Vol 17 No 10, October 2008
1674-1056/2008/17(10)/3678-09

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Elastic collisions of sulfur and hydrogen in their ground states at low temperatures and spectroscopic parameters of SH($X^2\Pi$) radical*

Shi De-Heng(施德恒)[a)b)†], Zhang Jin-Ping(张金平)[b)], Sun Jin-Feng(孙金锋)[a)], Liu Yu-Fang(刘玉芳)[a)], Zhu Zun-Lüe(朱遵略)[a)], Ma Heng(马 恒)[b)], and Yang Xiang-Dong(杨向东)[c)]

[a)] *College of Physics & Information Engineering, Henan Normal University, Xinxiang* 453007, *China*
[b)] *College of Physics & Electronic Engineering, Xinyang Normal University, Xinyang* 464000, *China*
[c)] *Institute of Atomic & Molecular Physics, Sichuan University, Chengdu* 610065, *China*

(Received 8 January 2008; revised manuscript received 21 March 2008)

This paper constructs the interaction potential of the SH($X^2\Pi$) radical by using the coupled-cluster singles-doubles-approximate-triples theory combining the correlation-consistent quintuple basis set augmented with the diffuse functions, aug-cc-pV5Z, in the valence range. Employing the potential, it accurately determines the spectroscopic parameters. The present D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e values are of 3.7767 eV, 0.13424 nm, 2699.846 cm^{-1}, 47.7055 cm^{-1}, 0.2639 cm^{-1} and 9.4414 cm^{-1}, respectively, which are in excellent agreement with those obtained from the measurements. A total of 19 vibrational states has been found when $J = 0$ by solving the radial Schrödinger equation of nuclear motion. The complete vibrational levels, classical turning points, initial rotation and centrifugal distortion constants when $J = 0$ are reported for the first time, which are in good accord with the experimental results. The total and various partial-wave cross sections are computed for the elastic collisions of sulfur and hydrogen in their ground states at low temperatures when two atoms approach each other along the SH($X^2\Pi$) potential energy curve. Over the impact energy range from 1.0×10^{-11} to 1.0×10^{-4} a.u., eight shape resonances have been found in the total elastic cross sections. For each shape resonance, the resonant energy is accurately calculated. Careful investigations have pointed out that these resonances result from the $l = 0$, 1, 2, 3, 4, 6, 7, 8 partial-wave contributions.

Keywords: elastic collision, total cross section, partial-wave cross section, shape resonance

PACC: 3440, 3430, 3400

1. Introduction

SH molecule has been one of the most studied free radicals. Because, on the one hand, as a chemical intermediate, this radical is expected to play an important role in many industrial processes, such as the coal combustion and atmospheric sulfur cycle; on the other hand, it is of astrophysical importance.[1] Up to now, several sulfur-containing molecules have already been found in space.[2−4] Since the isovalent OH radical has been observed in the interstellar medium, there is a strong possibility that the SH radical may also be found at such a place. It is well-known that the precise ground-state molecular parameters are required in a successful search. Therefore, it is not a surprise that these molecular parameters have been widely investigated by optical, infrared and far-infrared spectroscopy, by radio frequency transition and by mass spectroscopy.

For the reasons for which it is of fundamental importance in astrophysics and other fields, the SH radical has been the experimental subject of considerable spectroscopic investigations.[5−10] At the same time, the determinations of these spectroscopic parameters have also comprised a large body of theoretical work.[11−17] However in theory, the extracted spectroscopic properties are all incomplete. For example, the spectroscopic constants (D_e, R_e, ω_e, $\omega_e\chi_e$, α_e and B_e) are either inaccurate or incomplete. And we have found no complete calculations about its vibrational manifolds (vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants), which are very useful in the rovibrational transition calculations. Furthermore, since the elastic collision

*Project supported by the National Natural Science Foundation of China (Grant Nos 60777012 and 10574039) and the Science & Technology Innovation Talents in Universities of Henan Province in China (Grant No 2008HASTIT0 08).
†E-mail: dehengshi@yahoo.com.cn

properties, such as the total and various partial-wave cross sections, are very sensitive to the interaction potential over an extended range of internuclear separations, no investigations can be found about the elastic scattering between hydrogen and sulfur in their ground states in the cold regime due to the lack of accurate analytic potential energy function (APEF). In experiment, to the best of our knowledge, little information about its vibrational manifolds has been found for the vibrational levels higher than four. All these motivate us to perform the present calculations.

