Study on spectroscopic parameters and molecular constants of HCl($X^1\Sigma^+$) molecule by using multireference configuration interaction approach*

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Equilibrium internuclear separations, harmonic frequencies and potential energy curves (PECs) of HCl($X^1\Sigma^+$) molecule are investigated by using the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach in combination with a series of correlation-consistent basis sets in the valence range. The PECs are all fitted to the Murrell–Sorbie function, and they are used to accurately derive the spectroscopic parameters (D_e, D_0, $\omega_e\chi_e$, α_e and B_e). Compared with the available measurements, the PEC obtained at the basis set, aug-cc-pV5Z, is selected to investigate the vibrational manifolds. The constants D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e at this basis set are 4.4006 eV, 4.5845 eV, 0.12757 nm, 2993.33 cm^{-1}, 52.6273 cm^{-1}, 0.2981 cm^{-1} and 10.5841 cm^{-1}, respectively, which almost perfectly conform to the available experimental results. With the potential determined at the MRCI/aug-cc-pV5Z level of theory, by numerically solving the radial Schrödinger equation of nuclear motion in the adiabatic approximation, a total of 21 vibrational levels are predicted. Complete vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are reproduced, which are in excellent agreement with the available Rydberg–Klein–Rees data. Most of these theoretical vibrational manifolds are reported for the first time to the best of our knowledge.

Keywords: dissociation energy, spectroscopic parameter, vibrational level, inertial rotation constant

PACC: 3440, 3120C, 3520G

1. Introduction

Hydrogen chloride (HCl) is a molecule of fundamental importance. Because, on the one hand, it is one of secondary frequency standards for the far-infrared (FIR) region;[1,2] on the other hand, it has astrophysical relevance.[3−6] For example, it has been observed in the infrared (IR) region of the upper atmosphere[4] and in the IR absorption spectra of the atmospheres of Venus[5] and an S-type star.[6] For this reason, the spectroscopic properties of the molecule have been extensively investigated over the past several decades both experimentally and theoretically.

In experiment, the earlier spectroscopic investigations of the molecule were performed by Gordy's group in the 1950s and 1960s.[7−10] Since then, its spectroscopic properties have been widely studied by Lamb-dip spectroscopy,[2] FIR and tunable FIR (TuFIR) spectroscopy,[11,12] threshold ionisation spectroscopy,[13] photoelectron spectroscopy[14] and high resolution IR emission spectroscopy.[15] In theory, the earlier calculations of the molecule were made by Cade and Huo,[16] who used the self-consistent field (SCF) method with the optimised Slater-type functions (STF's) centred on both nuclei to calculate its potential energy curve (PEC). Since then, a number of theoretical investigations[17−28] have been carried out. Of particular interest is a comparison of these molecular constants between experiment and theory. As a whole, these theoretical predictions have presented a set of spectroscopic parameters, and they are in good agreement with the available experimental measurements.[9−13,29−34] However, the spectroscopic properties extracted from these theories and experiments were mainly based on some of the spectroscopic parameters (i.e. D_e, R_e, ω_e, $\omega_e\chi_e$, α_e, B_e and D_0). Little theoretical information is available about its vibrational manifolds (such as the vibrational levels, the classical turning points, the inertial rotation and centrifugal distortion constants), though these data are very useful in the rovibrational transition calculations. All these motivate us to do the present work.

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One of the main purposes of the present investigations is to calculate the spectroscopic parameter and vibrational manifold. The equilibrium internuclear separations, harmonic frequencies and PECs of the HCl ($X^1\Sigma^+$) molecule are evaluated by employing the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[35,36] in combination with a series of correlation–consistent basis sets[37−39] in the valence range. The PECs are fitted to the analytic Murrell–Sorbie (M–S) function with the least-squares fitting method, which are used to determine the spectroscopic parameters. With the interaction potential attained at the MRCI/aug-cc-pV5Z level of theory, by numerically solving the radial Schrödinger equation of nuclear motion in the adiabatic approximation with the Numerov method,[40] a total of 21 vibrational levels are predicted when the rotational quantum number J is equal to zero ($J = 0$). Complete vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are accurately reproduced for the first time, to the best of our knowledge. Generally, the present results are more complete and accurate than the previous ones,[16−28] and achieve much higher accuracy due to the employment of the large basis set.

2. Computational methods

We employ the MRCI approach to investigate the equilibrium internuclear distances R_e and the harmonic frequencies ω_e of the HCl($X^1\Sigma^+$) molecule. All the calculations are carried out with the full valence complete active space self-consistent field (CASSCF) method followed by the MRCI approach in MOLPRO 2008.1 program package[41] at a series of correlation–consistent basis sets, cc-pVnZ ($n = 2, 3, 4, 5, 6$)[37−39] in the valence range. Thus, the full valence CASSCF is adopted as a reference wavefunction for the MRCI calculations in the present investigations. Furthermore, the effects on the spectroscopic parameters by these basis sets augmented with diffuse functions, aug-cc-pVnZ ($n = 2, 3, 4, 5$), are also evaluated. The constants R_e and ω_e determined at these consistent–correlation basis sets are all listed in Table 1.

