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Coupled Cluster Predictions of Spectroscopic Parameters for (Potential) Interstellar Protonated Species

E. E. Etim[1,*], I. E. Mbakara[2], G. P. Khanal[3], E. J. Inyang, O. P. Ukafia and I. F. Sambo
[1]Department of Chemical Sciences, Federal University Wukari, Nigeria.
[2]Department of Chemistry, University of Ibadan, Ibadan.
[3]Department of Inorganic and Physical chemistry, Indian Institute of Science, 560012, Bangalore, India.

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ABSTRACT

Most of the interstellar protonated molecules that have been shown to be astronomically detectable based on recent studies could be termed as 'non-terrestrial' species as a number of them are yet to be probed in the terrestrial laboratory, thus, the rotational transitions required for their astronomical searches are not available. In this study, the coupled cluster variant CCSD(T) together with the aug-cc-pVTZ basis set has been used to predict the spectroscopic parameters of four known neutral interstellar molecules and their corresponding protonated analogues of which two; H_2NCO^+ and H_2COH^+ have been astronomically detected. The protonated analogues of H_2NCN and H_2CS are potential interstellar species from recent studies. The predicted rotational constants/transitions are in good agreement for those with known experimental data, thus, these spectroscopic parameters could guide the astronomical searches and laboratory measurement of these species without experimentally determined spectroscopic constants.

1.0 Introduction

Molecular hydrogen, H_2 is of course the most abundant molecule in the universe. However, under the conditions of the interstellar medium (ISM), neutral atoms and molecules tend to be unreactive with H_2; thus, the gas phase chemistry in ISM is driven largely by ion-molecule reactions with cosmic ray, UV radiation or X-rays from black hole or high speed shocks as ionization sources. Cosmic ray ionization of H_2 leads to H_2^+ which reacts with other H_2 molecules to form the protonated molecular hydrogen; H_3^+ - a stable but very reactive ion. This reactive and abundant protonated molecular hydrogen easily donates its proton to other neutral atoms and molecules; thus every interstellar molecule is subject to protonation.[1,2] The recombination of these protonated species with electron leads to the formation of neutral species and this is one of the main formation routes for interstellar molecules. Metastable isomers which are well known among interstellar molecules are believed to be formed via this route and as such, it suffices to say that for the neutral metastable isomers, their protonated analogues are also present and detectable in ISM.[3,4,5] These protonated species are not only helpful as major players in interstellar chemical reactions; they are also useful probes for their neutral non-polar analogues (that easily evade astronomical detection) and for chemical modeling of interstellar chemical processes.

Table 1 contains the list of all the currently known interstellar and circumstellar molecules; the protonated species represent only about 10% of all the known molecules in space despite their key role in the interstellar chemical processes. Availability of accurate rotational transitions remains one of the primary requirements for the astronomical searches for molecules.

Unlike the neutral molecules, having enough concentration of ions n gas phase to probe their rotational spectra is difficult. This of course is one of the reasons for the limited number of known ins among interstellar and circumstellar molecules. Thus, the astronomical detection of ions relying in matching of laboratory measured rotational transitions with emission lines from the ISM using radio telescope can be seen as a biased procedure as it places a limit to the ions that can be detected in ISM (only those with laboratory measured transitions).

However, every successful laboratory measurement of rotational transitions of neutral and other molecular species has always been a concerted effort between experiment and theory. Of course, theoretical tools have been shown to be effective in guiding successful astronomical detection of molecules with no laboratory measured transitions. That a number of molecules such as HNC, HCO^+, HOC^+, N_2H^+, C_3N, $HCNH^+$, C_2H, etc., were first detected in ISM before their identification in the terrestrial laboratory attests to this fact.[6,7,8,9,10,11,12] As simple as this may sound, not all theoretical predictions of rotational transitions can lead to successful astronomical detection. A very high accuracy is required for the predicted rotational transitions in order for such transitions to be able to guide astronomical searches and possible astronomical observation. This of course, places on constraint on the methods or levels of theory to be considered in order to achieve the desired high accuracy. In this regard, the CCSD(T)-the gold standard (used in this study) is unarguably good enough and highly sufficient in predicting rotational transitions to the desired accuracy.[13]

It is not news that the interstellar abundance of related molecular species is directly linked to their stability except