One of the present purposes is to construct the reliable APEF of the SH($X^2\Pi$) radical using the coupled-cluster singles-doubles-approximate-triples [CCSD(T)] theory[18] in combination with the correlation-consistent quintuple basis set augmented with the diffuse functions of Dunning and coworkers.[16,19−21] In the next Section, we briefly describe the theory and method about the low-energy elastic scattering. In Section 3, we first calculate the spectroscopic parameters (D_e, R_e and ω_e) at a series of correlation-consistent basis sets (cc-pVnZ and aug-cc-pVnZ). And then with the APEF obtained at aug-cc-pV5Z, we determine the rest spectroscopic parameters (B_e, α_e and $\omega_e\chi_e$) and compute the vibrational manifolds. In Section 4, we calculate the total and various partial-wave cross sections for the elastic collisions of hydrogen and sulfur in their ground states at low temperatures when two atoms approach each other along the SH($X^2\Pi$) potential energy curve (PEC). And in Section 5, concluding remarks are made. Atomic units are employed throughout this paper unless otherwise specified.

2. Theory and method

A partial-wave expansion reduces the problem of elastic scattering by a potential $V(r)$, where r is the internuclear distance of two atoms, to the determination of the radial solution of the lth partial-wave equation,[22]

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

where μ is the reduced mass of the colliding system, k is the wave number, which is determined in terms of the energy E of relative motion by $k^2=2\mu E/\hbar^2$, $V(r)$ is the diatomic interaction potential. The solutions must be regular and behave asymptotically as the following formula when $r\to\infty$,

$$u_l(r)\sim A_l[j_l(kr)+\tan\delta_l n_l(kr)]. \quad (2)$$

Where j_l and n_l are the spherical Bessel and Neumann functions, respectively. A_l is an arbitrary amplitude. And δ_l is the scattering phase shift of the lth partial wave. Alternatively, we can write

$$u_l(r)\sim A_l\sin(kr-\frac{1}{2}l\pi+\delta_l). \quad (3)$$

If A_l is chosen to be unity, the solution $u_l(r)$ satisfies the following integral equation,[23]

$$\tan\delta_l=\frac{-2\mu}{\hbar^2k}\int_0^\infty j_l(kr)V(r)u_l(r)\mathrm{d}r. \quad (4)$$

When l is equal to 0, 1, 2, ..., the scattering waves are usually called s partial wave, p partial wave, d partial wave, ..., respectively. The elastic cross section of lth partial wave, $\sigma_l(E)$, is defined by[24]

$$\sigma_l(E)=\frac{4\pi}{k^2}\cdot(2l+1)\sin^2\delta_l. \quad (5)$$

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

$$\sigma_T(E)=\sum_{l=0}^{\infty}\sigma_l(E)=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l. \quad (6)$$

With the accurate diatomic interaction potential derived from Gaussian 03 program package,[25] the $u_l(r)$ can be obtained by solving the radial Schrödinger equation (1). Once the $u_l(r)$ is determined, various partial-wave cross sections for the elastic collisions of the ground-state hydrogen and sulfur atoms in the cold regime can be calculated according to equations (5) and (6).

3. Interaction potential

For the calculation of harmonic frequencies and equilibrium structures, the CCSD(T) theory has been proved particularly successful. Especially in recent years, high-quality calculations have been reported for a variety of molecules.[26−30] In this paper, this theory is used to compute the harmonic frequency, equilibrium internuclear separation and PEC of the SH($X^2\Pi$) radical. The calculations are made in Gaussian 03 program package[25] at a series of correlation-consistent basis sets, cc-pVnZ (n=2, 3, 4, 5), of Dunning and co-workers[16,19−21] in the valence range. Furthermore, the effects on the spectroscopic parameters by these basis sets augmented with the diffuse functions, aug-cc-pVnZ (n=2, 3, 4, 5) are also investigated. The D_e, R_e and ω_e results are all tabulated in Table 1.

