Geometrical structures, vibrational frequencies, force constants and dissociation energies of isotopic water molecules (H_2O, HDO, D_2O, HTO, DTO, and T_2O) under dipole electric field*

Shi Shun-Ping(史顺平)[a)†], Zhang Quan(张 全)[b)], Zhang Li(张 莉)[a)], Wang Rong(王 蓉)[a)], Zhu Zheng-He(朱正和)[a)], Jiang Gang(蒋 刚)[a)], and Fu Yi-Bei(傅依备)[c)]

[a)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

[b)] *School of Mechanical Engineering & Automation, Xihua University, Chengdu* 610039, *China*

[c)] *China Academy of Engineering Physics, Mianyang* 621900, *China*

(Received 22 March 2010; revised manuscript received 29 April 2010)

The dissociation limits of isotopic water molecules are derived for the ground state. The equilibrium geometries, the vibrational frequencies, the force constants and the dissociation energies for the ground states of all isotopic water molecules under the dipole electric fields from −0.05 a.u. to 0.05 a.u. are calculated using B3P86/6-311++G(3df,3pf). The results show that when the dipole electric fields change from −0.05 a.u. to 0.05 a.u., the bond length of H–O increases whereas the bond angle of H–O–H decreases because of the charge transfer induced by the applied dipole electric field. The vibrational frequencies and the force constants of isotopic water molecules change under the influence of the strong external torque. The dissociation energies increase when the dipole electric fields change from −0.05 a.u. to 0.05 a.u. and the increased dissociation energies are in the order of H_2O, HDO, HTO, D_2O, DTO, and T_2O under the same external electric fields.

Keywords: isotopic water molecules, equilibrium geometry, vibrational frequencies, force constants, dissociation energies

PACS: 31.15.es, 31.30.Gs, 33.15.Dj, 33.15.Fm **DOI:** 10.1088/1674-1056/20/6/063102

1. Introduction

It is well known that hydrogen, deuterium and tritium are very useful in many areas, such as energy sources, environmental protection, nuclear materials, military affairs and so on. How to extract hydrogen, deuterium and tritium from all isotopic water molecules is an important problem. There are many methods to solve the problem, for example, the combined electrolysis catalytic exchange (CECE) process[1] and photodissociation.[2,3]

Many studies have been performed on the isotopic water molecules, such as the theory of Monte Carlo (MC),[4] molecular dynamics (MD) simulations,[5−9] Hartree–Fock (HF) calculations,[10,11] *ab initio* methods,[12−19] and density functional theory (DFT),[20−24] while experiments[2,25−40] have been devoted to the research of the microscopic structures, potential energy surfaces and dynamic properties for isotopic water molecules. Császár *et al.*[13] and Barletta *et al.*[14] used high accuracy *ab initio* studied adiabatic potential energy surfaces (PESs) of the ground electronic state for water molecules. The potential energy surfaces (PESs) and dipole moment functions of water molecules were investigated by Partridge and Schwemke[15] through using high quality *ab initio* calculation. The anharmonic potential energy surface of water molecule had been computed by Martin *et al* [19] through using an augmented coupled cluster method and various basis sets.

A lot of work focuses on the Born–Oppenheimer (BO) approximation,[41−46] but the greatest difficulty in deriving dissociation energies, vibrational frequencies and force constants of HDO, HTO, D_2O, DTO and T_2O lies in its identity with those of H_2O in the BO approximation. Hence we propose that the effects of nuclear motions (translational, rotational and vibration motions) should be considered for the calculation of dissociation energies, vibrational frequencies and force constants of isotopic water molecules,

*Project supported by the National Natural Science Foundation of China (Grant No. 10676022).

†Corresponding author. E-mail: shunping_999@163.com

© 2011 Chinese Physical Society and IOP Publishing Ltd

so those parameters of isotopic water molecules are obtained by using the nuclear motions energy correct electronic energies. In this paper the DFT method is used to study the structures, vibrational frequencies, force constants and dissociation energies of isotopic water molecules under the dipole electric field by calculating nuclear vibration energies for correcting electronic energies, which are obtained in the BO approximation. The properties of water molecules and aqueous solutions under the external electric field are also simulated in other documents.[47−49]

2. Calculation method

All this work is performed with Gaussian 03 W.[50] The B3P86 method[51] with the basis set 6-311++G (3df, 3pf)[52,53] is used to calculate a variety of structures, force constants, vibrational frequencies and dissociation energies of isotopic water molecules under the dipole electric field. At this level, the bond lengths of H–O and bond angles of H–O–H in the ground states of isotopic water molecules are computed. The results along with the available experimental data[19] and other theoretical values[10,13,15,38] are listed in Table 1.