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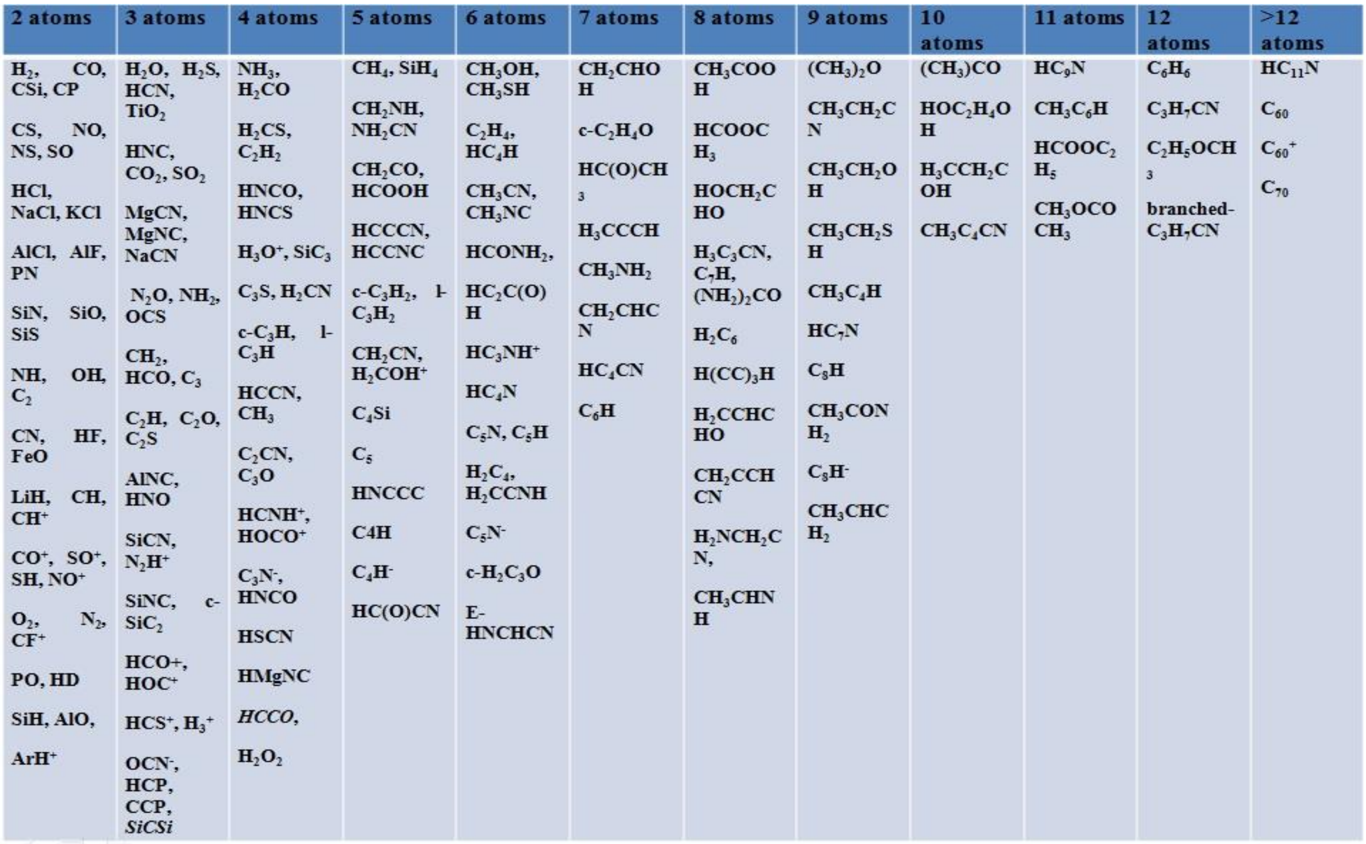
Tele:
E-mail address: emmaetim@gmail.com

Table 1. List of interstellar and circumstellar molecules[5].