Table 1. The equilibrium parameters for SH($X^2\Pi$) radical at the CCSD(T) level of theory and the 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	3.3994	0.13589	2692.583	aug-cc-pVDZ	3.4864	0.13609	2668.799
cc-pVTZ	3.6442	0.13455	2691.141	aug-cc-pVTZ	3.6838	0.13465	2687.156
cc-pVQZ	3.7356	0.13436	2697.244	aug-cc-pVQZ	3.7495	0.13436	2697.070
cc-pV5Z	3.7690	0.13421	2701.545	aug-cc-pV5Z	3.7767	0.13424	2699.846

The correlation-consistent basis sets are designed for correlation of the valence electrons. The cardinal number n determines the flexibility of the virtual excitation space. The basis set cc-pVnZ contains $(n+1)\times(n+1.5)\times(n+2)/3$ atomic orbitals (AOs). For example, the double-zeta basis set with the cardinal number n=2 contains 14 AOs of composition 3s2p1d, and the quintuple-zeta basis set with $n = 5$ contains 91 AOs of composition 6s5p4d3f2g1h. In these basis sets, atomic energy-optimized orbitals are added to the basis, from the beginning of cc-pVDZ, one shell at a time in the sense of the principal expansion. Therefore, at the same hierarchy of the coupled-cluster theory, the larger the cardinal number n, the smaller should be the D_e, R_e and ω_e differences between the calculated results and the experimental results. These can be clearly seen in Table 1.

By careful comparisons between the calculated D_e, R_e and ω_e values and the experimental values,[5−10] we are certain that the cc-pV5Z and the aug-cc-pV5Z are both excellent basis sets to calculate the spectroscopic parameters. Here, we choose the aug-cc-pV5Z basis set for further computations. The reason is that the PEC calculated at the aug-cc-pV5Z basis can satisfy the need of the investigations on collisions between atoms at low and ultralow temperatures. Because the diffuse functions can improve the description of long-range interactions, more accurate PEC can be obtained at larger internuclear separations at the basis set, aug-cc-pV5Z. It is well-known that, at low and ultralow temperatures, the collision processes between atoms are very sensitive to the details of the PEC, especially the details of PEC at larger internuclear distances. Thus, in order to obtain trustworthy total and various partial-wave cross sections, accurate PEC at larger internuclear distances is especially required. Since no aug-cc-pV6Z basis set is available in Gaussian 03 program package,[25] the aug-cc-pV5Z basis set is the largest one which is augmented with the diffuse functions in the valence range.

To be convenient for further comparisons, The D_e, R_e and ω_e results obtained at aug-cc-pV5Z together with the experiments[5−10] and other theories[11−17] are tabulated in Table 2.

Table 2. Spectroscopic parameter comparisons with measurements and other theories for SH ($X^2\Pi$) at the CCSD(T)/aug-cc-pV5Z level of theory.

Source	D_e/eV	R_e/nm	ω_e/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}
This work	3.7767	0.13424	2699.846	9.4414	0.2639	47.7055
Exp.[5]	–	0.13406	2696.2	9.6002	0.2799	48.74
Exp.[6]	3.7809±0.03	–	–	–	–	–
Exp.[7]	–	0.13404	2695.8	9.6036	0.2786	48.5
Exp.[8]	3.7163	0.13409	2711.6	9.4611	0.270	59.9
Exp.[9]	–	0.1341	2711.6	9.600	0.270	59.9
Exp.[10]	3.7005	0.1340	2702	9.611	0.300	60
Theory[11]	2.63	0.13298	2860	9.756	0.2494	42.32
Theory[12]	–	0.1343	2702	9.56	0.280	57
Theory[13]	3.53	0.1342	2739	9.59	0.29	55.1
Theory[14]	3.49	0.13468	2775.3	9.44	0.262	42.86
Theory[15]	3.7369	0.1345	2704.2	9.5482	0.2631	51.88
Theory[16]	3.7151	0.13411	2692.2	9.59	0.2777	47.5
Theory[17]	3.7757	0.1344	2697	9.557	0.276	50

In general, the PEC calculations are carried out at intervals of 0.02 nm over the internuclear separation ranging from 0.07 to 2.45 nm. Only near the equilibrium position, the interval is of 0.01 nm. The *ab initio* calculation points are fitted to the following Murrell–Sorbie (M-S) function,[30]

$$V(\rho) = -D_{\mathrm{e}}\left(1 + \sum_{i=1}^{n} a_i \rho^i\right)\exp(-a_1\rho). \qquad (7)$$

Where, $\rho = r - R_{\mathrm{e}}$, r is the internuclear distance of a diatomic molecule, R_{e} is its equilibrium internuclear separation and is regarded as a fixed parameter in the fitting process. The dissociation energy D_{e} and the parameters a_i are determined by fitting.