Table 1. Equilibrium parameters for HCl($X^1\Sigma^+$) at the MRCI level of theory and in different correlation–consistent basis sets, cc-pVnZ and aug-cc-pVnZ.

basis sets	D_e/eV	R_e/nm	ω_e/cm^{-1}	basis sets	D_e/eV	R_e/nm	ω_e/cm^{-1}
cc-pVDZ	4.9675	0.12486	3171.47	aug-cc-pVDZ	4.9048	0.12530	3131.35
cc-pVTZ	4.6190	0.12713	3025.82	aug-cc-pVTZ	4.6142	0.12727	3017.45
cc-pVQZ	4.5756	0.12753	2997.41	aug-cc-pVQZ	4.5770	0.12757	2993.62
cc-pV5Z	4.5818	0.12755	2996.68	aug-cc-pV5Z	4.5845	0.12757	2993.33
cc-pV6Z	4.5835	0.12758	2992.69				

The PEC is calculated at each basis set over the internuclear distance range from about 0.09 to 2.00 nm. The PEC calculations are carried out at an interval of 0.04 nm, except near the equilibrium position at an interval of 0.005 nm. The *ab initio* results at each basis set are all fitted to the M–S function with the least-squares fitting method. Therefore, the dissociation energy D_e and the analytic potential energy function (APEF) are derived. The D_e values fitted at present are also presented in Table 1 for comparison with the measurements. Based on the fitted APEF, force constants, quadratic f_2, cubic f_3 and quartic f_4, are deduced, thereby obtaining the spectroscopic parameters, $\omega_e\chi_e$, α_e, B_e and D_0.

For the $X^1\Sigma^+$ state of the HCl molecule, the recent experimental D_0 values were given by Martin and Hepburn[13] in 1998 and Michel *et al.*[34] in 2002, separately. Martin and Hepburn[13] determined the bond dissociation energy of the HCl($X^1\Sigma^+$) molecule by threshold ion-pair production spectroscopy to spectroscopic accuracy ($D_0 = 35748.2 \pm 0.8$ cm^{-1}). And Michel *et al.*[34] derived its dissociation energy via the lineshape analysis of a single rotational transition (D_0 = 35748.2±0.8 cm^{-1}). If we use these experimental results of ω_e and $\omega_e\chi_e$ determined by Parekunnel *et al.*[12] in 1999, we can deduce their dissociation energies to be 4.6166 eV[13] and 4.6165 eV,[34] respectively. Obviously, the present D_e values calculated at the cc-pV5Z, cc-pV6Z and aug-cc-pV5Z basis sets almost perfectly conform to these results, and the deviations from these two experiments are only within 0.754% at the cc-pV5Z, 0.717% at the cc-pV6Z and

0.695% at the aug-cc-pV5Z basis sets, respectively.

As to the results of R_e and ω_e at these basis sets, cc-pV5Z, cc-pV6Z and aug-cc-pV5Z, we also find that the excellent agreement exists between the present values and the available experimental data.[9,10,12,29−33] For example at the cc-pV5Z basis set, the deviations from the corresponding experimental ones are within 0.071%[29] for R_e and 0.123%[30] for ω_e, respectively. At the cc-pV6Z basis set, the deviations from the corresponding experimental ones are only within 0.094%[29] for R_e and 0.0587%[30] for ω_e, respectively. And at the aug-cc-pV5Z basis set, the deviations from the corresponding experimental ones also are only within 0.0863%[29] for R_e and 0.0781%[30] for ω_e, respectively. Thereupon, we are certain that these basis sets, cc-pV5Z, aug-cc-pV5Z and cc-pV6Z, are all suitable for determining the spectroscopic parameters of the HCl($X^1\Sigma^+$) molecule at the present level of accuracy. Because the diffuse functions can improve the description of long-range interactions, more accurate potential can be obtained at larger internuclear separations at the basis set, aug-cc-pV5Z. Therefore, we choose the PEC obtained at the aug-cc-pV5Z basis set for the calculation of the spectroscopic parameter and molecular constant. In addition, we find that the constants $\omega_e\chi_e$, α_e and B_e obtained at the aug-cc-pV5Z basis set are also in satisfactory agreement with the available experimental results.[9,10,12,30−33] These further approve that the interaction potential determined at the aug-cc-pV5Z basis set is the suitable one for vibrational manifold calculations.

