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Investigations on molecular constants of the CD($X^2\Pi$) radical and elastic collisions between ground-state C and D atoms at low temperatures*

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The potential energy curve of the CD($X^2\Pi$) radical is obtained using the coupled-cluster singles-doubles-approximate-triples [CCSD(T)] theory in combination with the correlation-consistent quintuple basis set augmented with diffuse functions, aug-cc-pV5Z. The potential energy curve is fitted to the Murrell–Sorbie function, which is used to determine the spectroscopic parameters. The obtained D_0, D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e values are 3.4971 eV, 3.6261 eV, 0.11197 nm, 2097.661 cm^{-1}, 34.6963 cm^{-1}, 0.2083 cm^{-1} and 7.7962 cm^{-1}, respectively, which conform almost perfectly to the available measurements. With the potential obtained at the UCCSD(T)/aug-cc-pV5Z level of theory, a total of 24 vibrational states have been predicted for the first time when $J = 0$ by solving the radial Schrödinger equation of nuclear motion. The complete vibrational levels, the classical turning points, the inertial rotation constants and centrifugal distortion constants are reproduced from the CD($X^2\Pi$) potential when $J = 0$, and are in excellent agreement with the available measurements. The total and the various partial-wave cross sections are calculated for the elastic collisions between the ground-state C and D atoms at energies from 1.0×10^{-11} to 1.0×10^{-4} a.u. when the two atoms approach each other along the CD($X^2\Pi$) potential energy curve. Only one shape resonance is found in the total elastic cross sections, and the resonant energy is 8.36×10^{-6} a.u. The results show that the shape of the total elastic cross section is mainly dominated by the s partial wave at very low temperatures. Because of the weak shape resonances coming from higher partial waves, most of them are passed into oblivion by the strong total elastic cross sections.

Keywords: elastic collision, total cross section, molecular parameter, vibrational level
PACC: 3520G, 3120C, 3420

1. Introduction

The CH radical has been one of the most studied free radicals. It plays an important role in many hydrocarbon combustion processes.[1] Now its presence has been revealed in a wide variety of energetic environments including the sun,[2] comets,[3] the interstellar medium,[4] stellar atmospheres,[5] flames and detonations.[6] For this reason, it has been the experimental[7−10] and theoretical[11−18] subject of extensive spectroscopic investigations over the past several decades.

By comparison with CH, only a few studies have been done on the deuterated isotopomer, CD, over the past several decades, though it is involved in a wide variety of chemical and physical systems and thought to be a significant intermediate in the evolution of interstellar molecules. In experiment, the electronic spectrum investigations on CD were first reported by Shindei[19] in 1936, later by Gerö[20] in 1941 and by Herzberg and Johns[21] in 1969. Although these studies served to locate several electronic states of the CD radical, they provided only rather inaccurate structural information. In 1989, Brown and Evenson[22] studied the far-infrared laser magnetic resonance (LMR) spectrum of the CD($X^2\Pi$) and provided the first really accurate measurements of several molecular parameters In 1995, Morino *et al*[23] observed the gas-phase vibration–rotation emission spectrum of the CD($X^2\Pi$) radical with a high-resolution Fourier transform interferometer (FTIR) and also determined several principal molecular parameters. Recently in 2003, Wienkoop *et al*[24] made two sepa-

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rate studies of this radical by the LMR technique and provided the most accurate measurements of several molecular parameters, even till today. In theory, on the one hand, relatively little attention has been paid to the spectroscopic constants (D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e) and the potential energy curve (PEC)[25] of this radical, let alone its vibrational manifolds (vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants); on the other hand, since the elastic collision properties, such as the total and the various partial-wave cross sections, are very sensitive to the interaction potential, no investigations can be found about the elastic collisions between the ground-state C and D atoms in the cold regime due to the lack of the accurate analytic potential energy function (APEF). All of this motivates us to perform the present investigations.

