Spectroscopic parameters and molecular constants of HI($X^1\Sigma^+$), DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$) isotope molecules*

Zhang Xiao-Niu(张小妞), Shi De-Heng(施德恒)†, Zhu Zun-Lue(朱遵略), and Sun Jin-Feng(孙金锋)

College of Physics and Information Engineering, Henan Normal University, Xinxiang 453007, *China*

(Received 4 May 2010; revised manuscript received 19 June 2010)

The potential energy curve (PEC) of HI($X^1\Sigma^+$) molecule is studied using the complete active space self-consistent field method followed by the highly accurate valence internally contracted multireference configuration interaction approach at the correlation-consistent basis sets, aug-cc-pV6Z for H and aug-cc-pV5Z-pp for I atom. Using the PEC of HI($X^1\Sigma^+$), the spectroscopic parameters of three isotopes, HI($X^1\Sigma^+$), DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), are determined in the present work. For the HI($X^1\Sigma^+$), the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 3.1551 eV, 3.2958 eV, 0.16183 nm, 2290.60 cm^{-1}, 40.0703 cm^{-1}, 0.1699 cm^{-1} and 6.4373 cm^{-1}, respectively; for the DI ($X^1\Sigma^+$), the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 3.1965 eV, 3.2967 eV, 0.16183 nm, 1626.8 cm^{-1}, 20.8581 cm^{-1}, 0.0611 cm^{-1} and 3.2468 cm^{-1}, respectively; for the TI ($X^1\Sigma^+$), the values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are of 3.2144 eV, 3.2967 eV, 0.16183 nm, 1334.43 cm^{-1}, 14.0765 cm^{-1}, 0.0338 cm^{-1} and 2.1850 cm^{-1}, respectively. These results accord well with the available experimental results. With the PEC of HI($X^1\Sigma^+$) molecule obtained at present, a total of 19 vibrational states are predicted for the HI, 26 for the DI, and 32 for the TI, when the rotational quantum number J is equal to zero ($J = 0$). For each vibrational state, vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ are determined when $J = 0$ for the first time, which are in excellent agreement with the experimental results.

Keywords: isotope effect, potential energy curve, spectroscopic parameter, molecular constant

PACC: 3520G, 3120A, 3120T

1. Introduction

The hydrogen halides are a very important chemical species which have broad applications in chemistry. Many disciplines in chemistry benefit from the unique characteristics of these molecules.[1] Iodide, as a heavier member of halide group, is of particular interest to those who study its dynamic behaviour due to its reactivity. Besides, iodide is the most critical radioactive contaminant with the potential short-term radiological consequences to the environments.[2] For these reasons, the spectroscopic and molecular properties of hydrogen iodine (HI) have been the subject of numerous investigations in the past several decades, both experimentally[1,3–9] and theoretically.[2,10–34]

In experiment, the earlier spectroscopic investigations of HI molecule were made by Naudé and Verleger[3] in 1950. Since then, the properties of HI have been studied by the resonance-enhanced multiphoton ionization (REMPI) spectra,[1] the infrared spectra,[3,4] the submillimeter-wave spectra,[5] the vacuum high-resolution spectrographs,[6] and so on. Some spectroscopic and molecular properties were summarized in Ref. [7] by Huber and Herzberg in 1979. However, as can be seen in the literature, the ground-state dissociation energy D_0 of HI is subject to considerable uncertainty. For example, the D_0 value determined by Naudé and Verleger[3] in 1950 is 4.2 eV. Whereas the D_0 value derived by Wilkinson[8] in 1963 is 3.057 eV. Obviously, a great difference exists between them.

In theory, the spectroscopic parameters and molecular constants were widely studied by a number of methods.[2,10–34] However, on the one hand, the D_e value still showed a wide variation, ranging from 1.95 eV to 3.5428 eV;[11–19,27–29,33] on the other hand, these theories mainly concentrated on the spectroscopic parameters (D_e, R_e, ω_e, $\omega_e\chi_e$, α_e, B_e and D_0) of HI rather than DI and TI. Furthermore, little theoretical information is available about vibrational manifolds (such as the vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ), though these data are very useful in the

*Project supported by the National Natural Science Foundation of China (Grant No. 10874064), and the Program for Science and Technology Innovation Talents in Universities of Henan Province of China (Grant No. 2008HASTIT008).

†Corresponding author. E-mail: scattering@sina.com.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

ro-vibrational transition calculation.