Finally, with the APEF obtained at the present MRCI/aug-cc-pV5Z level of theory, by numerically solving the radial Schrödinger equation of nuclear motion in the adiabatic approximation, all the vibrational states are determined. And complete vibrational levels, classical turning points, R_{min} and R_{max}, and inertial rotation and centrifugal distortion constants are evaluated.

3. Results and discussion

3.1. APEF of the HCl($X^1\Sigma^+$) molecule

The M–S function is a widely-used APEF. It can analytically describe the interaction potential of diatomic molecules well. In recent years, we have used this function to accurately deduce the APEFs for a number of diatomic molecules.[42−46] The common M–S function is expressed as[47]

$$V(\rho) = -D_e\left(1 + \sum_{i=1}^{n} a_i\rho^i\right)\exp(-a_1\rho), \qquad (1)$$

where $\rho = r - R_e$, r is the diatomic internuclear distance. R_e is its equilibrium internuclear distance and regarded as a fixed parameter in the fitting process. The dissociation energy D_e and the parameters a_i (i = 1, 2, ..., n) are floated in fitting.

Fitting Eq. (1) by the least-squares method, parameters a_i and D_e are determined. In order to attain a satisfactory result, of which the root mean square error is minimised and the extracted spectroscopic parameters from the fitted APEF are the closest to the experimental findings as a whole, we try to take the values of n ranging from 3 to 8. When comparing our results with the experimental ones (D_e, B_e, α_e, $\omega_e\chi_e$ and D_0),[9,10,12,13,29−34] we find that the favourable results can be derived at n = 4. The fitting results are listed in Table 2 together with the R_e value for integrality.

Table 2. M–S APEF parameters for HCl($X^1\Sigma^+$) at the MRCI/aug-cc-pV5Z level of theory.

D_e/eV	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	a_4/nm^{-4}	ΔE_{RMSE}/eV
4.5845	0.12757	35.77569	291.61853	1389.88026	–7901.70312	0.000913

To evaluate the fitting quality of the PEC, we calculate the root mean square error (ΔE_{RMSE}) in the fitting process,

$$\Delta E_{RMSE} = \sqrt{\frac{1}{N}\left\{\sum_{i=1}^{N}[V_{APEF}(i) - V_{ab\ initio}(i)]^2\right\}}, \qquad (2)$$

where $V_{APEF}(i)$ and $V_{ab\ initio}(i)$ are energies attained by the fitting and the *ab initio* calculations, respectively. N is the number of the fitting points (here N = 80). The present ΔE_{RMSE} for the M–S APEF is only 0.000913 eV. It shows that the present M–S function is very suitable for reproducing the PEC of the HCl($X^1\Sigma^+$) molecule,

and the fitting is of high quality. Therefore, the present APEF listed in Table 2 should be reliable and can be employed to accurately calculate the spectroscopic parameter and vibrational manifold, such as vibrational levels, classical turning points, the inertial rotation and centrifugal distortion constants.

4. Spectroscopic parameters (D_0, B_e, α_e and $\omega_e\chi_e$)

Now, we calculate the remaining spectroscopic parameters (B_e, α_e, $\omega_e\chi_e$ and D_0) of the HCl($X^1\Sigma^+$) molecule using the APEF tabulated listed in Table 2. According to the method and equations given in Ref. [42], we calculate these parameter values. The present B_e, α_e, $\omega_e\chi_e$ and D_0 values together with the R_e, ω_e and D_e results are given in Table 3. And those of the available experimental results[9,10,12,13,29–34] and other theoretical results[16–28] are also listed in Table 3 for comparison.