In the present paper, the harmonic frequencies, the equilibrium internuclear separations and the PECs of the CD($X^2\Pi$) radical are investigated using the CCSD(T) theory[26] in combination with a series of correlation-consistent basis sets[13,27,28] in the valence range, and then the rest of the spectroscopic constants are derived. Thirdly, with the potential obtained at the UCCSD(T)/aug-cc-pV5Z level of theory, a total of 24 vibrational states are predicted by solving the radial Schrödinger equation of nuclear motion with the Numerov method[29] when the rotational quantum number J is equal to zero ($J = 0$). The complete vibrational levels, the classical turning points, and the inertial rotation and centrifugal distortion constants are reproduced for the first time when $J = 0$. Finally, total and various partial-wave cross sections are calculated for the elastic collisions between the ground-state C and D atoms at low temperatures when the two atoms approach each other along the PEC of this CD($X^2\Pi$) radical. A comparison with recent measurements[24] shows that the present results achieve a much high accuracy due to the employment of the large basis set. Atomic units are used throughout this paper unless otherwise specified.

2. Computational methods

Here, we use the UCCSD(T) theory[26] in combination with a series of correlation-consistent basis sets[13,27,28] to calculate the harmonic frequencies ω_e, the equilibrium internuclear distances R_e and the PECs of the CD($X^2\Pi$) radical. For such calculations, the UCCSD(T) theory[26] has proved to be particularly successful. Especially in recent years, a number of high-quality theoretical results have been reported for a variety of molecules.[30−34] These calculations are made by using an unrestricted Hartree–Fock reference wavefunction in the Gaussian 03 program package[35] only in a valence range. The R_e and ω_e values obtained at this level of theory are tabulated as shown in Table 1.

Table 1. Equilibrium parameters for the CD($X^2\Pi$) radical at the UCCSD(T) level of theory and different correlation-consistent basis sets.

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	3.2754	0.11432	2067.253	aug-cc-pVDZ	3.3502	0.11401	2066.752
cc-pVTZ	3.5324	0.11224	2085.548	aug-cc-pVTZ	3.5694	0.11219	2088.026
cc-pVQZ	3.6005	0.11203	2095.437	aug-cc-pVQZ	3.6137	0.11203	—
cc-pV5Z	—	0.11196	2098.418	aug-cc-pV5Z	3.6261	0.11197	2097.661

In general, the PEC calculations are performed at intervals of 0.02 nm over the internuclear distance range from 0.077 to 2.47 nm at various correlation-consistent basis sets. Only near the equilibrium position will the interval be 0.05 nm. The *ab initio* calculation points at each set are all fitted to the Murrell–Sorbie (M–S) function with the least-squares fitting method. Therefore, the D_e and the APEF are derived. Here the D_e values are also collected in Table 1. By careful comparison between the present D_e, R_e and ω_e values and the experimental results,[21,23,24] we are certain that the correlation-consistent quintuple basis set augmented with diffuse functions, aug-cc-pV5Z, is the most suitable one to determine its spectroscopic

parameters. Therefore, the APEF obtained at this set will be used for further calculation.

On the one hand, the APEF obtained at the aug-cc-pV5Z basis set is employed to determine the spectroscopic parameters, i.e. $\omega_e\chi_e$, α_e B_e and D_0. The obtained values of $\omega_e\chi_e$, α_e B_e and D_0 are in excellent agreement with the available measurements[21,23,24] To more strictly compare our results with measurements, this APEF is further used to predict all the vibrational states by solving the radial Schrödinger equation of nuclear motion with the Numerov method.[29] On the other hand, this APEF is also used to calculate the total and the various partial-wave cross sections of two ground-state atoms, C and D, along the CD($X^2\Pi$) PEC. To calculate the total and the various partial-wave cross sections, we must obtain the radial solution u_l of the lth partial-wave equation. In order to obtain the radial solution u_l of the lth partial-wave equation, we must solve the following radial Schrödinger equation:[33]

$$\frac{\mathrm{d}^2u_l}{\mathrm{d}r^2}+\left[k^2-\frac{2\mu V(r)}{\hbar^2}-\frac{l(l+1)}{r^2}\right]u_l(r)=0, \qquad (1)$$

where $V(r)$ is the APEF obtained here; μ is the reduced mass of the colliding system, C and D atoms; k is the wave number, which is determined in terms of the energy E of relative motion by $k^2=2\mu E/\hbar^2$. Having obtained u_l, the scattering phase shift δ_l of the lth partial wave can be determined by

$$\tan\delta_l=\frac{-2\mu}{\hbar^2k}\int_0^\infty j_l(kr)V(r)u_l(r)\mathrm{d}r. \qquad (2)$$