One of the main purposes in the present study is to determine the accurate potential energy curve (PEC) of HI($X^1\Sigma^+$) molecule employing the full valence complete active space self-consistent field (CASSCF) method followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[35,36] in combination with very large correlation-consistent basis sets,[37−39] aug-cc-pV5Z-pp for I and aug-cc-pV6Z for H atom. The spectroscopic parameters and vibrational manifolds are determined for the HI. Furthermore, using the PEC of HI($X^1\Sigma^+$) molecule obtained here, with the help of VIBROT module presented in MOLCAS 7.4 program package,[40] the spectroscopic and the molecular properties for the two isotope molecules, DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), are also determined. Comparison with the available experimental results shows that the present spectroscopic parameters and molecular constants are both reliable and accurate.

2. Computational methods

It is well known that the relativistic effects must be taken into consideration when we undertake the reliable theoretical investigations on molecules which include heavy atoms. Here a balance should be considered between accuracy and economy because the relativistic calculations will consume more CPU time. Now, it can be well solved by using the effective core potential (ECP) approach. Thus, to obtain the reliable and accurate PEC of the HI, in the present paper we choose a very large ECP basis set, aug-cc-pV5Z-pp (ECP28MDF_AV5Z), for I atom to perform such an investigation.

The PEC of HI($X^1\Sigma^+$) molecule is investigated by the CASSCF approach, which is followed by the MRCI calculations. Therefore, the full valence CASSCF is used as the reference wavefunction for the MRCI calculations in the investigations. The present PEC calculations of HI($X^1\Sigma^+$) molecule are carried out in MOLPRO 2008.1 program package[41] by using the correlation-consistent basis sets, aug-cc-pV5Z-pp for I and aug-cc-pV6Z for H atom. For the calculations of such a kind, the MRCI theory[35,36] has proved particularly successful. Especially in recent years, a number of high-quality results have been reported for a variety of diatomic molecules.[42−47]

In MOLPRO only the Abelian point group symmetry is used. For molecules with degenerate symmetry, an Abelian subgroup must be employed. That is to say, for the diatomic molecule such as HI with $C_{\infty v}$ symmetry, it will be substituted by C_{2v} symmetry with the order of the irreducible representations as $a_1/b_1/b_2/a_2$. In the CASSCF and subsequent MRCI calculations, four kinds of states are evaluated. Specifically for the HI($X^1\Sigma^+$), five molecular orbitals (MOs) are put into the active space, including three a_1's, one b_1 and one b_2 symmetry MOs, which correspond to the 5s5p shells of I and 1s shell of H atom. The rest of the electrons in the HI molecule are put into the closed-shell orbitals, including four a_1's, two b_1's, two b_2's and one a_2 symmetry MOs. In the present paper, we use only these MOs (seven a_1's, three b_1's, three b_2's, one a_2) to calculate the PEC of HI($X^1\Sigma^+$), and find that the obtained PEC is smooth and convergent over the present internuclear distance range.

In general, the PEC calculations of HI($X^1\Sigma^+$) molecule are made in intervals of 0.02 nm over an internuclear distance range from 0.08 nm to 0.575 nm. Near the equilibrium position, we choose the interval to be of 0.005 nm, so that the properties of the PEC are displayed more clearly. The PEC is smooth and converges rapidly with the internuclear separation increasing. With the PEC determined at the basis aug-cc-pV5Z-pp for I and aug-cc-pV6Z for H atom, the spectroscopic parameters and molecular constants are evaluated for the three isotopes, HI($X^1\Sigma^+$), DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), using the VIBROT module presented in MOLCAS 7.4 program package.[40]

3. Results and discussion

3.1. Spectroscopic parameters

In order to conveniently compare the present results with other existing results available in the literature, we collect the spectroscopic parameters together with the experimental results[1,3−8] and other theoretical results[2,10−34] in Table 1 for the HI($X^1\Sigma^+$) and in Table 2 for the DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), respectively.

The earlier calculations were carried out by Ungemach *et al.*[10] in 1977. In their investigations, the multiconfiguration SCF (MCSCF) approach was employed to obtain the non-relativistic electronic properties of HI($X^1\Sigma^+$). Obviously, their R_e is much larger than the present one when compared with the experimental results.[1,3,5,7] And limited spectroscopic parameters were determined.