Table 1. Experimental data and theoretical values for water molecule.

Method and basis set/model	R_{OH}/Å	θ/(°)	Source
B3P86/6-311++G(3df,3pd)	0.9592	104.83	this work
Hartree–Fock/(6s5p2d/3s1p)	0.957	104.52	Ref. [10]
ab initio/PES	0.9578	104.490	Ref. [13]
Fitted empirical/PES	0.9578	104.509	Ref. [15]
B3LYP/ 6-311++ G**	0.9620	105.165	Ref. [38]
Experiment	0.957	104.5	Ref. [19]

These water molecular geometry parameters were optimized in a series of calculations,[10,13,15,38] which gave good agreements with the experimental values.[19] As it is shown in Table 1, the O–H bond length is 0.9592 Å (1 Å=0.1 nm) with a bond angle is 104.833° and the corresponding experimental equilibrium bond length and bond angle are 0.957 Å and 104.5°, respectively.[19] Clearly, the differences are very small. So we expect that the DFT is suited to predict the bond lengths and bond angles of water molecules not only in the absence but also in the presence of the external field. There are many stable structures that are obtained with our method and shown in Table 2.

Table 2. Computed values of bond length R_{OH} (Å) and bond angle θ (°) for water molecules under the dipole electric field.

Z (field)/10^{-4} a.u.		0	100	200	300	400	500
Parameters	R_{OH}/Å	0.9592	0.9606	0.9623	0.9644	0.9668	0.9698
	θ/(°)	104.83	103.59	102.34	101.09	99.83	98.57
Z (field)/10^{-4} a.u.		0	–100	–200	–300	–400	–500
Parameters	R_{OH}/Å	0.9592	0.9583	0.9578	0.9576	0.9574	0.9573
	θ/(°)	104.83	106.09	107.34	108.60	109.86	111.22

It is clear from this table that there are significant differences between the bond length and the bond angle of the water molecules under the dipole electric field. The bond length is 0.9698 Å under the dipole electric field of 0.05 a.u. and it is 0.0106 Å longer than that (0.9592 Å) without the dipole electric field. Also, the bond angle is about 6.26° smaller than that (104.83°) without the dipole electric field. The bond length is 0.9573 Å under dipole electric field of −0.05 a.u. and it is 0.0019 Å shorter than that (0.9592 Å) without the dipole electric field and the bond angle is about 6.39° bigger than that (104.83°) without the dipole electric field. Zhu *et al.*[47] indicated that the O–H bond length is stretched while the H–O–H bond angle contracts upon application of the electric field. Jung *et al.*[48] analysed the structure change of water by using an external electric field. From the simulations under various strengths of the electric field, they obtained the threshold for the significant structural change to be 0.15 Å to 0.2 Å.

3. Results and discussion

3.1. Dipole electronic field of dipole water molecule

The isotopic water molecule with an electric dipole moment is of C_{2v} symmetry, which is schemat-

ically shown in Fig. 1. Both the dipole electronic field and the isotopic water molecule are orientated along the z axis. Although the water molecule is in thermal motion, however, there will be two most possibilities of orientation, i.e. "head to tail" and "head to head". It is obvious that the energy of water molecules will increase for "head to head" orientation and decrease for "head-to-tail" orientation.

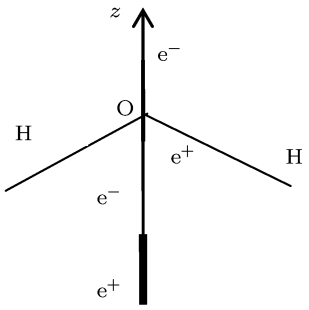


Fig. 1. Interaction of dipole electronic field with dipole H_2O.

3.2. Vibrational frequencies of water molecule

There are three vibrational modes and three rotational modes for an isotopic water molecule. The vibrational states can be described by normal mode and local mode. The three standard modes are denoted as ν_1 (symmetric stretch), ν_2 (bend) and ν_3 (asymmetric stretch). Previous spectral studies[16,17,2,23,32−36] demonstrated that local modes could much better describe the higher states. The average vibrational frequencies of the isotopic water molecules are obtained by averaging over the system and compared with the experimental data and other calculations in Table 3.