Fitting equation (7) by the least-squares fitting method, we obtain the parameters a_i and D_{e}. In order to obtain satisfactory results, we try it from n=3 to n=8, and find the best results at n=6. The fitting results are tabulated in Table 3 together with the R_{e} value for integrality.

Table 3. The M-S APEF parameters for SH($X^2\Pi$) at the CCSD(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
3.7767	0.13424	36.3960	330.543	1723.296	–15836.66	–206317.09	1005113.30	0.00497

To evaluate the fitting quality of the M-S APEF, we calculate the ΔE_{RMSE} in the fitting process,

$$\Delta E_{\mathrm{RMSE}} = \sqrt{\frac{1}{N}\left[\sum_{i=1}^{N}(V_{\mathrm{APEF}} - V_{ab\ initio})^2\right]}. \qquad (8)$$

Where V_{APEF} and $V_{ab\ initio}$ are energies attained by the fitting and by the *ab initio* calculations, respectively. N is the number of fitting points (here N=124). The present ΔE_{RMSE} is of only 0.00497 eV (about 0.1148 Kcal/mol). Obviously, the present fitting accuracy is greatly superior to the chemical one (1.0 Kcal/mol).[31] It shows that the M-S function is very suitable for reproducing the PEC of the SH($X^2\Pi$) radical, and the fitting process is of high quality. So, we think that the present APEF collected in Table 3 is credible.

Based on the relationships between the spectroscopic parameters and the M-S APEF,[32–34] the spectroscopic parameters, B_{e}, α_{e} and $\omega_{\mathrm{e}}\chi_{\mathrm{e}}$, are calculated. To be conveniently compared with the measurements and other theories, these results are tabulated in Table 2, too. In Table 2, one can find that the R_{e}, ω_{e}, B_{e}, $\omega_{\mathrm{e}}\chi_{\mathrm{e}}$ and α_{e} values are in excellent agreement with the recent measurements,[5,7] and the D_{e} is also in good accord with the recent experiments.[6] According to these, we conclude that the present APEF is accurate.

A number of theoretical investigations[11–17] have been made for the spectroscopic parameters of the SH($X^2\Pi$) radical. Among these investigations, the earlier one was carried out by Cade and Huo.[11] They used the self-consistent field (SCF) method with the optimized Slater-type functions to obtain the PEC of this radical. From Table 2, one can find that their D_{e} is too small when compared with the experiments.[6,8,10] Senekowitsch *et al*[12] performed the R_{e}, ω_{e}, B_{e}, α_{e} and $\omega_{\mathrm{e}}\chi_{\mathrm{e}}$ calculations employing the internally contracted MCSCF-CI method with the basis set 14s11p4d1f centred on sulfur and 8s3p1d centred on hydrogen. Unfortunately, they did not calculate the D_{e} value. Furthermore, their ω_{e} value deviating from the measurements[5,7] is too large. Bruna and Hirsch[13] used the standard multi-reference double-excitation (MRD-CI) method with a complex basis set to calculate the spectroscopic parameters. However, their ground-state D_{e} result is still small when compared with the recent experiments.[5] Park and Sun[14] used the second-order *ab initio* effective valence shell Hamiltonian and the basis set,[35] which consists of 6s4p Gaussian functions contracted from primitive 12s9p for sulfur and 2s contracted from primitive 4s for hydrogen, to determine the accurate spectroscopic constants. Resende and Ornellas[15] employed the CASSCF combined with the contracted CI method and the aug-cc-pV5Z basis set to compute the molecular parameters. However, their D_{e} values deviate from the measurements[5] at least by 7.6%[14] and 1.16%,[15] respectively. Whereas in the present paper, the D_{e} is in excellent agreement with the RKR data[5] and the deviation between them is of only 0.11%. Woon and Dunning[16] have made a series of benchmark calculations using the CASSCF+1+2 method and a very large correlation-consistent basis set, cc-pV5Z. Hirata *et al*[17] combined the DK3-CCSD, DK3-CCSDT and DK3-CCSDTQ theories with the cc-PVTZ, cc-PVQZ and cc-PV5Z basis sets to make the sophisticated calculations. From Table 2, one can find that there is a very close similarity between the present calculations

and their results. However, we should notice that they both did not give the APEF, which is very useful in the investigations of elastic collisions. And they either did not make the vibrational manifold calculations, which are very useful in the computations of the rovibrational transitions. As a whole, the present investigations are more complete and accurate when compared with these theories.[11−17]