Table 3. Spectroscopic parameter comparison between experimental measurements and other theoretical calculations for the HCl ($X^1\Sigma^+$) at the MRCI/aug-cc-pV5Z 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	4.5845	0.12757	2993.33	52.6273	10.5841	0.2981	4.4006
Exp.[9]	–	0.12745	–	–	10.6074	–	–
Exp.[10]	–	0.12746	–	–	10.6064	–	–
Exp.[12]	–	–	2990.925	52.8000	10.5933	0.3070	–
Exp.[13]	–	–	–	–	–	–	4.4328
Exp.[29]	–	0.12746	2991.799	–	–	–	–
Exp.[30]	–	–	2990.993	52.8510	10.5933	0.3070	–
Exp.[31]	–	–	2990.966	52.8364	10.5934	0.3072	–
Exp.[32]	4.6175	0.12746	2990.946	52.8186	10.5934	0.3072	4.4336
Exp.[33]	–	–	2990.946	52.8185	10.5934	0.3072	–
Exp.[34]	–	–	–	–	–	–	4.4327
theory[16]	3.48	0.12642	3181	47.76	10.767	0.2682	3.2843
theory[17](CEPA)	4.43	0.1278	2977.2	53.2	10.54	0.309	4.4271
(PNO-CI)	4.31	0.1273	3034.0	50.1	10.62	0.297	4.1234
theory[18]	–	0.12967	3030.4	99.57	10.228	0.2646	–
theory[19]	4.2332	0.12888	3004.9	50.65	10.36	–	4.0485
theory[20] (SCF)	–	0.1267	3133	45	10.72	0.275	–
(SCEP/CEPA)	–	0.1278	2987	53	10.54	0.304	–
theory[21]	4.34	0.1282	2961	–	10.46	–	–
theory[22]	4.62	0.1277	3023	52.9	10.67	0.338	4.4342
theory[23]	4.6199	0.12765	3025.6	54.45	10.571	0.310	4.4341
theory[24] (GVB+1+2)	4.5465	0.12760	2993.5	52.9	10.57	0.3066	4.3625
(CAS+1+2)	4.5768	0.12760	2990.7	52.0	10.57	0.2973	4.3930
theory[25]	4.5937	0.1278	2991	55	10.541	0.304	4.41
theory[26] (O3/SDC)	4.6309	0.12801	2971.18	45.81	–	0.3038	4.4481
theory[27]	4.5099	0.12768	3010.5	–	–	–	–
theory[28]	–	0.1277	2993	–	–	–	–

A number of theoretical investigations[16–28] are carried out on the spectroscopic parameters of the HCl ($X^1\Sigma^+$) molecule. Of these investigations, the earlier one was performed by Cade and Huo,[16] who used the SCF method with the optimised STF's centred on both nuclei to calculate its PEC. As given in Table 3, the D_0, D_e and $\omega_e\chi_e$ values are far from the experimental values.[12,13,30–34] Meyer and Rosmus[17] computed the spectroscopic parameters by the coupled electron pair approach (CEPA) and the pseudo natural orbital–configuration interaction (PNO–CI) method with the Gaussian-type orbitals (GTO's), which is comprised of 4s4p2d1f functions for Cl and 4s2p1d for H atom. From Table 3, it is

not difficult to find that their D_0, D_e and ω_e results are fairly accurate compared with the experimental results.[12,13,29−34] Bonifacic and Huzinaga[18] made the R_e, ω_e, $\omega_e\chi_e$, B_e and α_e calculations by using a large scale CI method in a double-zeta polarisation GTO's basis set, however, their values of ω_e and $\omega_e\chi_e$ are larger than the experimental results.[12,29−33] Hirst and Guest[19] carried out the CI calculations with the 11s7p/6s4p basis set for Cl and the 4s/2s basis set for H atom, which were augmented with a single set of d functions on Cl and a single set of p functions on H. Obviously, their D_0 value is too small compared with the experimental one.[13,32] Werner and Rosmus[20] performed the spectroscopic parameter calculations by several methods with the 14s11p3d1f basis set for Cl and the 7s2p1d$_{\sigma 2}$ basis set for H atom. However, an important parameter, D_e, was not evaluated in their work.

Afterwards, Bettendorff *et al.*[21] calculated D_e, R_e, ω_e and B_e by using the multireference CI (MRD–CI) approach with the atomic orbital (AO) basis set, which consists of 43 contracted cartesian gaussian functions. From Table 3, one can easily see that their D_e is still small when compared with the available experimental results.[13,32] Shortly afterwards, Wright and Buenker[22] performed its PEC and spectroscopic parameter calculations by the MRD–CI method and the basis set which contains the nuclear-centred double-zeta set augmented with the single polarisation (d on Cl and p on H atom) functions. Barclay and Wright[23] carried out its PEC and spectroscopic parameter calculations by the MRD–CI method with two basis sets, DZP (double-zeta plus single polarisation basis) and BF1 [the DZP basis augmented by a set of (s, p) bond functions]. And they found that the better results were obtained at the BF1 basis set. Woon and Dunning[24] also made the PEC and spectroscopic parameter calculations by the MRD–CI method based on the generalised valence bond (GVB) and CASSCF wave functions with a series of correlation–consistent basis sets. Comparing our results with the available measurements,[9,10,12,13,29−34] we find that the favourable results were obtained at the GVB+1+2/aug- cc-pV5Z and the CAS+1+2/aug-cc-pV5Z levels of theories. However, the molecular vibrational manifolds, such as vibrational levels, inertial rotation and centrifugal distortion constants, were not computed in their investigations.[22−24]