The vibrational frequencies of six different isotopically substituted water molecules are listed in Table 3, which are in good agreement both with the experimental values[23,32−36] and with the previous theoretical values.[15−17,23]

It is expected that this calculation may be suited to predict the vibrational frequencies of water molecules under the dipole electric field as given in Table 4. The variations of vibrational frequencies (ν_1, ν_2, ν_3) with dipole electric field are divided into two cases: one is that as the dipole electric field changes from 0 a.u. to 0.05 a.u., the ν_1 increases while ν_2 and ν_3 decrease for all isotopic water molecules, the other is that as the dipole electric field changes from 0 a.u. to −0.05 a.u., the ν_1 decreases for all isotopic water molecules However, the variations of calculated values of ν_2 and ν_3 are not monotonic. The ν_2 values of H_2O, D_2O, and T_2O decrease, whereas the ν_2 values of HDO, HTO, and DTO first increase and then decrease again; the ν_3 values of H_2O, D_2O, T_2O first decrease and then increase while the ν_3 values of HDO, HTO, DTO first increase and then decrease.

Table 3. Calculated values of vibrational frequencies of water molecules, experimental data and theoretical values for water molecule.

Parameter		*ab initio*[a]	SC[b]	CCSD(T)[c,d]	This work	Exp.[e−j]
H_2O	ν_2 (cm^{-1})	1594.7	1777.7	1652.3	1614.8	1648.47
	ν_1 (cm^{-1})	3657.1	4147.7	3828.9	3888.9	3832.17
	ν_3 (cm^{-1})	3755.9	4253.0	3937.7	3994.1	39442.53
HDO	ν_2 (cm^{-1})	1403.5	1558.2	1403.52	1426.4	1442.10
	ν_1 (cm^{-1})	2723.7	3051.6	2723.66	2832.1	2824.32
	ν_3 (cm^{-1})	3707.5	4202.6	3707.48	3900.5	3889.84
D_2O	ν_2 (cm^{-1})	1178.4	1301.0	1209.3	1182.0	1206.39
	ν_1 (cm^{-1})	2671.7	2989.0	2760.1	2803.0	2783.80
	ν_3 (cm^{-1})	2787.7	3118.0	2885.1	2927.3	2888.78
HTO	ν_2 (cm^{-1})	1332.5	1477.5	1332.49	1352.6	1332.48
	ν_1 (cm^{-1})	2299.8	2560.3	2299.81	2375.7	2299.77
	ν_3 (cm^{-1})	3716.6	4201.7	3716.72	3899.5	3716.58
DTO	ν_2 (cm^{-1})		1202.4		1100.8	
	ν_1 (cm^{-1})		2552.5		2368.1	
	ν_3 (cm^{-1})		3062.8		2842.3	
T_2O	ν_2 (cm^{-1})	995.4	1094.5	1017.3	994.5	995.33
	ν_1 (cm^{-1})	2237.2	2488.8	2298.0	2333.3	2237.15
	ν_3 (cm^{-1})	2366.6	2634.3	2436.1	2472.3	2366.60

[a]Ref. [16], [b]Ref. [23], [c]Ref. [17], [d]Ref. [15], [e]Ref. [21], [f]Ref. [32], [g]Ref. [33], [h]Ref. [34], [i]Ref. [35], [j]Ref. [36].

Table 4. Computed values of vibration frequencies (ν_1, ν_2, ν_3) of water molecules (H_2O, HDO, HTO, D_2O, DTO, T_2O) under externally dipole electric field.