The more stringent way to compare the *ab initio* results with the measurements is to attempt to reproduce the RKR data: the vibrational levels, classical turning points, initial rotation and centrifugal distortion constants. Since only in that way, it can be clearly demonstrated whether the APEF accurately describes the corresponding PEC. In order to attain the vibrational manifolds, first of all, we must solve the following radial Schrödinger equation of nuclear motion in the adiabatic approximation,

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\Psi_{\nu.J}(r) =E_{\nu,J}\Psi_{\nu.J}(r). \quad (9)$$

Where $V(r)$ is the adiabatic rotationless APEF tabulated in Table 3, ν and J are the vibrational and rotational quantum numbers, respectively, μ is the reduced mass of the SH radical. The rotational sublevel of a given vibrational level is represented by the following power series:[36]

$$E_{\nu,J} =G(\nu)+B_\nu[J(J+1)]-D_\nu[J(J+1)]^2 +H_\nu[J(J+1)]^3+L_\nu[J(J+1)]^4 +M_\nu[J(J+1)]^5+O_\nu[J(J+1)]^6. \quad (10)$$

By solving equation (9), we have obtained the total of 19 vibrational states for the SH($X^2\Pi$) radical with zero angular momentum (J=0). For each vibrational level [$G(\nu)$], 1 inertial rotation constant (B_ν) and 6 centrifugal distortion constants (D_ν, H_ν, L_ν, M_ν, N_ν and O_ν) are attained. Here, the vibrational levels and the classical turning points, $R_{\max}$ and $R_{\min}$, are tabulated in Table 4. The inertial rotation constants together with the available measurements[5] and theories[15] are tabulated in Table 5. And the six centrifugal distortion constants are tabulated in Table 6.

Table 4. Vibrational levels and classical turning points for SH($X^2\Pi$) when J=0.

υ	$G(\upsilon)$/cm^{-1}	$R_{\min}$/nm	$R_{\max}$/nm	υ	$G(\upsilon)$/cm^{-1}	$R_{\min}$/nm	$R_{\max}$/nm
0	1315.937	0.12387	0.14689	10	23193.453	0.10039	0.22517
1	3885.248	0.11751	0.15783	11	24809.299	0.09956	0.23397
2	6380.276	0.11365	0.16634	12	26284.823	0.09884	0.24381
3	8798.327	0.11080	0.17396	13	27602.860	0.09822	0.25521
4	11135.965	0.10852	0.18116	14	28739.089	0.09771	0.26919
5	13389.096	0.10662	0.18816	15	29654.287	0.09730	0.28832
6	15552.975	0.10501	0.19513	16	30261.919	0.09704	0.32468
7	17622.156	0.10362	0.20219	17	30400.865	0.09698	0.46378
8	19590.370	0.10240	0.20946	18	30470.926	0.09695	0.59945
9	21450.338	0.10133	0.21707				

Table 5. Initial rotation constants of SH($X^2\Pi$) when J=0 at the CCSD(T)/aug-cc-pV5Z level of theory.

CCSD(T)/aug-cc-pV5Z			Theory[15]	Exp.[5]	CCSD(T)/aug-cc-pV5Z			Theory[15]
υ	$G(\upsilon)$/cm^{-1}	B_υ/cm^{-1}	B_υ/cm^{-1}	B_υ/cm^{-1}	υ	$G(\upsilon)$/cm^{-1}	B_υ/cm^{-1}	B_υ/cm^{-1}
0	1315.937	9.4439172	9.4173	9.46051	10	23193.453	6.6430283	6.4741
1	3885.248	9.1765429	9.1493	9.18203	11	24809.299	6.2797343	6.1069
2	6380.276	8.9151384	8.8735	8.90402	12	26284.823	5.8756180	5.7025
3	8798.327	8.6559888	8.5949	8.62564	13	27602.860	5.4126965	5.2460
4	11135.965	8.3959000	8.3150	8.34584	14	28739.089	4.8568718	4.7160
5	13389.096	8.1319486	8.0308		15	29654.287	4.1250934	
6	15552.975	7.8612684	7.7413		16	30261.919	2.8168108	
7	17622.156	7.5808429	7.4439		17	30400.865	1.2429916	
8	19590.370	7.2872675	7.1368		18	30470.926	0.7979667	
9	21450.338	6.9764307	6.8149					

In experiment, only the B_ν, D_ν and H_ν values of the first 5 vibrational levels can be found in the literature.[5] From the B_ν comparisons tabulated in Table 5, we find that the largest deviation between them does not exceed 0.6%. Furthermore, the present D_ν and H_ν values are also in excellent agreement with the corresponding RKR data.[5] It is necessary to explain that, for the sake of clarity of this paper, we do not tabulate these D_ν and H_ν data in Table 6.