When l is equal to 0, 1, 2, ..., the elastic cross section of lth partial wave, $\sigma_l(E)$, is defined by

$$\sigma_l(E)=\frac{4\pi}{k^2}\cdot(2l+1)\sin^2\delta_l. \qquad (3)$$

Then, the total elastic cross section, $\sigma_T(E)$, can be calculated from

$$\sigma_T(E)=\sum_{l=0}^{\infty}\sigma_l(E)=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l. \qquad (4)$$

Therefore, once the u_l is determined, various partial-wave cross sections for the elastic collisions of the ground-state C and D atoms in the cold regime can be calculated from expressions (3) and (4).

Now, we briefly discuss the spin contamination at the SCF level, which arises from the unrestricted *ab initio* calculations. The spin contamination comes about when the ground-state wavefunction mingles with the wavefunctions of some excited states. In general, high spin contamination will influence the molecular structure, especially the density of spin. The spin contamination can be validated by comparing the total S_1 prospective value with the calculated one. S_1 is equal to $s(s+1)$, where s is the total spin value of the ground-state CD radical. Generally, the result is acceptable if the deviation is not beyond 10%.

From Table 2, we can find that the prospective value of total spin is absolutely identical with the calculation result. It proves that no spin contamination exists in the present calculations.

Table 2. Spin contamination for the CD($X^2\Pi$) radical at the UCCSD(T)/aug-cc-pV5Z level of theory.

multiplicity	state	expectance value S_1 of spin	calculation value S_2 of spin
2	$X^2\Pi$	2.00	2.00

3. APEF of the CD($X\ ^2\Pi$) radical

The M–S function is a widely-used APEF. It well describes the interaction potential energies of neutral diatomic molecules. The common M–S function is in the following form:

$$V(\rho)=-D_e\left(1+\sum_{i=1}^{n}a_i\rho^i\right)\exp(-a_1\rho), \qquad (5)$$

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

Fitting Eq.(5) by the least-squares method yields the parameters a_i and D_e. In order to attain a satisfactory result, in which the root mean square error (ΔE_{RMSE}) is minimized and the extracted spectroscopic parameters are the closest to the experiments[21,23,24] as a whole, we try it from $n = 3$ to $n = 8$. Compared with the spectroscopic experimental values (D_e, B_e, α_e $\omega_e\chi_e$ and D_0),[21,23,24] our most favourable results can be derived at $n = 6$. The fitting results are collected in Table 3 together with the R_e value for integrality.

Table 3. Parameters of M–S APEF for the CD($X^2\Pi$) radical at the UCCSD(T)/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}	a_5/nm^{-5}	a_6/nm^{-6}	ΔE_{RMSE}/eV
3.6261	0.11197	24.7189	–63.7275	638.5640	–23657.726	136941.276	–213340.545	0.00629

In order to evaluate the fitting quality of the M–S APEF, we calculate the ΔE_{RMSE} in the fitting process according to the formula given in Refs.[33] and [34]. By calculation, we determine that the present ΔE_{RMSE} is only 0.00629 eV (about 0.145 kcal/mol). Obviously, the present fitting accuracy is greatly superior to the chemical one (1.0 kcal/mol).[36] It shows that the M–S function is very suitable for reproducing the PEC of this radical, and the fitting process is of high quality. Therefore, we think that the parameter values of APEF collected in Table 3 should be credible and accurate and can be used to carry out the spectroscopic and vibrational manifold calculations.