Z (field)/10^{-4} a.u.			100	200	300	400	500
H_2O	ν_1 (cm^{-1}) A_1	1614.8	1652.2	1674.0	1692.5	1707.8	1719.8
	ν_2 (cm^{-1}) A_1	3888.9	3837.7	3822.3	3801.7	3775.2	3742.4
	ν_3 (cm^{-1}) B_2	3994.1	3924.9	3894.4	3858.3	3815.9	3766.9
HDO	ν_1 (cm^{-1}) A_1	1426.4	1448.9	1468.5	1485.4	1499.4	1510.5
	ν_2 (cm^{-1}) A_1	2832.1	2820.1	2804.0	2783.7	2759.0	2729.5
	ν_3 (cm^{-1}) B_2	3900.5	3882.5	3859.0	3830.1	3795.2	3753.9
HTO	ν_1 (cm^{-1}) A_1	1182.0	1374.8	1394.2	1411.0	1425.0	1436.3
	ν_2 (cm^{-1}) A_1	2803.0	2365.6	2351.9	2334.8	2314.0	2289.1
	ν_3 (cm^{-1}) B_2	2927.3	3881.7	3858.3	3829.5	3794.8	3753.6
D_2O	ν_1 (cm^{-1}) A_1	1352.6	1208.8	1224.3	1237.4	1248.2	1256.6
	ν_2 (cm^{-1}) A_1	2375.7	2767.5	2757.5	2743.5	2725.2	2720.1
	ν_3 (cm^{-1}) B_2	3899.5	2874.9	2851.4	2823.8	2791.8	2755.0
DTO	ν_1 (cm^{-1}) A_1	1100.8	1117.2	1131.5	1143.7	1153.7	1161.6
	ν_2 (cm^{-1}) A_1	2368.1	2359.2	2346.6	2330.4	2310.4	2286.2
	ν_3 (cm^{-1}) B_2	2842.3	2827.9	2809.7	2787.6	2761.2	2730.3
T_2O	ν_1 (cm^{-1}) A_1	994.5	1016.5	1029.2	1039.9	1048.6	1055.5
	ν_2 (cm^{-1}) A_1	2333.3	2305.0	2297.5	2286.6	2272.0	2253.4
	ν_3 (cm^{-1}) B_2	2472.3	2426.9	2406.2	2382.1	2354.4	2322.7
Z (field)/10^{-4} a.u.			–100	–200	–300	–400	–500
H_2O	ν_1 (cm^{-1}) A_1	1614.8	1599.0	1557.6	1532.1	1492.6	1445.2
	ν_2 (cm^{-1}) A_1	3888.9	3851.3	3849.0	3841.9	3829.7	3817.9
	ν_3 (cm^{-1}) B_2	3994.1	3968.3	3980.6	3988.2	3990.4	3993.6
HDO	ν_1 (cm^{-1}) A_1	1426.4	1401.2	1372.9	1314.2	1305.8	1263.2
	ν_2 (cm^{-1}) A_1	2832.1	2839.6	2842.4	2841.7	2837.1	2832.9
	ν_3 (cm^{-1}) B_2	3900.5	3912.5	3981.4	3919.6	3915.6	3912.5
HTO	ν_1 (cm^{-1}) A_1	1182.0	1327.8	1300.3	1269.4	1234.8	1193.1
	ν_2 (cm^{-1}) A_1	2803.0	2382.1	2384.7	2384.2	2380.5	2377.1
	ν_3 (cm^{-1}) B_2	2927.3	3911.3	3917.0	3917.9	3913.6	3710.2
D_2O	ν_1 (cm^{-1}) A_1	1352.6	1170.9	1148.4	1123.1	1094.7	1060.6
	ν_2 (cm^{-1}) A_1	2375.7	2774.9	2771.9	2765.4	2755.0	2744.8
	ν_3 (cm^{-1}) B_2	3899.5	2909.3	2919.8	2926.7	2929.9	2933.9
DTO	ν_1 (cm^{-1}) A_1	1100.8	1082.2	1061.4	1038.0	1011.8	980.2
	ν_2 (cm^{-1}) A_1	2368.1	2373.2	2374.3	2372.3	2366.8	2361.4
	ν_3 (cm^{-1}) B_2	2842.3	2852.4	2858.1	2860.6	2859.4	2859.0
T_2O	ν_1 (cm^{-1}) A_1	994.5	985.5	967.0	946.2	922.8	894.6
	ν_2 (cm^{-1}) A_1	2333.3	2309.2	2305.5	2298.9	2289.0	2279.2
	ν_3 (cm^{-1}) B_2	2472.3	2457.8	2467.6	2474.6	2478.3	2482.9

Notation: A_1, A_2, B_2 are the irreducible representations for vibrations.

3.3. Force constants of water molecule

There are six force constants for an isotopic water molecule which are obtained by fitting the energy functions of the bond length and the bond angle, while they include the electronic energy and the nuclear vibration motion energy of isotope water molecules. In detail, we first calculate multi-point energy near the equilibrium position and then obtain the force constants, which are shown in Table 5.