Table 1. Spectroscopic parameter comparison with available measurements and other theoretical results for HI($X^1\Sigma^+$) at MRCI level of theory.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
this work	3.2958	0.16183	2290.60	40.0703	6.4373	0.1699	3.1551
Exp.[1]	–	0.1609	–	–	–	–	–
Exp.[3]	–	0.1604	2309.53	39.73	6.551	0.183	4.2
Exp.[4]	–	–	2308.96	39.5751	6.5116	0.1703	–
Exp.[5]	–	0.1609	–	–	6.5121	0.1714	–
Exp.[6]	–	–	2309.01	39.6435	6.5111	0.16886	–
Exp.[7]	3.1959	0.1609	2309.01	39.6435	6.42637	0.16886	3.054
Exp.[8]	–	–	–	–	–	–	3.057
theory[2]	–	0.16057	2352.2	34.1	–	0.073	–
theory[10]	–	0.16404	–	–	–	–	2.81
theory[11]	2.17	0.1635	2433	–	–	–	–
theory[12] (NR*)	2.383	0.1607	2442	–	–	–	–
(R†)	2.030	0.1601	2410	–	–	–	–
theory[13]	2.81	0.1616	2329	–	–	–	–
theory[14]	2.91	0.1598	2358	–	–	–	–
theory[15] (NR*)	3.5428	0.1613	2373	–	–	–	–
(R†)	3.2350	0.1607	2348	–	–	–	–
theory[16]	2.5552	0.1606	2466	–	–	–	–
theory[17]	3.3520	0.16128	2345.1	–	–	–	–
theory[18]							
NR-CCSD(T)	3.3564	0.1625	2334	–	–	–	–
DC-CCSD(T)	3.0312	0.1620	2297	–	–	–	–
theory[19]	3.4674	0.16111	2392	–	–	–	–
theory[20]	–	0.166	2305	–	–	–	2.93
theory[21]	–	0.1598	2354	–	–	–	–
theory[22]	–	0.1602	2436	–	–	–	–
theory[23]	–	0.15998	2354.7	–	–	–	–
theory[24]	–	0.1604	2302	–	–	–	–
theory[25]	–	0.16135	2318	–	–	–	–
theory[26]	–	0.1610	2316	–	–	–	–
theory[27]	3.2393	0.163	–	–	–	–	–
theory[28] (NR)	2.35	0.1606	–	–	–	–	–
(R)	2.29	0.1596	–	–	–	–	–
theory [29] (NR)	2.37	0.1606	–	–	–	–	–
(R)	1.95	.1597	–	–	–	–	–
theory[30]	–	0.1616	2364	47	6.46	0.182	–
theory[31]	–	0.1606	2419	–	6.538	–	–
theory[32]	–	0.16136	2332	38.8	6.475	–	–
theory[33] (av5z-pp)	3.4487	0.16150	2320.0	38.2	–	–	–
(av5z-dk)	3.4405	0.16174	2316.4	38.2	–	–	–
theory[34]	–	0.1609	2328	40	6.515	0.161	3.05

*NR = non-relativistic calculation results; †R = relativistic calculation results.

Similar to Ref. [10], a number of theories[11−20] only determined the values of D_e R_e and ω_e, and their results are also inferior to the present ones, especially for the ω_e.[11−19] For example, Seijo[13] performed the calculation of relativistic *ab initio* model potential including spin–orbit effects through the Wood–Boring Hamiltonian. By comparison with the experiments, we find that their favourable results were obtained at the spin–orbit corrected basis set. As can be seen in Table 1, their D_e is too small and the ω_e is too large compared with the present ones. Visscher *et al.*[18] made the benchmark calculations of D_e, R_e and ω_e at various levels of theories. Here we select

their favourable results obtained at the NR-CCSD(T) and DC-CCSD(T) levels of theory for comparison. Their D_e seems superior to ours, but other constants have no obvious improvements. In the investigations,[11−20] only ω_e obtained by Chapman *et al.*[20] is superior to the present one, whereas their R_e greatly deviates from the available experimental results.[1,3]

Table 2. Comparison between spectroscopic parameters with available measurements and other theoretical results for DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$) at MRCI level of theory.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
DI							
this work	3.2967	0.16183	1626.88	20.8581	3.2468	0.0611	3.1965
Exp.[5]	–	0.1609	–	–	3.2842	0.0614	–
Exp.[6]	–	–	1639.66	19.873	3.2839	0.0608	–
TI							
this work	3.2967	0.16183	1334.43	14.0765	2.1850	0.0338	3.2144
Exp.[5]	–	0.1609	–	–	2.2102	0.0339	–

A number of investigations[21−26] even determined only two spectroscopic parameters, R_e and ω_e, but the two parameters are still not satisfactory. For example, Kellö and Sadlej[21] in 1990 estimated the relativistic contributions to the two parameters, however, they are both far from the experimental results[1,3−7] compared with the present ones. Saue *et al.*[22] in 1996 took into consideration the relativistic effects on R_e and ω_e using the four-component Dirac–Hartree–Fock (DHF) theory. Feller *et al.*[23] in 2003 estimated R_e and ω_e at the complete basis set (CBS). Although various corrections have been included in their investigations,[22,23] their ω_e results[22,23] are still inferior to the present one. Alekseyev *et al.*[24] in 2000 made the *ab initio* CI calculations including the spin–orbit coupling to determine the accurate spectroscopic parameters of low-lying electronic states of HI molecule. Martin and Sundermann[25] in 2001 used the valence correlation-consistent basis sets and Stuttgart–Dresden–Bonn (SDB) relativistic ECPs to calculate the values of R_e and ω_e for many molecules. And Hirata *et al.*[26] in 2007 used the high-order electron-correlation method with scalar relativistic and spin–orbit corrections to perform the R_e and ω_e calculations for several molecular systems containing heavy elements. As can be seen in Table 1, their results[24−26] are at most equivalent to the present one in the sense of accuracy.