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

Now, we calculate the rest of the spectroscopic parameters (B_e, α_e $\omega_e\chi_e$ and D_0) of the CD($X^2\Pi$) radical according to the parameter values of APEF indicated in Table 3. By using expression (5), we can derive the expressions of the force constants, quadratic f_2, cubic f_3 and quartic f_4, at the equilibrium position. Then, the spectroscopic parameters B_e, α_e $\omega_e\chi_e$ and D_0 can be determined from the following expressions (6)–(9):

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \tag{6}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3 R_e}{3f_2} + 1\right), \tag{7}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4 R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right], \tag{8}$$

$$D_0 = D_e - \left(\frac{1}{2}\omega_e - \frac{1}{4}\omega_e\chi_e\right). \tag{9}$$

The present B_e, α_e $\omega_e\chi_e$ and D_0 together with the R_e, ω_e and D_e values are listed in Table 4. For the convenience of further comparison, we also collect the available measurements[21,23,24] in this Table

Table 4. Comparison of spectroscopic parameter between our results and the measurements for the CD($X^2\Pi$) radical at the UCCSD(T)/aug-cc-pV5Z level of theory.

source	D_e/eV	D_0/eV	R_e/nm	ω_e/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}
this work	3.6261	3.4971	0.11197	2097.661	7.7962	0.2083	34.6963
Exp.[21]	3.6291	3.500	0.11190	2099.75	7.806	0.208	34.02
Exp.[23]	—	—	0.11179	2100.346	7.8078	0.2123	34.1558
Exp.[24]	—	—	0.11189	2101.052	7.8080	0.2122	34.7279

The latest spectroscopic experiments of the CD($X^2\Pi$) radical were performed by Wienkoop *et al*[24] in 2003. Wienkoop *et al*[24] investigated the vibrationally excited levels of this ground-state CD radical by the LMR technique. In their experiments, transitions in the (1, 0), (2, 1) and (3, 2) bands have been detected. All these data combined with the (1, 0) and (2, 1) bands, which were observed by Morino

et al[23] using the FTIR, have been employed to determine an improved set of molecular parameters for the CD($X^2\Pi$) radical. This group of spectroscopic parameters has been thought to be the most accurate experimental results till today. From Table 4, it is not difficult to see that the spectroscopic parameters, R_e and ω_e which are directly obtained from the UCCSD(T)/ aug-cc-pV5Z calculations in the Gaussian 03 program package,[35] are in excellent agreement with the measurements,[24] and the deviations are 0.071% and 0.162%, respectively. The rest of the spectroscopic parameters, such as D_e, B_e, $\omega_e\chi_e$ and D_0, which are reproduced from the APEF fitted in this paper, also accord well with the measurements[24] and the deviations are only 0.083%, 0.151%, 0.091% and 0.083%, respectively. It further proves that the present M–S APEF is credible and accurate, and it can be used to make vibrational manifold calculations.

3.2. Vibrational manifolds

In order to obtain the vibrational eigenvalues, we must solve the radial Schrödinger equation of nuclear motion. In the adiabatic approximation, the radial Schrödinger equation of nuclear motion can be written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\Psi_{\nu.J}(r) = E_{\nu,J}\Psi_{\nu.J}(r), \tag{10}$$

where $V(r)$ is the rotationless APEF in Table 3; r is the internuclear distance of two atoms, C and D; μ is the reduced mass of the CD radical; υ and J are the vibrational and the rotational quantum numbers, respectively; $E_{\nu,J}$ and $\Psi_{\nu,J}(r)$ are the eigenvalues and eigenfunctions of the potential $J(J+1)\cdot\hbar^2/2\mu r^2 + V(r)$, respectively. The rotational sublevel of a given vibrational level is represented by the following power series:

$$\begin{aligned}E_{\nu,J} = {} & G(\nu)+B_\nu[J(J+1)]-D_\nu[J(J+1)]^2 \\ & +H_\nu[J(J+1)]^3+L_\nu[J(J+1)]^4 \\ & +M_\nu[J(J+1)]^5+N_\nu[J(J+1)]^6 \\ & +O_\nu[J(J+1)]^7,\end{aligned} \tag{11}$$