2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2, CO, CSi, CP CS, NO, NS, SO HCl, NaCl, KCl AlCl, AlF, PN SiN, SiO, SiS NH, OH, C_2 CN, HF, FeO LiH, CH, CH^+ CO^+, SO^+, SH, NO^+ O_2, N_2, CF^+ PO, HD SiH, AlO, ArH^+	H_2O, H_2S, HCN, TiO_2 HNC, CO_2, SO_2 MgCN, MgNC, NaCN N_2O, NH_2, OCS CH_2, HCO, C_3 C_2H, C_2O, C_2S AlNC, HNO SiCN, N_2H^+ SiNC, c-SiC_2 HCO+, HOC^+ HCS^+, H_3^+ OCN^-, HCP, CCP, *SiCSi*	NH_3, H_2CO H_2CS, C_2H_2 HNCO, HNCS H_3O^+, SiC_3 C_3S, H_2CN c-C_3H, l-C_3H HCCN, CH_3 C_2CN, C_3O $HCNH^+$, $HOCO^+$ C_3N^-, HNCO HSCN HMgNC *HCCO*, H_2O_2	CH_4, SiH_4 CH_2NH, NH_2CN CH_2CO, HCOOH HCCCN, HCCNC c-C_3H_2, l-C_3H_2 CH_2CN, H_2COH^+ C_4Si C_5 HNCCC C4H C_4H^- HC(O)CN	CH_3OH, CH_3SH C_2H_4, HC_4H CH_3CN, CH_3NC $HCONH_2$, $HC_2C(O)H$ HC_3NH^+ HC_4N C_5N, C_5H H_2C_4, H_2CCNH C_5N^- c-H_2C_3O E-HNCHCN	CH_2CHOH c-C_2H_4O $HC(O)CH_3$ H_3CCCH CH_3NH_2 CH_2CHCN HC_4CN C_6H	CH_3COOH $HCOOCH_3$ $HOCH_2CHO$ H_3C_3CN, C_7H, $(NH_2)_2CO$ H_2C_6 $H(CC)_3H$ $H_2CCHCHO$ CH_2CCHCN H_2NCH_2CN, CH_3CHNH	$(CH_3)_2O$ CH_3CH_2CN CH_3CH_2OH CH_3CH_2SH CH_3C_4H HC_7N C_8H CH_3CONH_2 C_8H^- CH_3CHCH_2	$(CH_3)CO$ HOC_2H_4OH H_3CCH_2COH CH_3C_4CN	HC_9N CH_3C_6H $HCOOC_2H_5$ CH_3OCOCH_3	C_6H_6 C_3H_7CN $C_2H_5OCH_3$ branched-C_3H_7CN	$HC_{11}N$ C_{60} C_{60}^+ C_{70}

where other effects like interstellar hydrogen bonding, different formation routes, etc, dominate. The stability of protonated species is directly related to the magnitude to which the proton is bonded to the neutral molecule. Thus, neutral molecules with high proton binding energies (PBEs) will definitely have more stable protonated analogues than those with low PBEs. This has been well demonstrated in a recent study.[14] Where a neutral molecule is protonated from two different positions in the molecular structure, the protonated species resulting from a high PBE is more stable than its counterpart with low PBE from the same molecule. The more stable protonated species is also more abundant in ISM. The case of HCO^+ and HOC^+ is a perfect example where the reported interstellar abundances confirm the fact that the protonated species from a high PBE (HCO^+) is more abundant than the one from a low PBE (HOC^+).[8,15]

In the present study, four neutral interstellar molecules; H_2CO, H_2CS, HNCO, H_2NCN and their protonated analogues are considered. The protonated analogues of H_2CO and HNCO have been detected in the interstellar medium.[16,17,18,19]. The high PBEs for these neutral molecules whose protonated analogues are yet to be astronomically observed as compared to those with known protonated analogues strongly suggest the protonated analogues of these neutral molecules as potential interstellar molecules. However, there is little or death of information regarding the rotational transitions of some of these protonated species (either experimentally or theoretically) to warrant their astronomical searches. The present study therefore aims at predicting accurate rotational constants, rotational transitions and dipole moments for all the neutral species and their protonated analogues considered in this study at the CCSD(T) level of theory with the Dunning's aug-cc-pVTZ basis set.[13,20,21] The predicted spectroscopic parameters are meant to guide the laboratory measurement and astronomical searches of these protonated species whose rotational spectra have not been reported while the species with known experimental spectroscopic parameters are used as references in checking the accuracy of our predictions.