Of these investigations,[10−34] there are three groups of calculations[27−29] in which only the D_e and R_e parameters are determined. Concretely, Dunning[27] calculated the values of D_e and R_e using several approaches, and the best results were determined by the GVB+1+2 method with the basis sets, 15s11p7d for I and 4s for H. The R_e value is 1.31% larger than the experimental result,[1] whereas the present one is only 0.58% larger than the same experimental result. Schwerdtfeger *et al.*[28,29] investigated the relativistic and correlated effects on the spectroscopic parameter calculations for a number of diatomic molecules. Their R_e values[28,29] at the non-relativistic and relativistic effects are quite accurate, but the D_e results[28,29] are much smaller than the present one when compared with all the available measurements.

Only a few theoretical investigations[30−34] are involved with the spectroscopic parameters $\omega_e\chi_e$, α_e and B_e. Werner *et al.*[30] in 1981 calculated the PEC of HI($X^1\Sigma^+$) by the self-consistent electron pair approach/coupled electron pair approach (SCEP/CEPA) and MCSCF method with a Gaussian-type basis set comprised of a total of 109 functions contracted to 89 groups. And their most favourable results were determined by the SCEP/CEPA. As shown in Table 1, their R_e and B_e values are in excellent agreement with the available measurements, whereas the values of ω_e, $\omega_e\chi_e$ and α_e are much poorer than the present ones. Watanabe and Matsuoka[31] in 1998 carried out the Dirac–Fock–Roothaan calculations in the relativistic reduced frozen-core approximation (RFCA). Obviously, their ω_e value is worse than the present one. Hennum *et al.*[32] in 2001 used several approaches to study the electron correlation and relativistic effects on the spectroscopic parameters of hydrogen halides. And their most favourable results were obtained at the CCSD(T)+DPT(SCF)/TZ level of theory. Peterson *et al.*[33] in 2003 made the all-electron calculations by using the Douglas–Kroll–

Hess Hamiltonian and correlation-consistent basis sets with the relativistic pseudo-potential. By comparison with the experimental results,[3,7] we find that the favourable results were determined at two basis sets, the aug-cc-pV5Z-PP and the aug-cc-pV5Z-PP. However, their D_e value becomes worse than the present one. Hirata *et al.*[34] in 2004 made the spectroscopic calculations by using the third-order Douglas–Kroll relativistic coupled-cluster theory through the connected single, double, triple and quadruple substitutions for more than twenty molecules. For the HI($X^1\Sigma^+$), we have found that their results are equivalent to the present ones in the sense of accuracy, but they do not perform any calculations on the molecular constants.

From the above comparison, for the HI($X^1\Sigma^+$), we say that the present results are more accurate and complete than the previous theoretical results. For example, the spectroscopic parameters, R_e, ω_e, $\omega_e\chi_e$, B_e and α_e, deviate from the experimental results[7] only by 0.58%, 0.80%, 1.08% , 0.17% and 0.62%, respectively. Whereas none of these investigations[2,10−34] can achieve so high accuracy as a whole, in particular for ω_e and D_e.

For the HI($X^1\Sigma^+$) molecule, the recent experimental D_0 value was given by Wilkinson[8] in 1963. His D_0 value is 3.057 eV. And the experimental D_0 value collected in Ref. [7] by Huber and Herzberg in 1979 is 3.054 eV, which is very close to that obtained by Wilkinson.[8] The present D_0 value calculated at the largest correlation-consistent basis sets, aug-cc-pV5Z-pp for I and aug-cc-pV6Z for H atom, is 3.1551 eV. Obviously, this result accords well with the D_0 experimental values.[7,8] Because the basis sets used here are largest, and the approach used here is reliable and accurate, we have reasons to believe that the present results are reliable and accurate. Therefore, we think that the D_0 values given in Refs. [7] and [8] should be reliable experimental ones.