where $G(\upsilon)$ is the vibrational level; B_υ is the inertial rotation constant; D_υ, H_υ, L_υ, M_υ, N_υ and O_υ are the centrifugal distortion constants. We employ the Numerov method[29] with automatic step-size selection to solve Eq.(10) numerically, and have obtained a total of 24 vibrational states for the CD($X^2\Pi$) radical when the rotational quantum number J is set to equal zero. For each vibrational state, 1 vibrational level, 1 inertial rotation constant and 6 centrifugal distortion constants are obtained. Here, the vibrational levels, the classical turning points and the inertial rotation constants are all collected in Table 5, and the centrifugal distortion constants are all listed in Table 6.

Table 5. Vibrational levels, classical turning points and initial rotation constants of CD($X^2\Pi$) when $J = 0$ at the UCCSD(T)/aug-cc-pV5Z level of theory.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$	$R_{\min}$/nm	$R_{\max}$/nm	$B_\upsilon/\mathrm{cm}^{-1}$	υ	$G(\upsilon)/\mathrm{cm}^{-1}$	$R_{\min}$/nm	$R_{\max}$/nm	$B_\upsilon/\mathrm{cm}^{-1}$
0	1022.648	0.10309	0.12273	7.690569	12	21147.672	0.08102	0.19781	5.272540
1	3020.759	0.9760	0.13200	7.483896	13	22410.864	0.08038	0.20454	5.046518
2	4962.280	0.09425	0.13919	7.281873	14	23598.884	0.07980	0.21152	4.808893
3	6847.322	0.09177	0.14559	7.083281	15	24707.207	0.07929	0.21904	4.556226
4	8675.686	0.08977	0.15159	6.886996	16	25730.170	0.07883	0.22731	4.283599
5	10446.887	0.08811	0.15736	6.691959	17	26660.430	0.07842	0.23662	3.983455
6	12160.177	0.08669	0.16301	6.497148	18	27487.957	0.07807	0.24717	3.642931
7	13814.545	0.08545	0.16861	6.301554	19	28197.839	0.07778	0.26089	3.236407
8	15408.716	0.08435	0.17423	6.104143	20	28764.099	0.07755	0.27958	2.694595
9	16941.143	0.08338	0.17993	5.903822	21	29114.142	0.07740	0.32248	1.525981
10	18409.973	0.08251	0.18574	5.699397	22	29183.808	0.07738	0.42240	1.039610
11	19813.014	0.08172	0.19174	5.489506	23	29270.474	0.07734	0.47109	0.898465

In experiment, only the B_υ and D_υ values of the first three vibrational levels can be found in the literature[23] to our knowledge. These B_υ and D_υ values have been collected in Table 7 for the convenience of compar-

ison. From Table 7, it is not difficult to find that the present B_υ theories conform almost perfectly to the measurements[23] and the deviations between them are only 0.147%, 0.094% and 0.006% when $\upsilon = 0$, 1 and 2, respectively. It is also easy to see that the present D_υ theories agree very well with the experiments,[23] and the discrepancies between them are only 0.825%, 0.080% and 0.906% when $\upsilon = 0$, 1 and 2, respectively. According to this, we conclude that the parameter values of M–S APEF shown in Table 3 are reliable and accurate.

Table 6. Centrifugal distortion constants for CD($X^2\Pi$) at the UCCSD(T)/aug-cc-pV5Z level of theory when $J = 0$.

