Theoretical and experimental studies on hydrogen migration in dissociative ionization of methanol monocation to molecular ions H_3^+ and H_2O^+

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1. Experimental Details

The femtosecond laser system consists of an ultrafast Ti:Sapphire oscillator (Micra-5, Coherent) and an amplifier (Legend Elite, Coherent). The output laser pulses from the oscillator are stretched, amplified, and compressed to produce linearly femtosecond laser pulses with central wavelength of 800 nm (~40 nm bandwidth), pulse duration of 35 fs, repetition rate of 1 KHz, and the maximum single-pulse energy of 3.5 mJ. The output laser pulses are focused onto gaseous methanol by a quartz lens. The focal length of the quartz lens is 40 cm. A combination of a half-wave plate and a glan laser polarizer is inserted into the laser beam path to change the injection energies. For this experiment, the laser polarization direction is kept perpendicular to the time-of-flight axis by a half-wave plate. The pulse duration of the injection laser is determined by the measured value of PluseSout Autocorrelator (Spectra-Physics) dividing a value by $\sqrt{2}$, and the calculated pulse duration is 120 fs. The intensity of femtosecond laser is calculated by formula: $I = (f \times \tau \times A)^{-1} \times P$. In this formula, f, τ, A, and P represent repetition rate, pulse width, focal area and average power respectively. The value of focal area A is obtained by formula: $A = 4\pi f^2 \lambda^2 / D^2$, where λ, D represent central wavelength and laser spot diameter before being focused onto gaseous methanol. The calculated laser intensity is calibrated by Ar^{2+}/Ar^{+} ratio

proposed by Guo *et al.*[45], and the calibrated intensities at focal point are in the range of 2.7×10^{13} ~ 1.4×10^{14} W/cm^2.

The experiment is performed in our home-built dc slice imaging system, as schematically shown in Fig. 1. The experimental apparatus mainly consists of a home-built time-of-flight (TOF) mass spectrometer and a two-dimensional (2D) position sensitive detector. The TOF mass spectrometer is divided into two components by a skimmer, which are source chamber and main chamber. The details of our experimental setup are as follows:

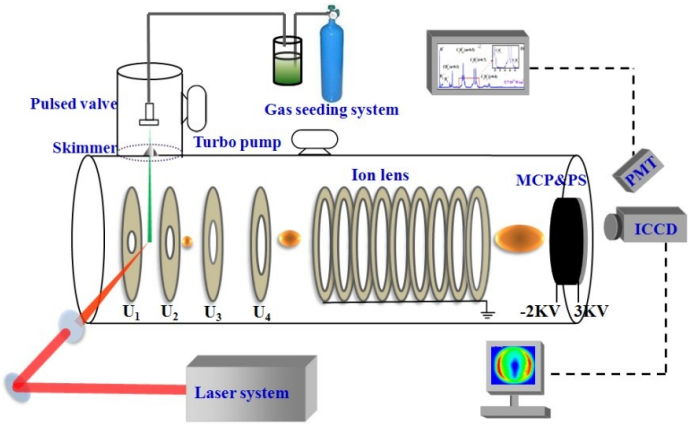


Figure 1. Schematic of our home-built dc slice imaging apparatus.

The source chamber is pumped by backing vacuum pump (TriScroll-600, Agilent Technologies Inc.) and turbo molecular pump (TMH/U 276, Pfeiffer Vacuum). The main chamber is pumped by backing vacuum pump (TriScroll-600, Agilent Technologies Inc.) and turbo molecular pump (TMH/U 5, Pfeiffer Vacuum). The background pressures for the source and main chambers are 3.0×10^{-7} and 4.2×10^{-8} mbar respectively. After the molecular beam is introduced, the corresponding pressures for the source and main chambers increase to 4.2×10^{-6} and 2.9×10^{-7} mbar respectively. The methanol sample is custom-made from Sinopharm Chemical Reagent Co., Ltd. It is anhydrous grade, 99.9+% purity, and the water content in methanol would not exceed 0.005%. The methanol sample at room temperature is mixed with helium (He) gas at 1 atm with the ratio of 1:9. The gas mixtures are introduced into the source chamber by pulsed valve to form a supersonic molecular beam. The piezoelectric pulsed valve (general valve, Parker) operates at 100 Hz with a duration time of 100 μs and has an orifice with diameter of 0.2 mm. A skimmer with diameter of 1 mm is mounted under the nozzle with the distance of 20 mm to separate the source chamber from the main chamber, and is used to align the supersonic molecular beam. After going through the