Recently, Hirata *et al.*[25] carried out the spectroscopic parameter calculations by third-order Douglas–Kroll (DK3) relativistic coupled-cluster theory with a series of correlation-consistent basis sets. And the best favourable results were determined by the extrapolation of DK3-CCSD, DK3-CCSDT and DK3-CCSDTQ in combination with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. Ramachandran[26] performed the PEC and spectroscopic parameter calculations by several density functional theory (DFT) with the cc-pVTZ basis set, and found that the good results could be derived at the O3LYP/the scaled dynamical correlation (O3/SDC) level of theory. Unfortunately, some important molecular constants, such as vibrational levels, inertial rotation and centrifugal distortion constants, were still not evaluated in these investigations.[25,26]

In order to accurately investigate the properties of this molecule, most recently, Haiduke *et al.*[27] performed the DKH2 calculations with the electronic correlation treated at the CCSD(T) level. In their relativistic calculations, the triple-, quadruple- and quintuple-zeta basis sets were employed. However, only D_e,R_e and ω_e were evaluated. Hirata *et al.*[28] used a high-order electron-correlation method with scalar relativistic and spin-orbit corrections at the complete basis set (CBS) extrapolation based on the cc-pVDZ-DK, cc-pVTZ-DK and cc-pVQZ-DK sets. Among the spectroscopic parameters, however, only R_e and ω_e were calculated. In the present work, we calculate not only the spectroscopic parameters but also the vibrational manifolds, thus, the present spectroscopic calculations are the most complete one up to now among all the theoretical studies.[16−28]

As listed in Table 3, spectroscopic parameters, R_e and ω_e, which are directly determined by the MRCI/aug-cc-pV5Z calculations in the MOLPRO 2008.1 program package,[41] are in excellent agreement with the available experimental results.[9,10,12,29−33] And the remaining spectroscopic parameters, such as D_0, D_e, α_e, B_e and $\omega_e\chi_e$, which are reproduced from the APEF fitted at present, also accord well with the available experimental measurements.[9,10,12,29−33] For example, the deviations from the experiments are only 0.715%[32] for D_e, 0.088%[30] for B_e and 0.396%[30] for $\omega_e\chi_e$. These further prove that the present M–S APEF is credible and accurate, and can be employed in the vibrational manifold calculations. Additionally, these also show that the present spectroscopic properties are basically accurate compared with the previous theoretical investigations.[16−28]

5. Vibrational manifolds

The more stringent way to compare the *ab initio* results with the measurements is to reproduce the RKR data: the vibrational levels and their corresponding classical turning points. Only in that way, can it be clearly demonstrated whether the present APEF accurately describes the PEC for the HCl($X^1\Sigma^+$) molecule. In order to obtain the vibrational eigenvalues, we solve the radial Schrödinger equation of nuclear motion. In the adiabatic approximation, the radial Schrödinger equation of nuclear motion can be written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\Psi_{v.J}(r) = E_{v,J}\Psi_{v.J}(r), \quad (3)$$

where $V(r)$ is the rotationless APEF presented in Table 2; r is the internuclear distance between two atoms, Cl and H; μ is the reduced mass of the HCl molecule; v and J are the vibrational and the rotational quantum numbers, respectively; $E_{v,J}$ and $\Psi_{v,J}(r)$ are the eigenvalues and eigenfunctions of the potential $J(J+1)\cdot\hbar^2/2\mu r^2+V(r)$, respectively. The rotational sublevel at a given vibrational level is represented by the following power series:[48]

$$\begin{aligned}E_{v,J} = {} & G(v)+B_v[J(J+1)]-D_v[J(J+1)]^2 \\ & +H_v[J(J+1)]^3+L_v[J(J+1)]^4 \\ & +M_v[J(J+1)]^5+N_v[J(J+1)]^6 \\ & +O_v[J(J+1)]^7, \end{aligned} \quad (4)$$

where $G(v)$ is the vibrational level, B_v is the inertial rotation constant, and D_v, H_v, L_v, M_v, N_v and O_v are the centrifugal distortion constants. In order to calculate the rotational and the centrifugal distortion constants when we solve Eq. (1) numerically, different values of rotational quantum number J have been taken into account. Using the Numerov method[40] with the automatic step-size selection to solve Eq. (1), we obtain a total of 21 vibrational levels for the HCl($X^1\Sigma^+$) molecule. For each vibrational level, one vibrational level, one inertial rotation constant and six centrifugal distortion constants are obtained. Here, the vibrational levels and their corresponding classical turning points are all presented in Table 4. And the inertial rotation constant B_v and the centrifugal distortion constants D_v and H_v are listed in Table 5.