As to the DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$) isotope molecules, to the best of our knowledge, no theoretical spectroscopic results are available in the literature, and only two groups of experiments[5,6] can be found up to date. In order to make a convenient comparison with these experimental results, we also collect them in Table 2. By comparison, we have found that excellent agreement exists between the present results and these RKR data. For example for the DI($X^1\Sigma^+$) the deviations of the present values of R_e, B_e and α_e from the experiments[5] are 0.58%, 1.14% and 0.49%, respectively. And the deviations of the present values of ω_e, $\omega_e\chi_e$, B_e and α_e from the experimental results[6] are 0.78%, 4.96%, 1.13%, and 0.49%, respectively. For the TI($X^1\Sigma^+$), the deviations of the present values of R_e, B_e and α_e from the only experimental results[5] are 0.58%, 1.14% and 0.29%, respectively. Because of the accurate spectroscopic results of the HI($X^1\Sigma^+$) and their excellent agreement with the RKR data[5,6] of the DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), we think that the PEC of HI($X^1\Sigma^+$) molecule is reliable. According to these, we believe that all the theoretical results listed in Table 2 are both reliable and accurate.

3.2. Vibrational manifolds

Using the PEC of the HI($X^1\Sigma^+$) obtained by the MRCI approach and the correlation-consistent basis sets, aug-cc-pV5Z-pp for I and aug-cc-pV6Z for H atom, we determine the values of vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ of the three isotope molecules, HI($X^1\Sigma^+$), DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), with the aid of VIBROT module presented in MOLCAS 7.4 program package.[40] By calculations, a total of 19 vibrational states for the HI($X^1\Sigma^+$), 26 for the DI ($X^1\Sigma^+$) and 32 for the TI($X^1\Sigma^+$) have been predicted, respectively. And for each vibrational state, the $G(\upsilon)$, B_υ and D_υ are determined. For the convenient comparison with the available RKR data,[5,9] these results are all listed in Tables 3–5, respectively.

Table 3 shows the present values of $G(\upsilon)$, B_υ and D_υ for the HI($X^1\Sigma^+$). Up to now there have been only two groups of experiments[5,9] involved with them. For the purpose of comparison, we also present these RKR results given in Ref. [9] in Table 3. Table 3 shows the excellent agreement between the RKR data[9] and the present ones. For example for the vibrational levels, the present results deviate from those experimental results[9] only by 0.42%, 0.27%, 0.05% ,0.26% and 0.35% when υ = 0, 1, 3, 5 and 7, respectively. And for the inertial rotation constant B_υ, the deviations of the present values from the experimental results[9] are also only 1.15%, 1.19%, 1.23% , 1.20% and 1.03% when υ = 0, 1, 3, 5 and 7, respectively. Although the deviations of D_υ from the experimental results[9] are a little large in the sense of high-class small quantity, we think that the agreement between them is still very satisfactory on the whole.

Table 3. Comparisons of vibrational levels and molecular constants with available experimental results for the HI($X^1\Sigma^+$) when $J = 0$ at the MRCI level of theory.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$		$B_\upsilon/\mathrm{cm}^{-1}$		$10^4 D_\upsilon/\mathrm{cm}^{-1}$	
	this work	Exp.[9]	this work	Exp.[9]	this work	Exp.[9]
0	1150.02	1145.2436	6.35225	6.4263643	1.98876	2.068672
1	3384.03	3374.8252	6.18107	6.2552378	2.01023	2.064996
2	5530.08	5524.4701	6.00906	6.0829499	2.02739	2.066559
3	7589.76	7593.2780	5.83606	5.9088108	2.04321	2.074726
4	9564.06	9579.9517	5.66157	5.7319726	2.06083	2.091303
5	11453.28	11482.7165	5.48483	5.5513815	2.08348	2.118734
6	13256.96	13299.218	5.30481	5.365710	2.11457	2.16040
7	14973.86	15026.386	5.12022	5.173257	2.15787	2.22110
8	16601.94		4.92948		2.21790	
9	18138.25		4.73065		2.30052	
10	19578.89		4.52133		2.41389	
11	20918.82		4.29840		2.57023	
12	22151.68		4.05773		2.78905	
13	23269.36		3.79343		3.10393	
14	24261.46		3.49668		3.57848	
15	25114.14		3.15289		4.35009	
16	25808.09		2.73461		5.78476	
17	26313.79		2.17642		9.34643	
18	26576.26		1.16576		45.4793	

