Molecular Astrophysics 8 (2017) 27–35

Contents lists available at ScienceDirect

Molecular Astrophysics

journal homepage: www.elsevier.com/locate/molap

Research Paper

On the spectroscopic constants, first electronic state, vibrational frequencies, and isomerization of hydroxymethylene ($HCOH^+$)

Riley A. Theis, Ryan C. Fortenberry*

Georgia Southern University, Department of Chemistry & Biochemistry, Statesboro, GA 30460, U.S.A.

ARTICLE INFO

Article history:
Received 5 April 2017
Revised 1 June 2017
Accepted 1 June 2017
Available online 3 June 2017

Keywords:
Rovibrational spectroscopy
Quartic force fields
Adiabatic effects
Quantum chemistry
Astrochemistry
Radical cations

ABSTRACT

The hydroxymethylene cation ($HCOH^+$) is believed to be chemically independent of the more stable formaldehyde cation isomer in interstellar chemistry and may likely be a precursor to methanol in chemical reaction networks. Previous work is corroborated here showing that the *trans* conformer of $HCOH^+$ is 3.48 kcal/mol lower than the *cis* on the potential energy surface. The small energy difference between the conformers and the much larger dipole moment of *cis*-$HCOH^+$ (2.73 D) make this conformer more likely to be observed than *trans*-$HCOH^+$ via telescopic rotational spectroscopy. A strong adiabatic shift is also predicted in the first electronic excitation into the $1\,^2A''/2\,^2A$ state out of either conformer into a C_1 structure reducing the excitation wavelength from the near-ultraviolet all the way into the near-infrared. The full set of fundamental vibrational frequencies are also computed here at high-level. The 3306.0 cm^{-1} and 3225.3 cm^{-1} hydroxide stretches, respective of bare *trans*- and *cis*-$HCOH^+$, are in agreement with previous theory but are significantly higher than the frequencies determined from previous experiment utilizing argon tagging techniques. This shift is likely because the proton-bound complex created with the argon tag reduces the experimental frequencies. Lower-level computations including the argon tag bring the hydroxide stretches much closer to the experimental frequencies indicating that the predicted frequencies for bare $HCOH^+$ are likely well-described.

1. Introduction

Second to water, methanol may be the most significant molecule for astrobiology. Naturally, methanol may act as an organic solvent, but it may also participate in chemical reactions itself, especially in interstellar ices, leading to more complicated, organic, prebiotic molecules and even amino acids and DNA bases (Bernstein et al., 2002; 1995; Cronin and Pizzarello, 1997; Lee et al., 2009; Muñoz Caro et al., 2002; Öberg, 2016; Sorrell, 2001). The interstellar formation of methanol itself is still somewhat of a mystery, but recent work has suggested that it could form from the hydroxymethylene radical cation ($HCOH^+$) (Mauney et al., 2016). Until this most recent study, very little was known about this small organic cation (Berkowitz, 1978; Burgers et al., 1983; Wesdemiotis and McLafferty, 1981), but its isomeric cousin, formaldehyde cation, is more widely known.

Even though formaldehyde is known (Snyder et al., 1969) in the interstellar medium (ISM), the collision of various, small, known, and abundant interstellar species including H_2O^+ (Ossenkopf et al., 2010) and methylidyne, (McKellar, 1940; Swings and Rosenfeld, 1937) for example, could create the hydroxymethylene cation, as well. Then, the $HCOH^+$ could be deposited onto ice grains where it could engage in condensed phase chemistry or form into methanol. In any case, the presence of $HCOH^+$ in the ISM is highly likely due to its simplicity and likely formation pathways. However, the spectral and relative energetics of this fascinating little radical cation are only just now coming to the fore of physical and astrochemistry.