υ	$D_\upsilon(\times10^{-4})/\mathrm{cm}^{-1}$	$H_\upsilon(\times10^{-9})/\mathrm{cm}^{-1}$	$L_\upsilon(\times10^{-13})/\mathrm{cm}^{-1}$	$M_\upsilon(\times10^{-17})/\mathrm{cm}^{-1}$	$N_\upsilon(\times10^{-21})/\mathrm{cm}^{-1}$	$O_\upsilon(\times10^{-25})/\mathrm{cm}^{-1}$
0	4.312178	20.22220	–7.984439	1.452949	–3.242112	4.103689
1	4.287158	19.18178	–8.799247	2.328688	–3.066113	2.732749
2	4.174491	18.10648	–9.397729	2.947189	–3.343767	1.757503
3	4.077855	17.00867	–9.868183	3.281338	–3.923676	0.970735
4	3.996642	15.88885	–10.28949	3.311335	–4.764432	0.109737
5	3.930455	14.73743	–10.73657	3.002577	–5.925774	–1.158520
6	3.879199	13.53506	–11.28802	2.284782	–7.583234	–3.321821
7	3.843156	12.25168	–12.03661	1.024895	–10.08075	–7.205632
8	3.823069	10.84360	–13.10485	–1.016991	–14.05150	–14.35415
9	3.820285	9.248087	–14.66973	–4.268094	–20.67586	–27.85998
10	3.836955	7.373757	–17.00553	–9.499740	–32.24002	–54.28821
11	3.876360	5.083658	–20.56260	–18.15046	–53.40493	–108.4586
12	3.943450	2.164637	–26.12195	–33.03377	–94.28473	–226.2882
13	4.045757	–1.730832	–35.12050	–60.00644	–178.5608	–502.6957
14	4.195051	–7.202495	–50.39233	–112.2729	–367.1857	–1217.220
15	4.410533	–15.36168	–78.03573	–222.8383	–837.3087	–3316.533
16	4.725569	–28.46746	–132.7640	–486.3720	–2194.500	–10668.33
17	5.203697	–51.73451	–256.1976	–1232.295	–7042.334	–43911.28
18	5.983782	–99.69532	–597.9103	–3999.344	–31319.67	–270025.2
19	7.447503	–227.9379	–1969.786	–20861.68	–259247.3	–3583825
20	11.28997	–863.7040	–15834.55	–382717.6	-1.09424×10^7	-3.47518×10^8
21	45.33346	–8041.911	994347.2	1.21378×10^8	-2.87006×10^7	-1.22976×10^{12}
22	14.29528	4945.745	–1052094	-1.15106×10^8	3.96821×10^8	1.24374×10^{12}
23	4.461521	1423.627	–161478.2	-3.17876×10^7	-3.96821×10^9	-2.15158×10^{12}

Unfortunately, for the ground-state CD radical, energy levels and classical turning points are not yet available; neither is the information about the inertial rotation constants and the centrifugal distortion constants when the energy level is higher than two, experimentally or theoretically, to the best of our knowledge. But according to the high-quality fitting process of the APEF, the excellent agreement between the present spectroscopic parameters and the available measurements, and the good accordance between the present B_υ and D_υ values and the available measurements, we have reason to believe that the results collected in Tables 5 and 6 are all reliable and accurate. Consequently, we can further conclude that the parameter values of M–S APEF listed in Table 3 are also reliable and accurate.

Table 7. B_υ and D_υ experimental results[23] for the CD($X^2\Pi$) radical with $\upsilon = 0$, 1 and 2 when $J = 0$.

	$\upsilon = 0$	$\upsilon = 1$	$\upsilon = 2$		$\upsilon = 0$	$\upsilon = 1$	$\upsilon = 2$
$B_\upsilon/\mathrm{cm}^{-1}$	7.701868	7.490970	7.281429	$D_\upsilon(\times10^{-4})/\mathrm{cm}^{-1}$	4.27689	4.2906	4.1370

In addition, we have used the present program codes to calculate the vibrational level, the inertial rotation constants and the centrifugal distortion constants of the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states of $^7Li_2$ molecule[37,38] and the $X^3\Sigma$ state of NH radical.[33] Favourable agreement has been obtained when these calculations are compared with the available Rydberg–Klein–Rees (RKR) data. These investigations show that the present calculation method is reliable and accurate.