Table 4. Comparisons of vibrational levels and molecular constants with available experimental results for DI($X^1\Sigma^+$) when $J = 0$ at the MRCI level of theory.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$		$B_\upsilon/\mathrm{cm}^{-1}$		$10^5 D_\upsilon/\mathrm{cm}^{-1}$	
	this work	Exp.[9]	this work	Exp.[9]	this work	Exp.[9]
0	821.94	815.2239	3.23844	3.2534870	5.12081	5.26303
1	2432.14	2414.9868	3.17660	3.1922888	5.16330	5.25393
2	3997.26	3974.5792	3.11455	3.1308625	5.19854	5.25090
3	5518.01	5493.7505	3.05227	3.0690972	5.22921	5.25500
4	6994.92	6972.1612	2.98975	3.0068654	5.25811	5.26751
5	8428.39	8409.3710	2.92688	2.9440192	5.28815	5.29000
6	9818.64		2.86356		5.32232	
7	11165.69		2.79963		5.36365	
8	12469.39		2.73490		5.41529	
9	13729.36		2.66915		5.48062	
10	14945.06		2.60211		5.56337	
11	16115.68		2.53350		5.66784	
12	17240.23		2.46297		5.79919	
13	18317.45		2.39012		5.96385	
14	19345.82		2.31449		6.17012	
15	20323.56		2.23551		6.42910	
16	21248.50		2.15250		6.75611	
17	22118.14		2.06458		7.17305	
18	22929.46		1.97066		7.71251	
19	23678.89		1.86925		8.42529	
20	24362.08		1.75830		9.39538	
21	24973.68		1.63481		10.7729	
22	25506.85		1.49406		12.8552	
23	25952.60		1.32789		16.3369	
24	26298.16		1.11969		23.3481	
25	26523.31		0.82176		46.3613	

Table 5. Comparisons of vibrational levels and molecular constants with available experimental results for TI($X^1\Sigma^+$) when $J = 0$ at the MRCI level of theory.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$		$B_\upsilon/\mathrm{cm}^{-1}$		$10^5 D_\upsilon/\mathrm{cm}^{-1}$	
	this work	Exp.[9]	this work	Exp.[9]	this work	Exp.[9]
0	674.59	669.4667	2.17943	2.1932550	2.30954	2.38406
1	2001.09	1987.7581	2.14541	2.1594867	2.32582	2.38029
2	3297.18	3279.0515	2.11128	2.1256276	2.33967	2.37830
3	4563.27	4543.2248	2.07706	2.0916386	2.35180	2.37833
4	5799.69	5780.1178	2.04274	2.0574758	2.36283	2.38067
5	7006.73	6989.5279	2.00829	2.0230899	2.37349	2.38565
6	8184.60	8171.2063	1.97370	1.9884251	2.38451	2.39367
7	9333.41		1.93891		2.39662	
8	10453.21		1.90387		2.41058	
9	11543.97		1.86851		2.42714	
10	12605.55		1.83277		2.44712	
11	13637.73		1.79655		2.47136	
12	14640.19		1.75977		2.50079	
13	15612.53		1.72231		2.53644	
14	16554.23		1.68405		2.57951	
15	17464.68		1.64487		2.63142	
16	18343.14		1.60460		2.69387	
17	19188.76		1.56306		2.76899	
18	20000.57		1.52006		2.85945	
19	20777.44		1.47535		2.96875	
20	21518.06		1.42865		3.10150	
21	22220.96		1.37960		3.26397	
22	22884.42		1.32777		3.46497	
23	23506.47		1.27262		3.71712	
24	24084.77		1.21342		4.03944	
25	24616.60		1.14921		4.46185	
26	25098.66		1.07863		5.03441	
27	25526.90		0.99968		5.84816	
28	25896.16		0.90916		7.08882	
29	26199.65		0.80138		9.20969	
30	26427.65		0.66421		13.7372	
31	26564.40		0.45747		33.0553	

By the way, in order to avoid congestion in Table 3, we do not list the RKR data presented in Ref. [5] in the table. By comparison, we also find that excellent agreement still exists between the present results and these RKR data.[5]

Table 4 shows the present values of $G(\upsilon)$, B_υ and D_υ of DI($X^1\Sigma^+$) isotope molecule and their comparison with the available experimental results.[9] To the best of our knowledge, only two groups of experimental results[5,9] can be found in the literature up to date. In order to avoid congestion, in a similar way to that in Table 3, we also omit the experimental results presented in Ref. [5] in this table. By comparison with the available experimental results presented by Lucia *et al.*,[5] it is not difficult to find that the good accordance can be found between the experimental results[5] and the present ones. As to the experimental findings reported by Coxon and Hajigeorgiou,[9] an excellent agreement still exists between experimental data[9] and the present ones. For example for the $G(\upsilon)$, the differences between them are only 0.82%, 0.71%, 0.44% and 0.23% when $\upsilon = 0$, 1, 3 and 5, respectively. For the B_υ, the differences between them are only 0.46%, 0.49%, 0.55% and 0.58% when $\upsilon = 0$, 1, 3 and 5, respectively. And for the D_υ, although the differences between them go up to 2.70%

and 1.72% when $\upsilon =$ and 1, respectively, these differences are both within 1.0% when the vibrational level is higher than one. Therefore we think that the agreement between the present results and the experimental results[9] is also satisfactory on the whole. According to these, we can still conclude that the present results of DI($X^1\Sigma^+$) isotope molecule, shown in Table 4 are accurate.