From Table 5 it follows that our results of quadratic force constants are in excellent agreement with the other results. The final results in the presence of the influence of the strong external torque are given in Table

6. The force constants ($f_{R_1\theta}$, $f_{R_2\theta}$, $f_{\theta\theta}$) increase while the force constants ($f_{R_1R_1}$, $f_{R_2R_2}$, $f_{R_1R_2}$) decrease with field strength increasing from 0 a.u. to 0.05 a.u. However, the opposite situation occurs when the field strength changes from 0 a.u. to −0.05 a.u.

Table 5. Comparison of force constants ($f_{R_1R_1}$, $f_{R_2R_2}$, $f_{\theta\theta}$, $f_{R_1R_2}$, $f_{R_1\theta}$, $f_{R_2\theta}$) of water molecule between the previous results and our predictions.

Method and basis set	f_{R1R1}, $f_{R_2R_2}$	$f_{\theta\theta}$	$f_{R_1R_2}$	$f_{R_1\theta}$, $f_{R_2\theta}$	Source
B3LYP/6-311++G**	0.5489	0.1460	–0.0067	0.0274	Ref. [40]
Hartree–Fock/4s3p/2s	0.6360	0.0566	–0.0050	0.0166	Ref. [2]
CCSD(T)/aug-cc-pVAZ(T)	0.5419	0.1644	–0.0063	0.0454	Ref. [2]
B3PB6/6-311++G(3df,3pd)	0.5462	0.1571	–0.0051	0.0302	this work

Table 6. Computed values of force constants ($f_{R_1R_1}$, $f_{R_2R_2}$, $f_{\theta\theta}$, $f_{R_1R_2}$, $f_{R_1\theta}$, $f_{R_2\theta}$) of water molecules (H_2O, HDO, HTO, D_2O, DTO, T_2O) under external electric field.

Z (field)/10^{-4} a.u.	0	100	200	300	400	500
$f_{R_1R_1}$, $f_{R_2R_2}$	0.5462	0.5418	0.5360	0.5289	0.5202	0.5100
$f_{R_1R_2}$	–0.0051	–0.0042	-0.0034	–0.0027	–0.0021	–0.0016
$f_{R_1\theta}$, $f_{R_2\theta}$	0.0302	0.0314	0.0327	0.0342	0.0360	0.0378
$f_{\theta\theta}$	0.1571	0.1628	0.1681	0.1732	0.1779	0.1823
Z (field)/10^{-4} a.u.	0	–100	–200	–300	–400	–500
$f_{R_1R_1}$, $f_{R_2R_2}$	0.5462	0.5489	0.5501	0.5519	0.5534	0.5572
$f_{R_1R_2}$	–0.0051	–0.0061	–0.0072	–0.0084	–0.0097	–0.0114
$f_{R_1\theta}$, $f_{R_2\theta}$	0.0302	0.0293	0.0285	0.0279	0.0276	0.0275
$f_{\theta\theta}$	0.1571	0.1511	0.1448	0.1380	0.1309	0.1230

3.4. Dissociation limit and dissociation energy of isotopic water molecules

In order to obtain the dissociation energies of isotopic water molecules, first, the ground electronic states and geometry parameters of water molecules are optimized and then the dissociation limit and the electronic state of the dissociation products are determined.

3.4.1. Dissociation limits of ground state for water molecule

By atomic and molecular reactive statics (AMRS),[54] we acquire the ground electronic states of all isotopic water molecules, whose structures belong to C_{2v} symmetry group with $\tilde{X}^1A_1$ state. If the ground states for H, D, T, and O are ^2S_g and ^3P_g, there will be no ground state $\tilde{X}^1A_1$ of water molecule, so it is impossible that H, D, T, and O are all in their ground electronic states. If O is in its first excited electronic state ^1D_g, then the ground electronic state $\tilde{X}^1A_1$ of water molecule may be found. Based on the same reason, OH, OD, and OT should be all in their first excited electronic state $A^2\Sigma^+$ and H, D, and T in their ground electronic states. The ground electronic state $\tilde{X}^1A_1$ of water molecule is obtained, too.