Table 4. Comparisons of the calculations of vibrational levels and classical turning points with the measurements for HCl ($X^1\Sigma^+$) when $J=0$ at the MRCI/aug-cc-pV5Z level of theory.

v	$G(v)/\mathrm{cm}^{-1}$		$R_{\min}$/nm		$R_{\max}$/nm	
	this work	Exp.[49]	this work	Ref.[22]	this work	Ref.[22]
0	1481.566	1483.879	0.11778	0.11772	0.13944	0.13934
1	4367.839	4369.856	0.11173	0.11172	0.14975	0.14973
2	7151.739	7151.862	0.10805	0.10807	0.15783	0.15789
3	9834.291	9830.657	0.10532	0.10536	0.16512	0.16526
4	12440.151	12406.708	0.10315	0.10321	0.17203	0.17223
5	14885.963	14880.153	0.10135	0.10141	0.17879	0.17902
6	17256.120	17250.741	0.09982		0.18553	
7	19527.790	19517.766	0.09849		0.19233	
8	21727.884		0.09734		0.19929	
9	23773.007		0.09632		0.20648	
10	25699.400		0.09542		0.21401	
11	27502.862		0.09463		0.22198	
12	29178.644		0.09393		0.23051	
13	30721.301		0.09331		0.23979	
14	32124.489		0.09277		0.25004	
15	33380.645		0.09230		0.26164	
16	34480.500		0.09190		0.27514	
17	35412.236		0.09157		0.29156	
18	36159.854		0.09131		0.31295	
19	36699.349		0.09112		0.34496	
20	36983.821		0.09102		0.42146	

Table 5. Comparisons of inertial rotation constant B_υ and centrifugal distortion constants D_υ and H_υ with measurements for HCl($X^1\Sigma^+$) when $J = 0$ at the MRCI/aug-cc-pV5Z level of theory.

υ	B_υ/cm^{-1}		$D_\upsilon(\times10^{-4})$/cm^{-1}			$H_\upsilon(\times10^{-8})$/cm^{-1}	
	this work	Exp.[49]	this work	Exp.[33]	Exp.[49]	this work	Exp.[49]
0	10.4332867	10.44019823	5.2863563	5.28281	5.2807523	1.6854518	1.670972
1	10.1445897	10.13618375	5.2025036	5.21572	5.2142668	1.6178790	1.615673
2	9.8542678	9.83459646	5.1369739	5.15662	5.154437	1.5321272	1.55125
3	9.5613939	9.53478936	5.0895031	5.10563	5.102647	1.4553511	1.47557
4	9.2650224	9.2360034	5.0603256		5.060637	1.3819835	1.38515
5	8.9641616	8.937332	5.0502218		5.03059	1.2813403	1.27494
6	8.6577440	8.637682	5.0606067		5.01532	1.1200624	1.13781
7	8.3445899	8.335721	5.0936784		5.01848	0.9570484	0.96363
8	8.0233623		5.1526509			0.6993491	
9	7.6925076		5.2421191				
10	7.3501748		5.3686361				
11	6.9941000		5.5416524				
12	6.6214356		5.7751034				
13	6.2284852		6.0902291				
14	5.8102692		6.5209180				
15	5.3597657		7.1247155				
16	4.8664637		8.0081981				
17	4.3132549		9.3955578				
18	3.6684374		11.866104				
19	2.8573106		17.665088				
20	1.4875352		79.994467				

In experiment, only $G(\upsilon)$ of the lower eight levels and the classical turning points of the lower six levels can be found in the literature[22,49], to the best of our knowledge. The $G(\upsilon)$, $R_{\min}$ and $R_{\max}$ results are also listed in Table 4 for convenient comparison. Note that these classical turning points given in Ref. [22] were calculated based on the experimental data reported by Rank *et al.*[33] It is easy to find that the present results given in Table 4 conform almost perfectly with the available measurements.[22,49] For example, the deviations from the corresponding experiments are only 0.156%, 0.045%, 0.037%, 0.039% and 0.051% for the $G(\upsilon)$ at $\upsilon = 0$, 1, 3, 5 and 7, respectively. The differences between the present $R_{\min}$ and the corresponding RKR data[22] are only 0.051%, 0.009%, 0.019%, 0.038%, 0.058% and 0.059% for $\upsilon = 0$, 1, 2, 3, 4 and 5 respectively. And the deviations between the present $R_{\max}$ and the corresponding RKR data[22] are also only 0.072%, 0.013%, 0.038%, 0.085%, 0.116% and 0.128% at $\upsilon = 0$, 1, 2, 3, 4 and 5, respectively. Therefore, we deduce that the remaining results listed in Table 4 are reliable and accurate.

To conveniently observe that the vibrational level varies with vibrational quantum number υ, we depict all the 21 bound levels in Fig. 1. And to clearly demonstrate the differences between our calculations and the experiments,[49] we present the deviations of our calculations from measurements [49] in Fig. 2.

