



Quantum chemical spectral characterization of CH_2NH_2^+ for remote sensing of Titan's atmosphere



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ABSTRACT

Cassini has shown that CH_2NH_2^+ is likely present in relatively high abundance in Titan's upper atmosphere. Relatively little is known about this molecule even though it contains the same number of electrons as ethylene, a molecule of significance to Titan's chemistry. Any studies on CH_2NH_2^+ with application to Titan or its atmospheric chemistry will have to be done remotely at this point with the end of the fruitful *Cassini* mission. Consequently, trusted quantum chemical techniques are utilized here to produce the rotational, vibrational, and rovibrational spectroscopic constants for CH_2NH_2^+ for the first time. The methodology produces a tightly fit potential energy surface here that is well-behaved indicating a strong credence in the accuracy for the produced values. Most notably, the 884.1 cm^{-1} NH_2 out-of-plane bend is the brightest of the vibrational frequencies reported here for CH_2NH_2^+ , and an observed and unattributed feature in this spectral region has been documented but never assigned to a molecular carrier. Follow-up IR or radio observations making use of the 540 GHz to 660 GHz range with the 0.45 D molecular dipole moment will have to be undertaken in order to confirm this or any attribution, but the data provided in this work will greatly assist in any such studies related to CH_2NH_2^+ .

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1. Introduction

Cassini's Ion Neutral Mass Spectrometer (INMS) (Waite et al., 2005) reported peaks at nearly every m/z value falling between 12 and 57. One of these includes $m/z=30$ (Vuitton et al., 2006). This peak, in particular, has been attributed to the aminomethyl/methylenimmonium cation, CH_2NH_2^+ a species about which little is known. The lack of data for this cation is somewhat surprising since it is isoelectronic with a very common hydrocarbon of significance for Titan's atmospheric chemistry: ethylene or $\text{H}_2\text{C}=\text{CH}_2/\text{C}_2\text{H}_4$. Consequently, the chemistry of ethylene and the aminomethyl cation will have many similarities as well as some differences. The initial INMS readings put the upper atmospheric density of CH_2NH_2^+ at two orders of magnitude greater than the more terrestrially sensible methylaminy cation, CH_3NH_2^+ , making the aminomethyl cation one of the more abundant species in Titan's atmosphere at altitudes between 1000 km and 1200 km (Vuitton et al., 2006).

The nitrogen–hydrocarbon chemistry of Titan's atmosphere is one of the most complex chemical environments of the solar system (Hörst, 2017). The seemingly strange juxtaposition of a thick

atmosphere at sub-100 K temperatures creates chemical phenomena vastly different from those present on Earth in the current epoch. As a result, many of the chemicals observed thus far with *Cassini* and even its *Huygens* lander have had little classification since they are likely not naturally created in any notable amounts here on Earth. The most common examples are Carl Sagan's tholins which have only recently started to produce some chemical definition (Sciamma-O'Brien et al., 2017), but CH_2NH_2^+ is among this group of relatively obscure nitrogen–hydrocarbon combination molecules. This cation is one of the simplest systems to possess both an amine group and a N–C bond, two conditions necessary for the creation of amino acids and, potentially, life. As a result, its lack of analysis is somewhat surprising even with application beyond purely planetary science.

What is known about CH_2NH_2^+ is that this cation is believed to be formed in Titan's atmosphere through protonation of CH_2NH (Vuitton et al., 2006). The feeder radical has a high proton affinity and readily accepts an additional hydrogen atomic cation into its structure (de Oliveira et al., 2001). Differently, CH_2NH_2^+ is also created through hydrogen loss from the more thermodynamically stable methylaminy cation, CH_3NH_2^+ (Singh et al., 2010). However, the intrinsic translational kinetic energy in this latter process is too great for the CH_2NH_2^+ potential well to be populated over long timescales. As a result, HCNH^+ is created, in part, due to the loss

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of two hydrogen atoms likely in the form of the ubiquitous hydrogen molecule either from a concerted elimination or by a hydride shift followed by H_2 loss. The implied atmospheric abundances of Titan from the INMS results giving $[CH_3NH_2^+] < [CH_2NH_2^+] < [HCNH^+]$ ($1.08 \times 10^{-1} < 6.16 \times 10^1 < 2.76 \times 10^2$) support such a mechanism. The $HCNH^+ m/z=28$ Cassini INMS peak is actually the largest in the initial Titan flybys meaning that the smaller, tetraatomic $HCNH^+$ cation was the most abundant molecule detected (Vuitton et al., 2006). Consequently, $CH_2NH_2^+ m/z=28$ Cassini INMS peak is actually the largest in the initial Titan flybys meaning that the smaller, tetraatomic $HCNH^+$ cation was the most abundant molecule detected (Vuitton et al., 2006). Consequently, $CH_2NH_2^+$ appears to be of significance as an intermediate in the creation of $HCNH^+$ both in Titan's atmosphere and may even be such in the interstellar medium.

The corresponding CH_2NH_2 radical has also been analyzed for its electronic properties (Jansen et al., 1999) and as a photodissociation product of CH_3NH_2 (Muller et al., 2016). The latter study indicates that similar reaction schema are believed to take place in the radical as they do for the ionized species, as well (Singh et al., 2010). In any case, the $CH_2NH_2^+$ cation form is known to exist in Titan's stratosphere, but almost nothing beyond the general structure and these implied roles is known. With the end of Cassini in 2017, any studies of Titan's chemistry will have to be done remotely with instruments such as the Stratospheric Observatory for Infrared Spectroscopy (SOFIA) or the Atacama Large Millimeter Array (ALMA).