According to previous work, (Mauney et al., 2016) the *trans*-$HCOH^+$ form of this radical cation has been computed to lie 6.1 kcal/mol above the formaldehyde cation, but a 43.0 kcal/mol barrier separates the two conformers. The *cis* form of $HCOH^+$ lies 3.5 kcal/mol above the *trans*, and a 17.4 kcal/mol transition state with a 90° dihedral angle must be accessed in order to isomerize. Infrared spectral analysis was done via argon tagging techniques (Douberly et al., 2010; Duncan, 2003) for all three forms of $[H_2, C, O]^+$ in the experimental results, but the formaldehyde and hydroxymethylene cation isomers are isolated from one another due to the high isomerization barrier. The formaldehyde and hydroxymethylene cation isomers are subsequently almost certainly formed via different pathways in the ISM (Mauney et al., 2016). Furthermore, the Ar atoms appear preferentially to bind to the

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* Corresponding author.
E-mail address: rfortenberry@georgiasouthern.edu (R.C. Fortenberry).

http://dx.doi.org/10.1016/j.molap.2017.06.001

$HCOH^+$ conformers via the hydrogen in the hydroxide moiety in the argon tagged structures. Quantum chemical studies combined with the argon tagging experimental analysis has led to the assignment of the hydroxymethylene cation O–H stretches at 2757 cm^{-1} and 2803 cm^{-1}, respective of *cis*- and *trans*-$HCOH^+$ tagged with Ar, and the C–H stretches at 2833 cm^{-1} and 2952 cm^{-1}, respectively. While, argon tagging (Duncan, 2003) is a very powerful tool for the analysis of difficult molecular species, especially hard-to-access isomers of cations as in the case of $HCOH^+$, argon will engage in various levels of bonding (Filipek, II and Fortenberry, 2016; Fortenberry, 2017a; Frenking and Cremer, 1990; Grandinetti, 2011; Novak and Fortenberry, 2016; 2017; Theis and Fortenberry, 2016).

The intensities of the assigned O–H stretch in either argon tagged $HCOH^+$ conformer (Mauney et al., 2016) are quite large indicating that a proton-bound complex is forming between the argon atom and the formyl radical. Proton-bound complexes are of high interest themselves to the astrochemical community since the proton "shuttle" motion has a significant change in the center-of-charge with little change in the center-of-mass creating a very bright vibrational mode (Begum and Subramanian, 2016; Cotton et al., 2012; Fortenberry et al., 2016a; 2016b; 2015b; Mladenovcić and Roueff, 2014; Terrill and Nesbitt, 2010; Yu et al., 2015). Such complexes are known from both experiment and theory for noble gas clusters, as well (Borocci et al., 2011; Fortenberry, 2017b; Fridgen and Parnis, 1998; Grabowski et al., 2016; Legay-Sommaire and Legay, 1999; Lundell et al., 1999; McDonald II et al., 2016), especially for argon containining species which is much more polarizable than neon and helium (Pauzat et al., 2013; 2009; Rice et al., 1991; Taylor et al., 1989). Consequently, the O–H stretches reported are perturbed by the argon atom as is pointed out in Ref. Mauney et al. (2016). As a further example, the hydride stretch in the astronomically observed argonium cation (Barlow et al., 2013; Cueto et al., 2014; Schilke et al., 2014) drops by nearly 1600 cm^{-1} from 2592.7 cm^{-1} to less than 1000 cm^{-1} in the $ArHAr^+$ proton-bound complex (Fortenberry, 2017b; McDonald II et al., 2016). This is likely an extreme case due to the presence of the same atoms opposite one another around the proton, but characteristics of a proton-bound complex between the formyl radical and an argon atom are present in the $HCOH^+$-Ar complexes (Mauney et al., 2016).

While the argon-proton-bound complexes are likely of interest to astrochemistry in their own right, the spectral features of the isolated hydroxymethylene radical cations are still somewhat shrouded, especially with regards to the rotational and electronic transition energy regimes. The present work builds upon the previous (Mauney et al., 2016) by utilizing high-level, single-molecule computations to predict the gas phase spectra of *cis*- and *trans*-$HCOH^+$. Other quantum chemical studies on different molecules have utilized the methodology employed here, discussed in the next section, to provide vibrational frequencies to 5.0 cm^{-1} or better in many cases and rotational constants to within a few dozen MHz of gas phase experimental values (Fortenberry et al., 2014a; 2012; 2015a; Huang et al., 2013; Huang and Lee, 2008; 2009; Huang et al., 2011; Kitchens and Fortenberry, 2016; Zhao et al., 2014). Consequently, not only will vibrational frequencies for both conformers of $HCOH^+$ be included in the discussion, but the rotational and spectroscopic constants as well as discussion of the first electronically excited state will be provided for the first time. Further spectroscopic insights into the spectrum of this small, radical cation will be provided for subsequent comparison to observed astronomical spectra giving deeper insights into the potential role of the hydroxymethylene cation in interstellar chemistry.