2.0 Computational details

In order to achieve the desired high accuracy in this study, the well-known coupled cluster with single and double substitutions which includes connected triple substitution in a perturbative way, CCSD(T) is used. The CCSD(T) is used in conjunction with the Dunning's augmented correlation consistent basis set; aug-cc-pVTZ.[13,20,21] Gaussian 09 suit of programs is employed for all the calculations reported here.[22] The geometries of all the neutral molecules and their protonated analogues were optimized using the method and basis set mentioned above. Harmonic frequencies calculations were carried out to confirm stable equilibrium geometries with no imaginary frequency. After predicting the rotational constants for those molecules which define their frequency regions for radio astronomical searches and their laboratory measurement in the terrestrial laboratory, these rotational constants were used in predicting the rotational transitions with the help of the ASROT program (http://www.ifpan.edu.pl/~kisiel/prospe.htm). The neutral molecules and their protonated analogues are isoelectronic which represent enough similarities in terms of structural parameters and mass, thus, the same method that is able to predict accurate spectroscopic parameters for the neutral molecules by extension should be able to predict for the protonated analogues.

3.0 Results and discussion

3.1 H_2CO and H_2COH^+: Formaldehyde and its oxygen protonated are known interstellar molecular species.[18,23] As would be expected, the neutral species, H_2CO was first detected (in 1969) before the protonated analogue (in 1996). This trend in their astronomical observation could be traced to the available of the spectroscopic constants as the neutral species are easily studied as compared to the protonated analogues/ions. Table 1a contains the experimental and calculated rotational constants for H_2CO and H_2COH^+. The calculated rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ basis set are in good agreement with the experimentally measured rotational constants for both the neutral and protonated species. In both cases, the percentage deviation ranges from 0.009 to 1.13 for all the rotational constants. This high level of accuracy strongly supports the fact that the rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ could guide successful astronomical searches for these molecular species assuming the experimental values are not available. The rotational transitions obtained with the ASROT program are contained in Table 1b. The percentage deviation ranges from 0.02 to 0.96 for all the rotational transitions obtained for the two molecular species with known experimental parameters.

Table 1a. Rotational constants for H_2CO and H_2COH^+.

Rotational constants	Experiment (MHz)[a,b]	CCSD(T)/aug-cc-pVTZ (MHz)	Δ%
H_2CO			
A	281,968.90	285,165.26	1.13
B	38,836.11	38,553.00	0.73
C	34,002.21	33,961.56	0.12
H_2COH^+			
A	197,581.544	197,756.63	0.09
B	34,351.547	34,286.29	0.19
C	29,171.669	29,220.21	0.17

[a]Dangoisse et *al.*[24] ; [b]Dore et *al.*[25]

Table 1b. Rotational transitions for H_2CO and H_2COH^+.

Rotational transitions	Observed[a,b] (MHz)	Calculated (MHz)	Δ(GHz)
H_2CO			
1_{01}-0_{00}	72,837.97	72,514.56	0.32
2_{12}-1_{11}	140,839.65	140,437.68	0.40
2_{02}.1_{01}	145,603.08	144,965.60	0.64
2_{11}-1_{10}	150,498.45	149,620.56	0.88
2_{11}-2_{12}	14,488.65	13,774.32	0.71
3_{03}-2_{02}	218,222.19	217,289.69	0.93
3_{22}-2_{21}	218,475.66	217,543.68	0.93
3_{13}-2_{12}	211,211.43	210,617.09	0.59
3_{21}-2_{20}	218,760.07	217,797.67	0.96
H_2COH^+			
2_{12}-1_{11}	121,864.526	121,946.920	0.08
2_{11}-2_{02}	173,697.518	173,718.434	0.02
3_{03}-2_{02}	190,079.131	190,056.166	0.02
3_{13}-2_{12}	182,719.152	182,848.732	0.13
3_{12}-2_{11}	198,248.992	198,045.313	0.20
3_{22}-2_{21}	190,548.754	190,519.500	0.03
3_{21}-2_{20}	191,032.797	190,982.834	0.05
3_{12}-3_{03}	181,867.359	181,707.582	0.16

[a]Dangoisse et *al.*[24] ; [b]Dore et *al.*[25]

3.2 H_2CS and H_2CSH^+: These are the sulphur analogues of the H_2CO and H_2COH^+ discussed above. The H_2CS is a known interstellar molecule detected from the Sagittarius B2 molecular cloud [26] but the protonated analogue is yet to be astronomically observed and there are no literatures regarding its astronomically searches (whether successful or not). The reason for this could be traced to the lack of spectroscopic parameters for the protonated analogue (H_2CSH^+) that could warrant its astronomical searches. Table 2a contains the experimental and calculated rotational constants for H_2CS. It also contains the calculated rotational constants for H_2CSH^+ with no experimental data. The calculated rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ basis set are in good agreement with the experimentally measured rotational constants for the neutral molecule, H_2CS.