skimmer, the gas mixtures go into the ionization region of the main chamber. The multi-stage ion lens is installed in the main chamber, which has the similar geometry described by Suits.[22] The voltages applied on the electrodes are U_1=2500 V, U_2=2178 V, U_3=2076 V and U_4=0 V, which have been optimized according to the ion trajectory calculations simulated by SIMION 8.0 software. In such a condition, all ions with the same velocity vector can map on the same point of the detector. The temporal spread for ion cloud along TOF axis is about 350 ns, the space resolution is better than 1%, and the spatial magnification N for different ions with different kinetic energy is about 0.90±0.01.

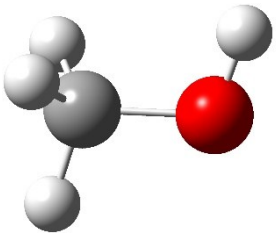
The laser and methanol molecular beam are crossed perpendicularly in the middle of the repeller and extractor plates of a multi-stage ion lens. The produced fragment ions are accelerated by ion lens and detected by two-stage microchannel plates (MCPs, Hamamatsu F2226-24) coupled to a P47 phosphor screen (PS) in a field-free region. The dc sliced images of ion cloud are obtained by an intensified charge coupled device (ICCD) camera (Princeton Instruments PI-MAXII, 512×512 pixels) with time gate of 4 ns. The TOF mass spectra are acquired by a photomultiplier tube (PMT, Hamamatsu H7732-10) connected to a digital oscilloscope and transferred to a computer for storage and analysis. Both sliced images and TOF spectra in this paper are treated for background subtraction, in order to eliminate the impact from impurities and water in the cavity. All the timing sequence control is optimized by a digital delay pulse generator (DG535, Stanford Research System).

(45) C. L. Guo, M. Li, J. P. Nibarger, G. N. Gibson, *Phys. Rev. A* **1998**, *58*, R4271-R4274.

2. GaussView Structures, Sum of electronic and zero-point Energies, Zero-point correction, Cartesian Coordinates for various isomers along dissociation pathway of methanol monocation calculated at b3lyp/6-311++G(d,p) level of theory and Electronic Energies at CCSD(T)/CC-pVTZ level of theory:

CH_3OH

GaussView Structure (Optimized at b3lyp/6-311++G(d,p) level of theory):

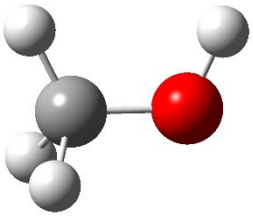


Sum of electronic and zero-point Energies = -115.713959
Zero-point correction= 0.051040
Energy at CCSD(T)/CC-pVTZ level= -115.53588769
Cartesian Coordinates:

C	0.66765200	-0.02036700	0.00010000
H	1.02916500	-0.54360700	0.89356500
H	1.02908500	-0.54545600	-0.89252400
H	1.08343600	0.98740500	-0.00164900
O	-0.74981300	0.12203800	0.00008100
H	-1.14908900	-0.75244100	-0.00063500

CH_3OH^+

GaussView Structure (Optimized at b3lyp/6-311++G(d,p) level of theory):

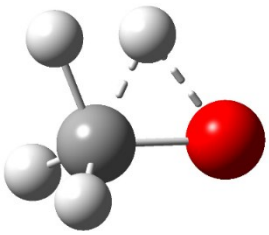


Sum of electronic and zero-point Energies = -115.324469
Zero-point correction= 0.047001
Energy at CCSD(T)/CC-pVTZ level= -115.14011006
Cartesian Coordinates:

C	0.63502200	0.06917800	-0.00020400
H	0.97650800	1.10102700	-0.00074100
H	1.05708500	-0.57636300	0.82558800
H	1.05745100	-0.57848400	-0.82368100
O	-0.70705700	-0.13191500	-0.00003200
H	-1.24472300	0.69407400	0.00031600

TS1

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

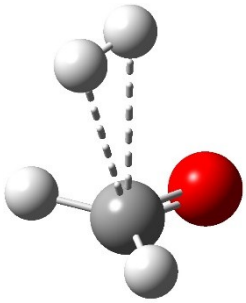


Sum of electronic and zero-point Energies = -115.220490
Zero-point correction= 0.041841
Energy at CCSD(T)/CC-pVTZ level= -115.03507461
Cartesian Coordinates:

C	0.57986400	-0.10590500	0.00015400
H	1.10528500	1.00274500	-0.00076600
H	0.96552000	-0.56411500	0.92354400
H	0.96651700	-0.56416200	-0.92281900
O	-0.82655100	-0.03755100	-0.00024300
H	0.09589600	1.06136700	0.00106300

S1

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

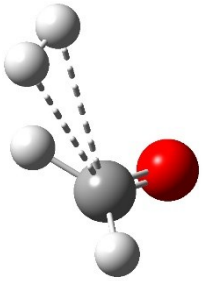


Sum of electronic and zero-point Energies = -115.254685
Zero-point correction= 0.036688
Energy at CCSD(T)/CC-pVTZ level= -115.09844286
Cartesian Coordinates:

C	0.09375000	-0.45863200	0.00009300
H	2.52055700	0.41870900	0.00533400
H	0.48180000	-0.85627700	0.96928300
H	0.47509100	-0.86327700	-0.96883900
O	-0.77571600	0.37191200	0.00027600
H	2.16578000	1.07733800	-0.00854100

TS2

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

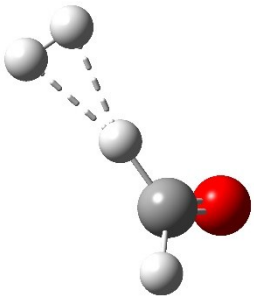


Sum of electronic and zero-point Energies = -115.288112
Zero-point correction= 0.035420
Energy at CCSD(T)/CC-pVTZ level= -115.09777664
Cartesian Coordinates:

C	0.05594200	0.40067700	-0.08261900
H	2.61384000	-0.89869100	0.20293200
H	0.81992200	0.22715700	-0.88493700
H	0.16502600	1.28712600	0.59286000
O	-0.85303300	-0.35207600	0.05227000
H	2.88982400	-0.20304700	0.16670200

S2

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

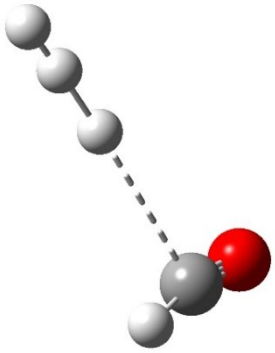


Sum of electronic and zero-point Energies = -115.291047
Zero-point correction= 0.036310
Energy at CCSD(T)/CC-pVTZ level= -115.09805256
Cartesian Coordinates:

C	0.03887000	0.40400000	-0.00009300
H	2.76825100	-0.44713800	-0.37794500
H	1.13022700	0.04583700	-0.00271400
H	-0.15810600	1.50610800	0.00255000
O	-0.84221600	-0.38418300	-0.00010600
H	2.76413700	-0.45534400	0.37951400

TS3

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

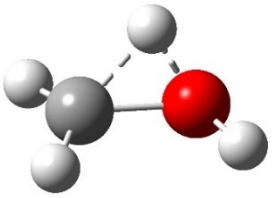


Sum of electronic and zero-point Energies = -115.24270749
Zero-point correction= 0.028944
Energy at CCSD(T)/CC-pVTZ level= -115.03870173
Cartesian Coordinates:

C	-0.32495400	0.46680300	-0.00004900
H	3.28791400	-0.27595100	-0.00030500
H	2.21293500	-0.09630900	0.00240100
H	0.08830500	1.47613600	-0.00022300
O	-0.96755500	-0.44177700	-0.00005100
H	4.10100900	-0.37047800	-0.00116700

TS4

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

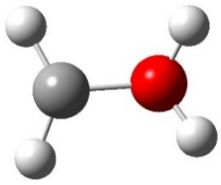


Sum of electronic and zero-point Energies = -115.276130
Zero-point correction= 0.044693
Energy at CCSD(T)/CC-pVTZ level= -115.09590297
Cartesian Coordinates:

C	0.74293200	0.03455100	0.00855900
H	1.24819000	-0.87102500	-0.30734800
H	1.14761500	1.03966700	-0.02267900
O	-0.69448700	-0.10488400	-0.08351200
H	-0.13466400	-0.29580400	0.98082400
H	-1.16283800	0.75892300	-0.03405400

$CH_2OH_2^+$

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

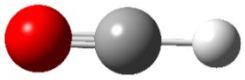


Sum of electronic and zero-point Energies = -115.326883
Zero-point correction= 0.049165
Energy at CCSD(T)/CC-pVTZ level= -115.15489461
Cartesian Coordinates:

C	-0.81155900	-0.00000500	0.08582300
H	-1.23125300	0.96755100	-0.14792600
H	-1.23127000	-0.96750600	-0.14812500
O	0.63968600	-0.00001100	-0.07907200
H	1.10719100	0.81045800	0.20671800
H	1.10720200	-0.81038600	0.20697100

CHO^+

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

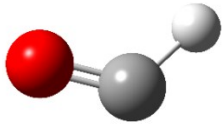


Sum of electronic and zero-point Energies = -113.565385
Zero-point correction= 0.016433
Energy at CCSD(T)/CC-pVTZ level= -113.37507152
Cartesian Coordinates:

C	0.00000000	0.00000000	-0.51518400
H	0.00000000	0.00000000	-1.61066700
O	0.00000000	0.00000000	0.58772100

CHO

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

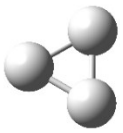


Sum of electronic and zero-point Energies = -113.878373
Zero-point correction= 0.012959
Energy at CCSD(T)/CC-pVTZ level= -113.878373
Cartesian Coordinates:

C	0.06177800	0.58369600	0.00000000
H	-0.86489400	1.22171500	0.00000000
O	0.06177800	-0.59048600	0.00000000

H_3^+

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):



Sum of electronic and zero-point Energies = -1.326274
Zero-point correction= 0.019951
Energy at CCSD(T)/CC-pVTZ level= -1.34149296
Cartesian Coordinates:

H	0.00000000	0.44084200	-0.25497300
H	0.00000000	-0.44084200	-0.25497300
H	0.00000000	0.00000000	0.50994600

H_3

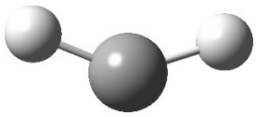
GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

Sum of electronic and zero-point Energies = -1.671447
Zero-point correction= 0.010349
Energy at CCSD(T)/CC-pVTZ level= -1.67215610
Cartesian Coordinates:

H	0.00000000	0.00000000	-1.53410400
H	0.00000000	0.00000000	-0.78985800
H	0.00000000	0.00000000	2.32396200

CH_2^+

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

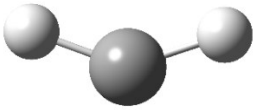


Sum of electronic and zero-point Energies = -38.766793
Zero-point correction= 0.016208
Energy at CCSD(T)/CC-pVTZ level= -38.69660696
Cartesian Coordinates:

C	0.00000000	0.00000000	0.09050800
H	0.00000000	1.03760500	-0.27152500
H	0.00000000	-1.03760500	-0.27152500

CH_2

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

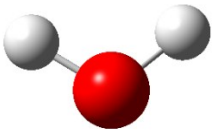


Sum of electronic and zero-point Energies = -39.130261
Zero-point correction= 0.016483
Energy at CCSD(T)/CC-pVTZ level= -39.05653815
Cartesian Coordinates:

C	0.00000000	0.00000000	0.17631300
H	0.00000000	0.86245300	-0.52893900
H	0.00000000	-0.86245300	-0.52893900

H_2O^+

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):

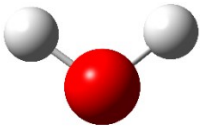


Sum of electronic and zero-point Energies = -75.974043
Zero-point correction= 0.018584
Energy at CCSD(T)/CC-pVTZ level= -75.87199217
Cartesian Coordinates:

O	0.00000000	0.00000000	0.11575200
H	0.00000000	0.82212800	-0.46300800
H	0.00000000	-0.82212800	-0.46300800

H_2O

GaussView Structure (Optimized at b3lyp/6-31g(d,p) level of theory):



Sum of electronic and zero-point Energies = -76.437252
Zero-point correction= 0.021279
Energy at CCSD(T)/CC-pVTZ level= -76.32446131
Cartesian Coordinates:

O	0.00000000	0.00000000	0.11707900
H	0.00000000	0.76357500	-0.46831600
H	0.00000000	-0.76357500	-0.46831600

3. Comparisons of GaussView Structures for various isomers along dissociation pathway of methanol monocation calculated at B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory.

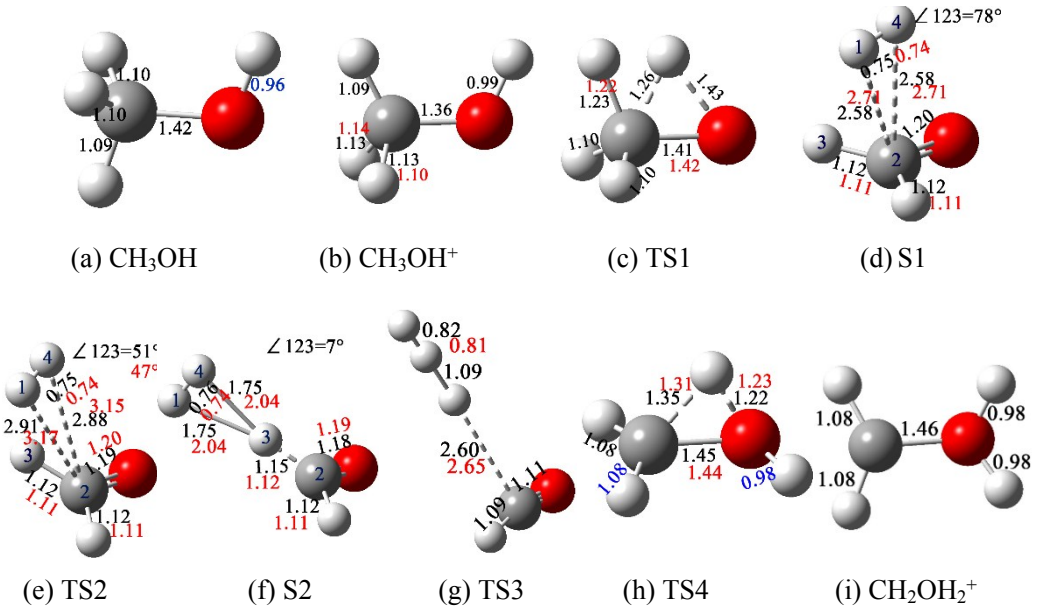


Figure 2. Comparisons of structures of CH_3OH, CH_3OH^+, TS1, S1, TS2, S2, TS3, TS4, and $CH_2OH_2^+$ ((a) – (i)) optimized at the theoretical levels of B3LYP/6-311++G (d, p) and MP2/6-311++G (d, p). The decimals represent the bond length of the corresponding chemical bond, and their units are in Å. The decimals in blue color represent the changes to the original manuscript. The chemical bond length and bond angle values in only black (blue) color represent that these values calculated at two different theoretical levels are the same. The chemical bond length and bond angle values in black (blue) and red color at the same time represent the different values are obtained for two different theoretical levels.