Table 5 shows the present $G(\upsilon)$, B_υ and D_υ of TI($X^1\Sigma^+$) isotope molecule and their comparisons with the experimental results.[9] Because the values of B and D_0 obtained by Lucia *et al.*[5] are very close to the results reported by Coxon and Hajigeorgiou,[9] we do not include them in the table. Obviously, the present results accord fairly well with the experimental results.[9] For example for the $G(\upsilon)$, the deviations from the experimental results[9] are only 0.77%, 0.67%, 0.44% and 0.25% when $\upsilon =$ 0, 1, 3 and 5, respectively. Hence, we can still say that the present results in Table 5 are accurate.

The molecular constants of HI, DI and TI are derived from the same PEC. However, due to the differences in mass among H, D and T, on the one hand, the total numbers of their vibrational states are different, with the isotope effect taken into consideration. As shown in Tables 3–5, there are 19 vibrational states for the HI, 26 for the DI and 32 for the TI. On the other hand, we also find that the level interval [$G(\upsilon)$–$G(\upsilon$–1)] becomes smaller when the mass of isotope atom becomes larger. The highest vibrational levels for HI, DI and TI are all lower than the ground-state dissociation energy 26589.6690 cm^{-1}

4. Conclusions

The CASSCF method and the subsequent MRCI approach are employed to investigate the PEC of HI($X^1\Sigma^+$) molecule over an internuclear distance range from 0.08 nm to 0.575 nm. Using the HI($X^1\Sigma^+$) PEC, the spectroscopic parameters of three isotope molecules, HI($X^1\Sigma^+$), DI($X^1\Sigma^+$) and TI($X^1\Sigma^+$), are accurately determined at the present level of theory. In order to acquire reliable and accurate PEC of HI($X^1\Sigma^+$) molecule, a very large relativistic effective core potential basis set for I and a very large valence basis set for H atom are used. For the HI($X^1\Sigma^+$), the present values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 3.1551 eV, 3.2958 eV, 0.16183 nm, 2290.60 cm^1, 40.0703 cm^{-1}, 0.1699 cm^{-1} and 6.4373 cm^{-1}, respectively; for the DI ($X^1\Sigma^+$), the present values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 3.1965 eV, 3.2967 eV, 0.16183 nm, 1626.8 cm^{-1}, 20.8581 cm^{-1}, 0.0611 cm^{-1} and 3.2468 cm^{-1}, respectively; and for the TI ($X^1\Sigma^+$), the present values of D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e are 3.2144 eV, 3.296 eV, 0.16183 nm, 1334.43 cm^{-1}, 14.0765 cm^{-1}, 0.0338 cm^{-1} and 2.1850 cm^{-1}, respectively. These results are compared with previous results reported in the literature. A good agreement is obtained between the experimental data and the present ones. With the PEC of HI($X^1\Sigma^+$) molecule determined here, a total of 19 vibrational states are predicted for the HI, 26 for the DI, and 32 for the TI, respectively, when $J = 0$. For each vibrational state, vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ are calculated for the first time. Comparison between the available experimental results and the present results demonstrates that the present spectroscopic parameters and molecular constants are both reliable and accurate.

References

[1] Wright S A and McDonald J D 1994 *J. Chem. Phys.* **101** 238

[2] Mečiarová K, Cantrel L and Črnušk I 2008 *Collect. Czech. Chem. Commun.* **73** 1340

[3] Naudé S M and Verleger H 1950 *Proc. Phys. Soc.* **63** 470

[4] Niay P, Bernage P, Coquant C and Fayt A 1978 *J. Mol. Spectrosc.* **72** 168

[5] Lucia D F C, Helminger P and Gordy W 1971 *Phys. Rev.* A **3** 1849

[6] Hurlock S C, Alexander R M, Rao K N, Derska S N, Pugh L A and R K Narahari 1971 *J. Mol. Spectrosc.* **37** 373

[7] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure* Vol. 4 *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold Company) p. 325