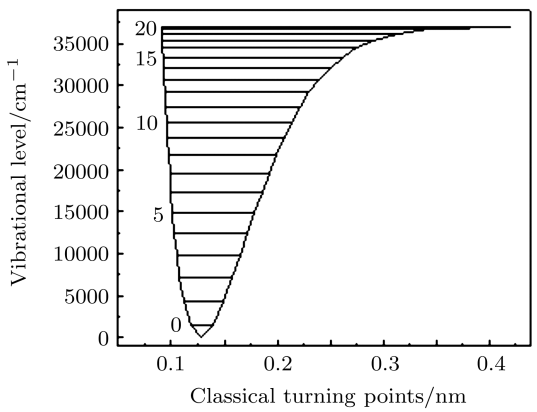


Fig. 1. 21 bound vibrational levels together with their classical turning points, with 0, 1, 2, ... 7 numbering the first 8 vibrational levels.

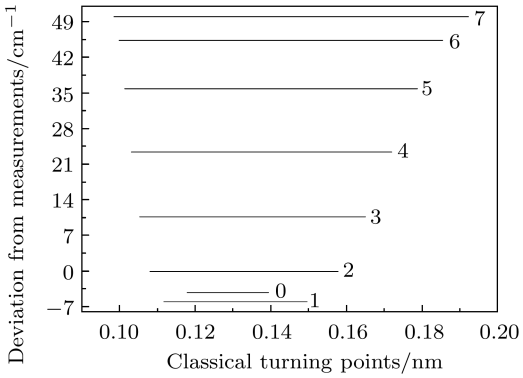


Fig. 2. Deviations of the theoretical vibrational levels from measurements, with 0, 1, 2, ... 7 numbering the first 8 vibrational levels.

As for B_υ, D_υ and H_υ, only the experimental results of the lower eight levels can be found, to our knowledge. The values of B_υ, D_υ and H_υ are also listed in Table 5 for convenient comparison. Table 5 that the present theoretical calculations accord well with these experimental measurements[33,49] as a whole. For example, their deviations from the corresponding experimental values are only 0.066%, 0.083%, 0.279%, 0.300% and 0.106% for the B_υ at υ = 0, 1, 3, 5 and 7, respectively. And the deviations from the corresponding experimental ones are only 0.106%, 0.226%, 1.482%, 0.390% and 1.498% for the D_υ at υ = 0, 1, 2, 5 and 7, respectively. Thus, we believe that the rest of results in Table 5 are also reliable and accurate. Further, we conclude that the M–S APEF given in Table 3 must be reliable and accurate.

6. Conclusions

The equilibrium internuclear separations, the harmonic frequencies and the PECs of the HCl ($X^1\Sigma^+$) molecule are investigated by employing the MRCI theory in combination with a series of correlation–consistent basis sets,[37−39] in the valence range. By careful comparison with the available measurements, the interaction potential obtained at the aug-cc-pV5Z basis set over the internuclear distance ranging from about 0.09 to 2.0 nm is chosen to determine the spectroscopic parameters, D_e, B_e, α_e, $\omega_\mathrm{e}\chi_\mathrm{e}$ and D_0. With the interaction potential obtained at the MRCI/aug-cc-pV5Z level of theory, by numerically solving the radial Schrödinger equation of nuclear motion with the Numerov method, a total of 21 vibrational levels are predicted for the first time. For each vibrational state, one vibrational level and its corresponding classical turning points, one inertial rotation constants and six centrifugal distortion constants are also reproduced. A comparison of our calculations with the available measurements shows that the present results are both reliable and accurate. The present results provide more complete and accurate investigations on the molecular parameters of the HCl($X^1\Sigma^+$) molecule so far.

References

[1] Guelachvili G, Birk M, Bordé C J, Brault J W, Brown L R, Carli B, Cole A R H, Evenson K M, Fayt A, Hausamann D, Johns J W C, Kauppinen J, Kou Q, Maki A G, Rao K N, Toth R A, Urban W, Valentin A, Vergès J, Wagner G, Wappelhorst M H, Wells J S, Winnewisser B P and Winnewisser M 1996 *IUPAC Pure Appl. Chem.* **68** 193

[2] Cazzoli G and Puzzarini C 2006 *J. Mol. Spectrosc.* **226** 161

[3] Weisstein E W and Serabyn E 1996 *Icarus* **123** 23

[4] Farmer C B, Carli B, Bonetti A, Carlotti M, Dinelli B M, Fast H, Evans W F J, Louisinard N, Alamichel C, Mankin W, Coffey M, Nolt I G, Murcray D G, Goldman A, Stokes G M, Johnson D W, Traub W A, Chance K V, Zander R, Roland G and Delbouille L 1990 *J. Atmos. Chem.* **10** 237

[5] Benedict W S, Connes J, Connes P and Kaplan L D 1967 *Astrophys. J.* **147** 1230