4. Total and partial-wave elastic cross sections

Using the parameter values of APEF in Table 3, the basic equation (1) can be numerically solved by the Numerov method[29] with automatic step-size selection. The partial-wave phase shift δ_l of the elastic collisions between two ground-state C and D atoms at low temperatures is evaluated according to expression (2) when two atoms approach each other along the PEC of the CD($X^2\Pi$) radical. Various elastic partial-wave cross sections and the total elastic cross sections are calculated from expressions (3) and (4) over the present impact energy range from 1.0×10^{-11} to 1.0×10^{-4} a.u. The collision energy dependence of the total elastic cross sections at low temperatures is depicted in Fig.1.

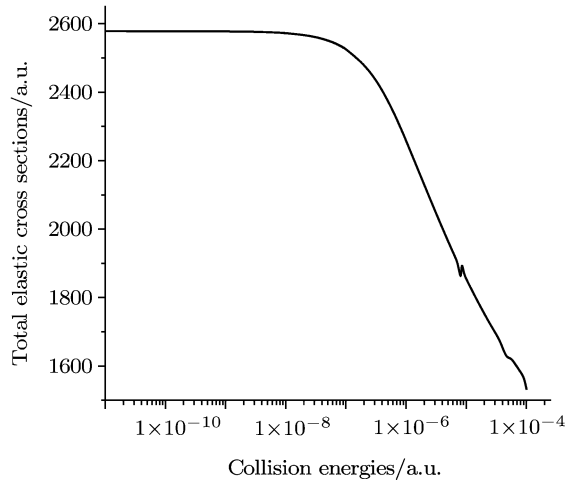


Fig.1. Total elastic cross section versus collision energy for scattering along the PEC of the ground state CD radical.

The collision energy dependences of elastic cross sections for various partial waves are presented in Figs.2–4, separately.

As shown in Fig.1, the total cross sections of elastic collisions between two atoms, C and D, in their ground states, are very large and are almost constant at ultralow temperatures. From Figs.2–4, we can see that the s-wave cross sections are significant but the p-, d-, f-, g- and h-wave cross sections are very small when the collision energy is below 10^{-6} a.u. Therefore, the elastic total cross sections are dominated by s-wave scattering in this impact energy regime. From Fig.2, we can clearly see that the s-wave cross sections tend to decrease rapidly as the energy increases. Due to the weakness of the p-, d-, f-, g- and h-wave cross sections, accordingly, the total elastic cross sections also go down with the rapid decrease of s-wave cross sections.

A weak structure can be found in Fig.1. From Figs.2–4, one can see that this weak structure results from the sharp shape resonance p-partial wave. Accurate calculations point out that the resonant position in the total elastic cross sections is at an energy of 8.36×10^{-6} a.u. It is strictly consistent with one of the resonant positions in the p-wave cross sections.

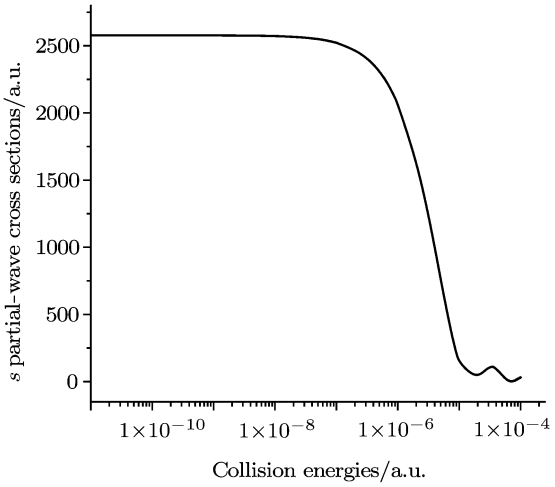


Fig.2. Curve for s partial-wave cross section versus collision energy for scattering along the PEC of the ground state CD radical.

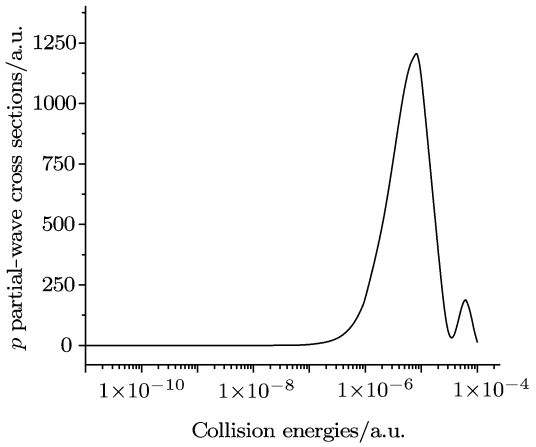


Fig.3. Curve for p partial-wave cross section versus collision energy for scattering along the PEC of the ground state CD radical.