Thus, the predicted rotational constants for the protonated species are believed to be accurate and could guide the astronomical searches for this species. The rotational transitions obtained with the ASROT program are presented in Table 2b. With respect to the possible presence of H_2CSH^+ in detectable amount in the interstellar or circumstellar medium, there exist some periodic trends among the known interstellar and circumstellar molecules. This relationship is conspicuously observed among the O and S containing interstellar and circumstellar molecular species. Of the 19 known S-containing molecules, 16 have the corresponding O-analogues as known interstellar and circumstellar molecules. Thus, the fact that the O-analogue of H_2CSH^+ is a known interstellar molecule suggests it possible presence and detectability in the interstellar medium. Hence, with the availability of spectroscopic parameters, this molecule could be successfully searched for in the various astronomical sources.

Table 2a. Rotational constants for H_2CS and H_2CSH^+.

Rotational constants	Experiment (MHz)[a]	CCSD(T)/aug-cc-pVTZ (MHz)	Δ%
H_2CS			
A	291,660.05±50	293,075.86	0.48
B	17,699.5551±0.0056	17,482.59	1.23
C	16,653.0621±0.0065	16,498.43	0.93
H_2CSH^+			
A	-	143,489.23	
B	-	17,137.91	
C	-	15,309.41	

[a]Johnson et *al.*[27]

Table 2b. Rotational transitions H_2CS and H_2CSH^+.

Rotational transitions	Observed[a] (MHz)	Calculated (MHz)	Δ(GHz)
H_2CS			
1_{01}-0_{00}	33,029.96	33,981.02	0.95
2_{02}-1_{01}	66,057.02	67,959.41	1.90
2_{12}-1_{11}	65,089.85	66,977.88	1.89
2_{11}-1_{10}	67,054.96	68,946.20	1.89
H_2CSH^+			
1_{01}-0_{00}	-	32,447.32	
2_{02}-1_{01}	-	64,874.94	
2_{12}-1_{11}	-	63,066.14	
2_{11}-1_{10}	-	66,723.14	
3_{03}-2_{02}	-	97,263.16	
3_{21}-2_{20}	-	97,420.75	
3_{13}-2_{12}	-	94,586.96	
3_{22}-2_{21}	-	97,341.96	

[a]Johnson et *al.*[27]

3.3 HNCO and H_2NCO^+: The neutral molecule HNCO belongs to the CHNO isomeric group in which three of the isomers; cyanic acid, isocyanic acid and fulminic acid are known interstellar molecular species.[28,29,30,31,32,33,34] The only isomer of the group that is yet to be astronomically observed is iso-fulminic acid which is the least stable among the isomers. Table 3a displays the experimental and calculated rotational constants for HNCO and H_2NCO^+. The protonated analogue of HNCO (H_2NCO^+) is a known interstellar molecular species.[19] The calculated rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ basis set are in good agreement with the experimentally measured rotational constants for both the neutral and protonated species except for the A rotational constant. The rotational transitions obtained with the ASROT program are contained in Table 3b. The percentage deviation ranges from 0.61 to 11.41% for all the rotational transitions obtained for the two molecular species with known experimental parameters.

This high level of accuracy obtained strongly supports the fact that the rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ could guide successful astronomical searches for these molecular species assuming the experimental values are not available as in the case of H_2NCNH^+ (discussed below).

Table 3a. Rotational constants for HNCO and H_2NCO^+.

Rotational constants	**Experiment (MHz)[a,b]**	**CCSD(T)/aug-cc-pVTZ (MHz)**	**Δ%**
HNCO			
A	912,712.288(136)	808,563.69	11.41
B	11,071.01027(62)	10,991.29	0.72
C	10,910.57748(64)	10,843.89	0.61
[c]H_2NCO^+			
A	319782(103)	321,817.6721	0.64
B	10278.6846(26)	10,198.2345	0.78
C	9948.9034(23)	9,884.9852	0.64

[a]Kewley et *al.*[35] ; [b]Winnewisser et *al.*[36], [c]Gupta et *al.*[19]

Table 3b. Rotational transitions for HNCO and H_2NCO^+.