2. Computational details

Quartic Force Fields (QFFs) can often provide highly accurate structural and spectroscopic data for molecules and are defined by the equation:

$$V = \frac{1}{2}\sum_{ij} F_{ij}\Delta_i\Delta_j + \frac{1}{6}\sum_{ijk} F_{ijk}\Delta_i\Delta_j\Delta_K + \frac{1}{24}\sum_{ijkl} F_{ijkl}\Delta_i\Delta_j\Delta_k\Delta_l. \tag{1}$$

in which the $F_{ij...}$ represents the force constants and Δ_i describe the displacements. The QFFs for the $HCOH^+$ molecule are constructed separately for both the *cis*- and *trans*- conformers. The spin restricted open-shell Hartree Fock (ROHF) reference wavefunctions; (Scheiner et al., 1987) coupled cluster singles, doubles, and perturbative triples [CCSD(T)]; (Crawford and Schaefer III, 2000; Raghavachari et al., 1989) and the PSI4 program (Turney et al., 2012) are used in the computations for all $HCOH^+$ QFFs.

The standard approach utilized in our group (Fortenberry et al., 2011; Huang and Lee, 2008; 2009; Huang et al., 2011) (defined below) is performed for each $\tilde{X}\ ^2A'$ $HCOH^+$ conformer ground state. The geometry is optimized with the aug-cc-pV5Z basis set (Dunning, 1989) and then corrected with optimized geometry differences including and excluding core electrons with the Martin-Taylor (MT) core correlating basis set (Martin and Taylor, 1994). Once the reference geometries for the two types of $\tilde{X}\ ^2A'$ ground states are computed, a grid of 743 symmetry unique points are used to describe each QFF. The displacements of the bond lengths are in increments of 0.005 Å and 0.005 rad for the bond angles. The internal coordinates for the *cis*- and *trans*-$HCOH^+$ molecules are as follows:

$$I_1(a') = H_\alpha - C \tag{2}$$

$$I_2(a') = C - O \tag{3}$$

$$I_3(a') = O - H_\beta \tag{4}$$

$$I_4(a') = \angle(H_\alpha - C - O) \tag{5}$$

$$I_5(a') = \angle(C - O - H_\beta) \tag{6}$$

$$I_6(a'') = \tau(H_\alpha - C - O - H_\beta) \tag{7}$$

with the hydrogen bonded to the carbon listed as H_α and H_β bonded to the oxygen giving the H_α–C–O–H_β reference atomic arrangement.

Single point energy computations are generated at each displaced geometry using the aug-cc-pVTZ, QZ, and 5Z basis sets. A three-point, total energy complete basis set (CBS) limit energy (Fortenberry et al., 2014b; Martin and Lee, 1996),

$$E(l) = A + B\left(l + \frac{1}{2}\right)^{-4} + C\left(l + \frac{1}{2}\right)^{-6}, \tag{8}$$

giving the first "C" term in our CcCR approach, is produced by extrapolating the three energies via a three-point formula. The differences in the MT basis set energies are, again, used to correct for core correlation ("cC"), and scalar relativity ("R") is also included from differences in the cc-pVTZ-DK basis set (de Jong et al., 2001; Douglas and Kroll, 1974) with relativity included and excluded. The "R" computations make use of the MOLPRO 2010.1 quantum chemistry code (Werner et al., 2010).

The equilibrium geometry is derived using a least squares approach for fitting the energy points. A refitting of the points is conducted to ensure a minimum is found on the potential energy surface, to create zeroed gradients, and to produce the quadratic, cubic, and quartic force constants terms that describe the QFF. The