Consequently, there exists a huge need to produce the infrared (IR) and radio spectral data for molecules detected by Cassini's INMS for which no such data currently exist. The vibrational frequencies of $CH_2NH_2^+$ have been produced harmonically with a modest level of quantum chemical theory (de Oliveira et al., 2001), but the quantitative correlation to actual observation or experiment would be mostly coincidental for such a computational level. Anharmonic corrections produce a more physically meaningful description of the atomic motions such that computational predictions of the vibrational (IR) and rotational (radio) spectra can accurately represent physical reality. High-level, quantum chemical, anharmonic, theoretical computations have been able to reproduce experimental vibrational frequencies to within as close as 1.0 cm^{-1} (0.01 microns) or better in many cases and rotational constants to within a few dozen MHz of gas phase experimental values (Huang and Lee, 2008; 2009; Huang et al., 2011; 2013a; Zhao et al., 2014; Fortenberry et al., 2012; 2014; 2015; Kitchens and Fortenberry, 2016). As a result, the same protocol will be employed for computing these values for $CH_2NH_2^+$.

The treasure trove of data generated from the Cassini mission related to Titan will continue to keep scientists busy for years to come, and the follow-up questions will not be answerable *insitu* for the foreseeable future. Hence, the data produced here will greatly assist in remote sensing observations related to $CH_2NH_2^+$ and the chemistry of its parent and daughter species in Titan's atmosphere and potentially even into the interstellar and interplanetary media.

2. Computational details

Proven quantum chemical techniques are employed in this work based on the "gold standard" of quantum chemistry (Helgaker et al., 2004): coupled cluster theory (Crawford and Schaefer III, 2000; Shavitt and Bartlett, 2009) at the singles, doubles, and perturbative triples level, CCSD(T) (Raghavachari et al., 1989). The most cost effective, in terms of computational cost for the garnered accuracy, means for producing rovibrational spectroscopic data comes in the form of quartic force fields (QFFs) (Fortenberry et al., 2013b). These descriptions of the electronic potential energy surface with respect to changes in nuclear position are fourth-order

Taylor series expansions for the potential portion of the internuclear Hamiltonian. These are utilized in the nuclear Schrödinger equation and are defined by the equation:

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l, \quad (1)$$

in which the $F_{ij\dots}$ represents the force constants and the Δ_i terms describe the displacements.

The initial geometry is optimized in order to produce as close to a minimum structure as possible. The CCSD(T) level of theory is utilized in conjunction with the aug-cc-pV5Z basis set (Dunning, 1989; Kendall et al., 1992; Peterson and Dunning, 1995) to do so. Optimizations with the Martin–Taylor (MT) core correlating basis set (Martin and Taylor, 1994) are also included where the core electrons are allowed to be represented in the coupled cluster wave function and where they are not. The difference in the two MT structures is then added to the CCSD(T)/aug-cc-pV5Z geometry. From this reference geometry, 4493 total points are generated to define the QFF. The coordinates, the i, j, \dots terms from Eq. (1), employed include:

$$S_1(a_1) = C - N \quad (2)$$

$$S_2(a_1) = \frac{1}{\sqrt{2}}[(C - H_1) + (C - H_2)] \quad (3)$$

$$S_3(a_1) = \frac{1}{\sqrt{2}}[(N - H_3) + (N - H_4)] \quad (4)$$

$$S_4(a_1) = \frac{1}{\sqrt{2}}[\angle(N - C - H_1) + \angle(N - C - H_2)] \quad (5)$$

$$S_5(a_1) = \frac{1}{\sqrt{2}}[\angle(C - N - H_3) + \angle(C - N - H_4)] \quad (6)$$

$$S_6(b_2) = \frac{1}{\sqrt{2}}[(C - H_1) + (C - H_2)] \quad (7)$$

$$S_7(b_2) = \frac{1}{\sqrt{2}}[(N - H_3) + (N - H_4)] \quad (8)$$

$$S_8(b_2) = \frac{1}{\sqrt{2}}[\angle(N - C - H_1) + \angle(N - C - H_2)] \quad (9)$$

$$S_9(b_2) = \frac{1}{\sqrt{2}}[\angle(C - N - H_3) + \angle(C - N - H_4)] \quad (10)$$

$$S_{10}(b_1) = \frac{1}{\sqrt{2}}[\tau(H_3 - N - C - H_1) - \tau(H_4 - N - C - H_2)] \quad (11)$$

$$S_{11}(b_1) = \frac{1}{\sqrt{2}}[\tau(H_4 - N - C - H_1) - \tau(H_3 - N - C - H_2)] \quad (12)$$

$$S_{12}(a_2) = \frac{1}{\sqrt{2}}[\tau(H_3 - N - C - H_1) + \tau(H_4 - N - C - H_2)] \quad (13)$$

with alternative qualitative definitions for the mathematical descriptions above of S_{10} as the CH_2 out-of-plane bend, S_{11} as the NH_2 out-of-plane bend, and S_{12} as the twisting motion along the $C=N$ bond. The numerical labels for the hydrogen atoms are given in Fig. 1 but can be summarized in that H_1 and H_2 are bonded to

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