[8] Wilkinson P G 1963 *Astrophys. J.* **138** 778

[9] Coxon J A and Hajigeorgiou P G 1991 *J. Mol. Spectrosc.* **150** 1

[10] Ungemach S R, Schaefer H F and Liu B 1977 *J. Mol. Spectrosc.* **66** 99

[11] Barandiarán Z and Seijo L 1986 *J. Chem. Phys.* **84** 1941

[12] Matsuoka O 1992 *J. Chem. Phys.* **97** 2271

[13] Seijo L 1995 *J. Chem. Phys.* **102** 8078

[14] Lee S Y and Lee Y S 1991 *Chem. Phys. Lett.* **187** 302

[15] Styszyński J 2000 *Chem. Phys. Lett.* **317** 351
[16] Styszyński J and Kobus J 2003 *Chem. Phys. Lett.* **369** 441
[17] Haiduke R L A, Comar M and da Silva A B F 2006 *Chem. Phys.* **331** 173
[18] Visscher L, Styszyñski J and Nieuwpoort W C 1996 *J. Chem. Phys.* **105** 1987
[19] Al-Saidi W A 2008 *J. Chem. Phys.* **129** 064316
[20] Chapman D A, Balasubramanian K and Lin S H 1987 *J. Chem. Phys.* **87** 5325
[21] Kellö V and Sadlej A J 1990 *J. Chem. Phys.* **93** 8122
[22] Saue T, Faegri K and Gropen O 1996 *Chem. Phys. Lett.* **263** 360
[23] Feller D, Peterson K A, de Jong W A and Dixon D A 2003 *J. Chem. Phys.* **118** 3510
[24] Alekseyev A B, Liebermann H, Kokh D B and Buenker R J 2000 *J. Chem. Phys.* **113** 6174
[25] Martin J M L and Sundermann A 2001 *J. Chem. Phys.* **114** 3408
[26] Hirata S, Yanai T, Harrison R J, Kamiya M and Fan P D 2007 *J. Chem. Phys.* **126** 024104
[27] Dunning T H 1984 *J. Phys. Chem.* **88** 2469
[28] Schwerdtfeger P, Szentpály L V, Vogel K, Silberbach H, Stoll H and Preuss H 1986 *J. Chem. Phys.* **84** 1606
[29] Schwerdtfeger P, Szentpály L V, Stoll H and Preuss H 1987 *J. Chem. Phys.* **87** 510
[30] Werner H J, Reinsch E A and Rosmus P 1981 *Chem. Phys. Lett.* **78** 311
[31] Watanabe Y and Matsuoka O 1998 *J. Chem. Phys.* **109** 8182
[32] Hennum A C, Halkier A and Klopper W 2001 *J. Mol. Struct.* **599** 153
[33] Peterson K A, Figgen D, Goll E, Stoll H and Dolg M 2003 *J. Chem. Phys.* **119** 11113
[34] Hirata S, Yanai T, de Jong W A, Nakajima T and Hirao K 2004 *J. Chem. Phys.* **120** 3297
[35] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803
[36] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514
[37] Peterson K A, Woon D E and Dunning T H 1994 *J. Chem. Phys.* **100** 7410
[38] Peterson K A, Kendall R A and Dunning T H 1993 *J. Chem. Phys.* **99** 1930
[39] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
[40] Krogh J W, Lindh R, Malmqvist P Å, Roos B O, Veryazov V and Widmark P O 2009 *User Manual*, Molcas Version 7.4 (Lund: Lund University)
[41] Werner H J, Knowles P J, Lindh R, Manby F R, Schütz M, Celani P, Korona T, Mitrushenkov A, Rauhut G, Adler T B, Amos R D, Bernhardsson A, Berning A, Cooper D L, Deegan M J O, Dobbyn A J, Eckert F, Goll E, Hampel C, Hetzer G, Hrenar T, Knizia G, Köppl C, Liu Y, Lloyd A W, Mata R A, May A J, McNicholas S J, Meyer W, Mura M E, Nicklass A, Palmieri P, Pflüger K, Pitzer R, Reiher M, Schumann U, Stoll H, Stone A J, Tarroni R, Thorsteinsson T, Wang M and Wolf A 2008 *MOLPRO*, version 2008.1, a package of *ab initio* program
[42] Shi D H, Zhang J P, Sun J F, Liu Y F and Zhu Z L 2009 *Acta Phys. Sin.* **58** 5329 (in Chinese)
[43] Zhang X N, Shi D H, Sun J F and Zhu Z L 2010 *Chin. Phys.* B **19** 013501
[44] Gao F, Yang C L, Hu Z Y and Wang M S 2007 *Chin. Phys.* **16** 3668
[45] Zhang L, Yang C L and Ren T Q 2008 *Mol. Phys.* **106** 615
[46] Wang X Q, Yang C L, Su T and Wang M S 2009 *Acta Phys. Sin.* **58** 6873 (in Chinese)
[47] Zhang X N, Shi D H, Zhang J P, Zhu Z L and Sun J F 2010 *Chin. Phys.* B **19** 053401