Hence, the reasonable dissociation limits for the ground electronic state $\tilde{X}^1A_1$ of water molecule can be written as

$$H_2O(\tilde{X}^1A_1) \rightarrow \begin{cases} H_2(X^1\Sigma_g^+) + O(^1D_g), \\ OH(A^2\Sigma^+) + H(^2S_g), \\ H(^2S_g) + H(^2S_g) + O(^1D_g). \end{cases} \quad (1)$$

In this paper, the third dissociation channel is taken into account in our calculation.

3.4.2. Dissociation energy of isotopic water molecules under the dipole electronic field

After a brief description of the possible dissociation channel, the dissociation energy is determined as follows:

$$\begin{aligned} D_e = {} & E_e(O) + 2E_e(H) - E_e(H_2O) + E_n(O) \\ & + 2E_n(H) - E_n(H_2O), \end{aligned} \quad (2)$$

where E_e is the electronic energy and E_n is the nuclear motion kinetic energy.

In Eq. (2) we report the core correlation contribution at the level of theory. The core correction is

defined as the difference in energy between core and valence electron calculations. In the so-called non-BO approximation, we have to consider the nuclear motion, i.e. translational, rotational and vibration motions. In this paper by calculating nuclear vibration energy to correct electronic energy obtained in the Born–Oppenheimer approximation, the dissociation energies are computed. There are of course, great differences in dissociation energy between water and its isotopic variants as pointed out. The dissociation energies of isotopic water molecules for the ground state are provided in Table 7.

Table 7. Computed dissociation energy (D_e) values of water molecules H_2O, HDO, HTO, D_2O, DTO and T_2O under external electric field.

Z (field)/10^{-4} a.u	–500	–400	–300	–200	–100	0	100	200	300	400	500
D_e (H_2O)/eV	11.60	11.82	12.04	12.26	12.47	12.66	12.86	13.06	13.25	13.43	13.61
D_e (HDO)/eV	11.67	11.90	12.12	12.33	12.54	12.74	12.94	13.14	13.33	13.51	13.69
D_e (HTO)/eV	11.71	11.93	12.15	12.37	12.58	12.78	12.97	13.17	13.36	13.54	13.72
D_e (D_2O)/eV	11.75	11.98	12.20	12.41	12.62	12.82	13.02	13.22	13.41	13.59	13.77
D_e (DTO)/eV	11.79	12.01	12.23	12.45	12.66	12.86	13.06	13.25	13.44	13.62	13.80
D_e (T_2O)/eV	11.82	12.04	12.26	12.48	12.69	12.89	13.09	13.28	13.47	13.66	13.84

The dissociation energies of ground states of isotopic water molecules are all shown in Fig. 2, from which it follows that the dissociation energies of water molecules increase with dipole electric field increasing from 0 a.u. to 0.05 a.u. while the dissociation energies of water molecules decrease as dipole electric field changes from 0 a.u. to −0.05 a.u. because of the charge transfer induced by the applied dipole electric field. It can also be seen from Fig. 2 that the differences in dissociation energy follow the differences in neutron number for all isotopic water molecules under the same dipole electric fields. The variation of the hydrogen isotopes dominates the behaviour of the dissociation energy of the water molecule, which reveals that the electric energy and nuclear motion kinetic energy strongly depend on dipole electric field.

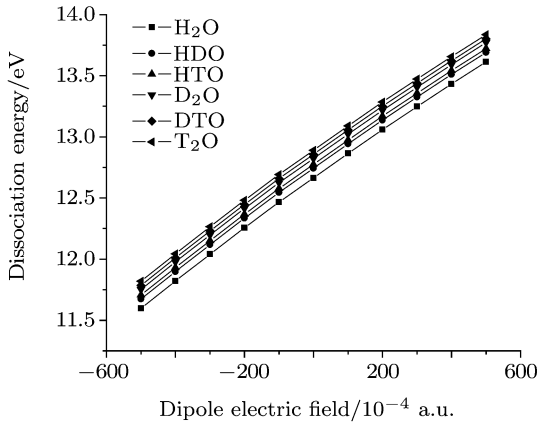


Fig. 2. Relationships between dipole electric field and dissociation energy of H_2O, HDO, HTO, D_2O, DTO, and T_2O.

