomic hydride cations in general are of considerable importance in astrophysics. They are important constituents of interstellar media [2, 3], cool stellar atmospheres [4], comets [3, 5], and the Sun [6]. The molecule CaH is present in sunspots [7] and almost all the calcium; at photospheric temperatures, exists in its first stage of ionization [8]. Further, the solar abundance of Mg and Ca are 7.58 and 6.36, respectively [9], whereas

the ionization potentials for the same are $I(\text{Mg})=7.646 \text{ eV}$ and $I(\text{Ca})=6.113 \text{ eV}$ [10]. Consequently, if one assumes MgH^+ as observable in the solar spectrum [11], it is only natural to believe that the CaH^+ is an astrophysically important molecule. The need for molecular data on CaH^+ was expressed earlier by Johnson and Sauval [4] and Sinha and Tripathi [12]. However, opposite to MgH^+ , there is no experimental data available on the spectroscopic constants of CaH^+ . On the theoretical side few efforts have been made but of a limited nature [13–17]. The objective of the present paper is therefore to present reliable theoretical values for the spectroscopic constants of CaH^+ with particular emphasis on the mi-

TABLE I. The calculated spectroscopic constants of MgH^+ and CaH^+ obtained at the fourth-order MBPT level.

	MgH^+		CaH^+	
	Present	Experiment [19]	Present	Other theoretical values
R_e (Å)	1.657	1.652	1.936	1.864, ^a 2.085, ^b 1.881, ^c 1.926, ^d 1.940 ^e
B_e (cm^{-1})	6.400	6.387	4.609	4.85 ^c
ω_e (cm^{-1})	1682	1699	1511.0	1468, ^a 1504, ^c 1482, ^d 1467 ^e
$\omega_e x_e$ (cm^{-1})	34.3	31.9	23.5	21.01 ^c
α_e (cm^{-1})	0.16	0.18	0.13	0.09 ^c
D_0^0 (cm^{-1})	14945.0	16780.0	14804	17000, ^a 16700, ^c 15500, ^d 15600 ^e

^aReference [17]: Pseudopotential two-electron valence configuration interaction (CI) and core polarization.

^bReference [13]: Two-electron frozen-core CI.

^cReference [14]: Single- and double-excitation CI (only single excitation from the core).

^dReference [15]: Density functional with pseudopotential.

^eReference [16]: Single- and double-excitation valence CI.

crowave and the vibrational constants. These results should be of great value in the possible laboratory or astrophysical observations of CaH^+ .

To assess the accuracy of our calculated values for CaH^+ the spectroscopic constants of MgH^+ will also be calculated using the same theoretical model. As the spectroscopic constants of MgH^+ are available from experiment [18, 19] a simple comparison will allow a direct measure of the reliability of our theoretical approach.

The calculations are performed within the many-body-perturbation-theory (MBPT) model [20] up to the complete fourth-order level MBPT(4) with inclusion of all single, double, triple, and quadruple substitutions.

All calculations were performed using the GAUSSIAN-86 program [21] with a basis of contracted Cartesian Gaussian set. For Ca the basis consists of $(14s\ 11p\ 2d\ | 8s\ 6p\ 2d)$ as described previously [22]. For Mg the basis is $(12s\ 8p\ 2d\ | 6s\ 4p\ 2d)$ as given in [23]. For H we have selected the $(9s\ 3p\ 1d\ | 4s\ 3p\ 1d)$ basis of Siegbahn and Liu [24]. For the MBPT calculations the core $(1s-2p)$ for Ca and $(1s)$ for Mg are kept frozen.

Table I summarizes the calculated values for the spectroscopic constants of MgH^+ and CaH^+ in their ground states. A comparison with the experimental values for MgH^+ shows an excellent agreement, particularly for the microwave (B_e) and vibrational (ω_e) constants. These are expected to be the most reliable calculated constants because MBPT(4) gives very accurate results for those properties related to the equilibrium internuclear distance. One also notes however that the calculated values for the anharmonic constant the rotation-vibration interaction constant $\omega_e x_e$ and the rotation-vibration interaction constant α_e are also in very good accord with experiment. For the binding energy D_0^0 the result is less accurate [19, 25, 26]. Our calculated value is obtained from independent calculations on MgH^+ at equilibrium and in the limit of separated atoms $\text{Mg}^+ + \text{H}$, taking into

TABLE II. The calculated rotational constant (in cm^{-1}) of MgH^+ and CaH^+ obtained at different levels of MBPT.

Method	MgH^+	CaH^+
SCF ^a	6.450	4.501
MBPT(2)	6.471	4.647
MBPT(3)	6.438	4.602
DQ-MBPT(4) ^b	6.410	4.609
MBPT(4)	6.400	4.609
Experiment [19]	6.387	

^aSCF denotes self-consistent field.

^bDQ represents double and quadrupole substitution.

account the zero vibrational energy.

Having in mind the accuracy of the present results for MgH^+ we now discuss the obtained values for CaH^+ . The calculated value for $B_e = 4.609\ \text{cm}^{-1}$, corresponding to the equilibrium internuclear distance value $R_e = 1.936\ \text{\AA}$, should be very reliable. Previous theoretical values [13–17] of R_e range from $1.864\ \text{\AA}$ to $1.940\ \text{\AA}$. The value of $1.940\ \text{\AA}$ obtained by Schilling, Goddard, and Beauchamp [16] is closest to our value. The recent result of Boutalib, Davdey, and Mouhtadi [17] of $1.864\ \text{\AA}$ is found to be somewhat too low. To illustrate the convergence of the calculated rotational constants Table II shows intermediate results of the MBPT calculations for MgH^+ and CaH^+ .

Judging from the accuracy of our results for MgH^+ and the usual performance of MBPT(4) in describing single-reference closed-shell systems at or near equilibrium distance, the present values for the spectroscopic constants of CaH^+ should be reliably useful in possible astronomical or laboratory observation of this diatomic hydride cation. In particular B_e and ω_e are good guides for microwave and vibrational spectra.

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