[6] Ridgway S T, Carbon D F, Hall D N B and Jewel J 1984 *Astrophys. J. Suppl.* **54** 177

[7] Burrus C A, Gordy W, Benjamin B and Livingston R 1955 *Phys. Rev.* **97** 1661

[8] Cowan M and Gordy W 1958 *Phys. Rev.* **111** 209

[9] Jones G and Gordy W 1964 *Phys. Rev.* **136** A1229

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

[11] Nolt I G, Radostitz J V, Dilonardo G, Evenson K M, Jennings D A, Leopold K R, Vanek M D, Zink L R, Hinz A and Chance K V 1987 *J. Mol. Spectrosc.* **125** 274

[12] Parekunnel T, Hirao T, Le Roy R J and Bernath P F 1999 *J. Mol. Spectrosc.* **195** 185

[13] Martin J D D and Hepburn J W 1998 *J. Chem. Phys.* **109** 8139

[14] Yencha A J, King G C, Lopes M C A, Bozek J D and Berrah N 1999 *Chem. Phys. Lett.* **315** 37

[15] LeBlanc R B, White J B and Bernath P F 1994 *J. Mol. Spectrosc.* **164** 574

[16] Cade P E and Huo W M 1967 *J. Chem. Phys.* **47** 649

[17] Meyer W and Rosmus P 1975 *J. Chem. Phys.* **63** 2356

[18] Bonifacic V and Huzinaga S 1975 *Chem. Phys. Lett.* **36** 573

[19] Hirst D M and Guest M F 1980 *Mol. Phys.* **41** 1483

[20] Werner H J and Rosmus P 1980 *J. Chem. Phys.* **73** 2319

[21] Bettendorff M, Peyerimhoff S D and Buenker R J 1982 *Chem. Phys.* **66** 261
[22] Wright J S and Buenker R J 1985 *J. Chem. Phys.* **83** 4059
[23] Barclay V J and Wright J S 1988 *Chem. Phys.* **121** 381
[24] Woon D E and Dunning T H 1993 *J. Chem. Phys.* **99** 1914
[25] Hirata S, Yanai T, de Jong W A, Nakajima T and Hirao K 2004 *J. Chem. Phys.* **120** 3297
[26] Ramachandran B 2006 *J. Phys. Chem.* A **110** 396
[27] Haiduke R L A, Comar M and da Silva A B F 2006 *Chem. Phys.* **331** 173
[28] Hirata S, Yanai T, Harrison R J, Kamiya M and Fan P D 2007 *J. Chem. Phys.* **126** 024104
[29] Klaus Th, Belov S P and Winnewisser G 1998 *J. Mol. Spectrosc.* **187** 109
[30] Clayton C M, Merdes D W, Plíva J, McCubbin T K and Tipping R H 1983 *J. Mol. Spectrosc.* **98** 168
[31] Guelachvili G, Niay P and Bernage P 1981 *J. Mol. Spectrosc.* **85** 271
[32] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure*, Vol.4, *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold) p290
[33] Rank D H, Rao B S and Wiggins T A 1965 *J. Mol. Spectrosc.* **17** 122
[34] Michel M, Korolkov M V and Weitzel K-M 2002 *Phys. Chem. Chem. Phys.* **4** 4083
[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] González J L M Q and Thompson D 1997 *Comput. Phys.* **11** 514
[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* programs
[42] Shi D H, Zhang J P, Sun J F, Zhu Z L, Yu B H and Liu Y F 2008 *J. Mol. Struct.* (*Theochem*) **851** 30
[43] Shi D H, Zhang J P, Liu Y F, Sun J F and Zhu Z L 2009 *Int. J. Quantum. Chem.* **109** 1159
[44] Shi D H, Chen Z Y, Zhang J P, Sun J F, Liu Y F and Zhu Z L 2009 *J. Mol. Struct.* (*Theochem*) **904** 98
[45] Shi D H, Sun J F, Zhu Z L, Ma H, Liu Y F and Zhu Z H 2007 *Int. J. Quantum. Chem.* **107** 1856
[46] Shi D H, Zhang J P, Sun J F, Liu Y F, Zhu Z L, Ma H and Yang X D 2008 *Chin. Phys.* B **17** 3678
[47] Murrell J N, Carter S, Farantos S C, Huxley P and Varandas J C 1984 *Molecular Potential Energy Functions* (Chichester: John Wiley & Sons) p9
[48] Shi D H, Zhang J P, Sun J F, Liu Y F and Zhu Z L 2009 *Acta Phys. Sin.* **58** 2369 (in Chinese)
[49] Coxon J A and Hajigeorgiou P G 2000 *J. Mol. Spectrosc.* **203** 49