Rotational transitions	**Observed[a] (MHz)**	**Calculated (MHz) CCSD(T)**	**Δ(GHz)**
HNCO			
1_{01}-0_{00}	21,981.470	21,835.180	0.15
2_{02}-1_{01}	43,963.000	43,670.340	0.29
2_{11}-1_{10}	44,119.757	43,817.760	0.30
2_{12}-1_{11}	43,798.873	43,522.960	0.27
3_{03}-2_{02}	65,944.301	65,505.458	0.44
3_{13}-2_{12}	65,698.262	65,284.427	0.41
3_{12}-2_{11}	66,179.531	65,726.627	0.45
3_{22}-2_{21}	65,294.015	65,505.540	0.21
4_{04}-3_{03}	87,925.252	87,340.516	0.58
4_{14}-3_{13}	87,597.342	87,045.879	0.55
4_{13}-3_{12}	88,239.039	87,635.479	0.60
H_2NCO^+			
1_{01}-0_{00}	20225.977(5)	20083.219700	
2_{12}-1_{11}	40122.510(5)	39853.190100	
2_{02}-1_{01}	40453.209(5)	40166.203353	

[a]Kewley et *al.*[35] ; [b]Winnewisser et *al.*[36]

3.4 H_2NCN and H_2NCNH^+: The H_2N_2C isomeric group has at least three possible isomers; H_2NCN, NH_2NC, CH_2N. Of these isomers, the H_2N_2C is a known interstellar molecular species.[34] The astronomically observed isomer is also found to be the most stable isomer of the group suggesting a possible link between the stability of a molecule and its astronomical observation. Table 4a contains the experimental and calculated rotational constants for H_2NCN.

Table 4a. Rotational constants for H_2NCN and H_2NCNH^+.

Rotational constants	**Experiment (MHz)[a,b]**	**CCSD(T) (MHz)**	**Δ%**
H_2NCN			
A	310885±450	310407.59	0.15
B	10130.62	10030.90	0.98
C	9866.422	9807.19	0.60
H_2NCNH+			
A		288,709.79	
B		9,566.00	
C		9,328.71	

[a]Kewley et *al.*[35] ; [b]Winnewisser et *al.*[36]

It also contains the calculated rotational constants for H_2NCNH^+ with no experimental data. The calculated rotational constants obtained at the CCSD(T) level with the aug-cc-pVTZ basis set are in excellent agreement with the experimentally measured rotational constants for the neutral molecule, H_2NCN with a percentage deviation in range of 0.15 to 0.98. Thus, the predicted rotational constants for the protonated species, H_2NCNH^+ are believed to be accurate and could guide the astronomical searches for this species. The rotational transitions obtained with the ASROT program are presented in Table 4b. For the neutral species with known experimental rotational constants, the percentage deviation for the predicted transition ranges from 0.14 to 0.42. This high accuracy for the predicted transition for the known neutral species strongly supports the use of the predicted transitions for the protonated species for its astronomical searches.

Table 4b. Rotational transitions for H_2NCN and H_2NCNH^+.

Rotational transitions	**Observed (MHz)**	**Calculated (MHz) CCSD(T)**	**Δ(GHz)**
H_2NCN			
1_{01}-0_{00}	19979.7	19838.1	0.14
2_{02}-1_{01}	39958.5	39676.1	0.28
2_{12}-1_{11}	39712.5	39452.5	0.26
2_{11}-1_{10}	40205.2	39899.9	0.30
3_{03}-2_{02}	59937.2	59513.8	0.42
H_2NCNH^+			
1_{01}-0_{00}		18894.7	
2_{02}-1_{01}		37789.3	
2_{12}-1_{11}		37552.1	
2_{11}-1_{10}		38026.7	
3_{03}-2_{02}		56683.5	

4. Conclusion

Ions play a profound role in interstellar chemical processes. This letter reports the rotational constants and dipole moment for four neutral interstellar molecules (with high proton binding energies) and their protonated analogues with the CCSD(T) (the gold standard) method. The CCSD(T) method gives excellent estimates of the rotational constants/transitions for the neutral and protonated species with known experimental values. These spectroscopic parameters are thus sufficiently accurate to guide the astronomical searches of these protonated species that are highly detectable and for probing these protonated species in the laboratory.

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