The dissociation energies of isotopic water molecules are obtained under the dipole electric field. Then we suppose that the electric dipole moment of water molecules and the dipole electric field be parallel. However, the electric dipole moment of water molecules and the dipole electric field are parallel or anti-parallel to each other with the same probabilities because of the thermal motion, the weighted average values for the dissociation energies for both cases of water molecules are adopted.

It can be seen clearly from Table 8 that the average dissociation energies decrease with dipole electric field increasing and the dissociation energies of water molecules are about 0.05, 0.06, 0.07, 0.06, 0.07, and 0.06 eV smaller than those of other hydrogen-isotope waters, respectively. It is important to dissociate water molecules as the dissociation energy decreases.

Table 8. Weighted average values for dissociation energies of hydrogen-isotope water in the dipole electric field.

Average dissociation energy/eV							
	H_2O	12.66	12.66	12.66	12.64	12.63	12.61
	HDO	12.74	12.74	12.74	12.72	12.70	12.68
	HTO	12.78	12.78	12.77	12.75	12.74	12.71
	D_2O	12.82	12.82	12.82	12.80	12.78	12.76
	DTO	12.86	12.86	12.85	12.84	12.82	12.79
	T_2O	12.89	12.89	12.88	12.87	12.85	12.83

4. Summary

The geometrical structures, the vibrational frequencies, the force constants and the dissociation energies of all isotopic water molecules are reported based on density functional theory with B3PB6 exchange–correlation potential under the dipole electric field. Owing to the influence of the dipole electric field, a new equilibrium structure is determined along with vibrational frequency, force constant and dissociation energy. On the other hand, we have systematically studied the interaction between electric energy and nuclear motion energy and the nuclear motion effect is taken into consideration in this paper. Combining with accurate variational nuclear motion computations, we provide a detailed probe of the vibrational energy level structure of isotopic water molecules within its drastic dissociation limit.

References

[1] Sugiyama T, Asakura Y, Uda T, Shiozaki T, Enokida Y and Yamamoto I 2006 *Fusi. Engi. Desi.* **81** 833

[2] Engel V, Staemmler V, Vander Wal R L, Crim F F, Sension R J, Hudson B andresen P, Hennig S, Weide K and Schinke R 1992 *J. Phys. Chem.* **96** 3201

[3] Meng N, Leung M K H, Leung D Y C and Sumathy K 2007 *Rene. Sust. Ener. Rev.* **11** 401

[4] Benedek N A, Snook I K, Towler M D and Needs R J 2006 *J. Chem. Phys.* **125** 104302

[5] Francesca I, Rossend R, Thomas E and James T H 2009 *J. Phys. Chem.* A **113** 6657

[6] Kim H D and Koji A 2009 *J. Chem. Phys.* **131** 064501

[7] Scott H, Thomas E M and David E M 2009 *J. Chem. Phys.* **131** 024501

[8] Zhu S B, Yao S, Zhu J B, Singh S and Robinson G W 1991 *J. Phys. Chem.* **95** 6211

[9] Lie G C and Clementi E 1986 *Phys. Rev.* A **33** 2679

[10] Thom H D, Russell M P and Soe A 1972 *J. Chem. Phys.* **57** 5044

[11] Ermler W C and Kern C W 1971 *J. Chem. Phys.* **55** 4851

[12] Falk M 1984 *Spec. Act.* **40** 43

[13] Császár A G, Czakó G, Furtenbacher T, Tennyson J, Szalay V, Shirin S V, Zobov N F and Polyansky O L 2005 *J. Chem. Phys.* **122** 214305

[14] Barletta P, Shirin S V, Zobov N F, Polyansky O L, Tennyson J, Valeev E F and Császár A G 2006 *J. Chem. Phys.* **125** 204307

[15] Partridge H and Schwenke D W 1997 *J. Chem. Phys.* **106** 4618

[16] Zobov N F, Polyansky O L, Sueur C R L and Tennyson J 1996 *Chem. Phys. Lett.* **260** 381

[17] Csaszar A G and Mills I M 1997 *Spec. Acta* Part A **53** 1101

[18] Jursic B S and Martin R M 1996 *Int. J. Quantum Chem.* **59** 495

[19] Martin J M L, Fraryois J P and Gijbels R 1992 *J. Chem. Phys.* **96** 15

[20] Benedict W S, Gailar N and Plyler E K 1956 *J. Chem. Phys.* **24** 1139

[21] Thiessen W E and Narten A H 1982 *J. Chem. Phys.* **77** 2656

[22] Soper A K 2000 *Chem. Phys.* **258** 121

[23] Krohn B J, Ermler W C and Kern C W 1974 *J. Chem. Phys.* **60** 22

[24] Ruan W, Luo W L, Zhang L, Zhu Z H and Fu Y B 2009 *Acta Phys. Sin.* **58** 1537 (in Chinese)