Figure 2 shows that a weak shape resonant peak exists in the s-partial wave and the resonant energy is 3.45×10^{-5} a.u. As this peak is too weak, it is passed

into oblivion by the strong total elastic cross sections.

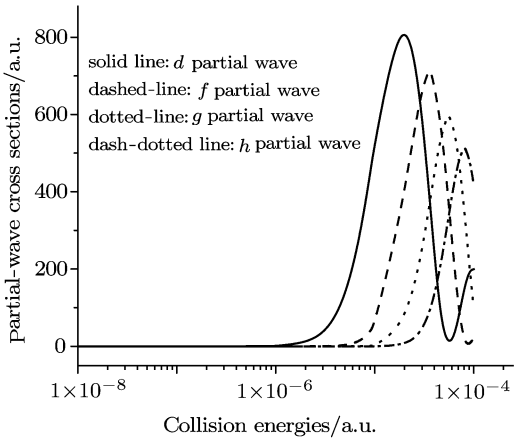


Fig.4. Curves for d, f, g and h partial-wave cross section versus collision energy for scattering along the PEC of the ground state CD radical.

As shown in Figs.3 and 4, several other sharp resonant peaks exist in the curves for p-, d-, f-, g- and h-wave cross sections and their resonant energies are 6.09×10^{-5} a.u. for the p-partial wave cross section, 1.91×10^{-5} a.u. for the d-partial wave cross section, 3.55×10^{-5} a.u. for the f-partial wave cross section, 5.55×10^{-5} a.u. for the g-partial wave cross section and 8.09×10^{-5} a.u. for the h-partial wave cross section. Compared with the s partial wave, all these waves have shape resonances but are very weak, thus they are passed into oblivion by the strong total elastic cross sections.

We have investigated the elastic collisions between two ground-state Li atoms at low and ultralow temperatures using the present theoretical method[39] The results are in excellent agreement with the measurements. Thus, the present method should be reliable. The interaction potential attained here is reliable and accurate, therefore, we believe that the total and the various elastic cross sections calculated in this paper are reliable and accurate, though neither experimental results nor theoretical results can be found for the elastic collisions between atoms C and D at low and ultralow temperatures. These results are expected to be detected experimentally and examined theoretically in the near future.

5. Conclusions

The equilibrium internuclear separations, the harmonic frequencies and the PECs of the CD($X^2\Pi$) radical have been investigated by employing the UCCSD(T) theory in combination with a series of correlation-consistent basis sets. The APEF obtained at the aug-cc-pV5Z basis set over the internuclear distance range from 0.077 to 2.47 nm in the valence range is chosen to determine the spectroscopic parameters, i.e. D_e, $\omega_e\chi_e$, α_e B_e and D_0. With the potential attained at the UCCSD(T)/aug-cc-pV5Z level of theory, on the one hand, a total of 24 vibrational states have been predicted by numerically solving the radial Schrödinger equation of nuclear motion with the Numerov method. For each vibrational state, the vibrational level, the classical turning points, the inertial rotation constants and the centrifugal distortion constants are also calculated for the first time when $J = 0$. On the other hand, the total and the various elastic cross sections of atom C and D collisions are investigated for the first time when the two atoms approach each other along the CD($X^2\Pi$) PEC. One weak shape resonance is found in the total elastic cross sections, and the resonant energy is of 8.36×10^{-6} a.u. The analyses show that the shape of the total elastic cross sections is mainly dominated by the s partial wave at very low temperatures. Because of the weak shape resonances coming from the higher partial waves, most of them are passed into oblivion by the strong total elastic cross sections.

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