[25] Botter R, Dibeler V H, Walker J A and Rosenstock H M 1966 *J. Chem. Phys.* **44** 1271

[26] McCulloh K E 1976 *Int. J. Mass Spec. Ion Phys.* **21** 333

[27] Wiedmann R T, Tonkyn R G, White M G, Wang K and McKay V 1992 *J. Chem. Phys.* **97** 768

[28] Van Lonkhuyzen H D and de Lange C A 1984 *Mol. Phys.* **51** 551

[29] Barr J D, Fanis A D, Dyke J M, Gamblin S D, Hooper N, Morris A, Stranges S, West J B and Wright T G 1999 *J. Chem. Phys.* **110** 345

[30] Pakoulev A, Wang Z H, Pang Y and Dlott D D 2003 *Chem. Phys. Lett.* **380** 404

[31] Carleer M, Jenouvrier A, Vandaele A C, Bernath P F, Merienne M F, Colin R, Zobov N F, Polyansky O L, Tennyson J and Savin V A 1999 *J. Chem. Phys.* **111** 2444

[32] Ulenikov O N, Cherepanov V N and Malikova A B 1991 *J. Mol. Spec.* **146** 97

[33] Cope S D, Russell D K, Fry H A, Jones L H and Barefield J E 1988 *J. Mol. Spec.* **127** 464

[34] Wilemski G 1978 *J. Quantum Spec. Radi. Tran.* **20** 291

[35] Fry H A, Jones L H and Barefield J E 1984 *J. Mol. Spec.* **103** 41

[36] Cope S D, Russell D K, Fry H A, Jones L H and Barefield J E 1986 *J. Mol. Spec.* **120** 311

[37] Odde S, Mhin B J, Lee S, Lee H M and Kim K S 2004 *J. Chem. Phys.* **120** 9524

[38] Ruan W, Luo W L, Zhang L and Zhu Z H 2009 *Sci. Chin.* G **52** 566

[39] Luo W L, Ruan W, Zhang L, Xie A D and Zhu Z H 2008 *Acta Phys. Sin.* **57** 4833 (in Chinese)

[40] Becke A D 1993 *J. Chem. Phys.* **98** 5648

[41] Xu M, Wang R K, Linghu R F and Yang X D 2007 *Acta Phys. Sin.* **56** 769 (in Chinese)

[42] Wang Q M, Ren T Q and Zhu J L 2009 *Acta Phys. Sin.* **58** 5266 (in Chinese)

[43] Wang Q M, Ren T Q and Zhu J L 2009 *Acta Phys. Sin.* **58** 5270 (in Chinese)

[44] Fan X W, Geng Z D and Zhang Y S 2005 *Acta Phys. Sin.* **54** 5614 (in Chinese)

[45] Li Q and Zhu Z H 2006 *Acta Phys. Sin.* **55** 102 (in Chinese)

[46] Zhu J L, Ren T Q and Wang Q M 2009 *Acta Phys. Sin.* 58 3047 (in Chinese)

[47] Zhu S B, Zhu J B and Robinson G W 1991 *Phys. Rev.* A **44** 2602

[48] Jung D H, Yang J H and Jhon M S 1999 *Chem. Phys.* **244** 331

[49] Rajgara F A, Dharmadhikari A K, Mathur D and Safvan C P 2009 *J. Chem. Phys.* **130** 231104

[50] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery Jr J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2003 *Gaussian* 03, Revison B02, (Pittsburgh: Gaussian, Inc. PA)

[51] Perdew J P 1986 *Phys. Rev.* B **33** 8822

[52] Clark T, Chandrasekhar J, Spitznagel G W and Ragué Schleyer P V 2004 *J. Comp. Chem.* **4** 294

[53] Frisch M J, Pople J A and Binkley J S 1984 *J. Chem. Phys.* **80** 3265

[54] Zhu Z H 1996 *Atomic and Molecular Reactive Statics* (Beijing: Science Press) (in Chinese)