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

ν	$D_\nu/10^{-4}\mathrm{cm}^{-1}$	$H_\nu/10^{-8}\mathrm{cm}^{-1}$	$L_\nu/10^{-12}\mathrm{cm}^{-1}$	$M_\nu/10^{-17}\mathrm{cm}^{-1}$	$N_\nu/10^{-20}\mathrm{cm}^{-1}$	$O_\nu/10^{-24}\mathrm{cm}^{-1}$
0	4.9354923	1.7168009	–0.1932432	–2.9716618	–0.94154027	0.92652665
1	4.7598675	1.5781689	–0.5871379	–0.2203339	–0.56312278	0.24028022
2	4.6319215	1.4232300	–0.8664468	1.3768534	–0.61539269	–0.15145792
3	4.5461864	1.2564104	–1.0968585	1.6724218	–0.89898611	–0.50441948
4	4.4993472	1.0743678	–1.3272184	0.50565104	–1.4005207	–1.1264115
5	4.4902616	0.86793931	–1.6025246	–2.5879314	–2.2471114	–2.4866392
6	4.5201277	0.62171461	–1.9770827	–8.6832468	–3.7627966	–5.5528155
7	4.5929537	0.31131767	–2.5328378	–20.067885	–6.6821267	–12.654757
8	4.7165518	–0.1027358	–3.4129761	–41.661300	–12.750746	–29.993874
9	4.9044861	–0.6879112	–4.8950185	–84.682760	–26.497804	–75.924347
10	5.1799361	–1.5679457	–7.5711917	–177.19745	–61.113759	–212.56558
11	5.5838276	–2.9912083	–12.855711	–399.02978	–161.36237	–691.24762
12	6.1937733	–5.5198805	–24.670246	–1021.9628	–515.26183	–2817.3734
13	7.1754545	–10.666186	–56.544462	–3256.1468	–2211.7991	–16493.770
14	8.9597140	–23.800483	–175.40027	–15567.169	–16197.729	–186976.31
15	13.191077	–78.118836	–1082.7234	–195236.97	–417989.66	–10039164
16	40.311911	1364.5342	–75985.837	–42882732	-1.89720×10^{8}	-9.01273×10^{8}
17	7.8804393	783.71406	23512.822	21644018	3.94804×10^{7}	-1.00711×10^{10}
18	52.712849	–8062.6779	–3088465.6	-1.5049×10^{10}	-8.54752×10^{11}	-5.36676×10^{14}

Unfortunately, to the best of our knowledge experimentally and theoretically, no energy levels and classical turning points have been found. And no information about the inertial rotation and centrifugal distortion constants exists for the SH($X^2\Pi$) radical up to date in the literature. 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 accord between the present B_υ, D_υ and H_υ values and the available experiments, we have reasons to believe that the results tabulated in Tables 4–6 are all accurate. Consequently, we conclude that the M-S APEF tabulated in Table 3 is accurate, too.

4. Total and partial-wave elastic cross sections

Using the APEF tabulated in Table 3, we can numerically solve equation (1) by the Numerov method[37] with the automatic step-size selection. The partial-wave phase shift δ_l of the elastic collisions of sulfur and hydrogen in their ground states at low temperatures is calculated according to the formula (4) when two atoms approach each other along the ground-state PEC of the SH radical. Various elastic partial-wave cross sections and the total elastic cross sections are calculated by equations (5) and (6) over the 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 evaluated at low temperatures is depicted in Fig.1. And the collision energy dependences of elastic cross sections for some selected partial waves are presented in Figs.2–5, respectively.

As shown in Figs.1–5, we see that the total cross sections of elastic collisions between two ground-state sulfur and hydrogen atoms when they approach each other along the PEC of the SH($X^2\Pi$) radical are almost constant at low temperatures, where only the s-wave cross sections are significant. At very low temperatures, the total and the s-wave cross sections increase slowly. Therefore, the total elastic cross sections are dominated by s-wave scattering when the collision energy is below 10^{-5} a.u. With the increase of the energy, the s-wave cross section tends to de-

crease, but the decrease is obviously overcome by the higher partial-wave contributions. As shown in Figs.1-5, we can see that more oscillations occur through the additions of higher partial waves.

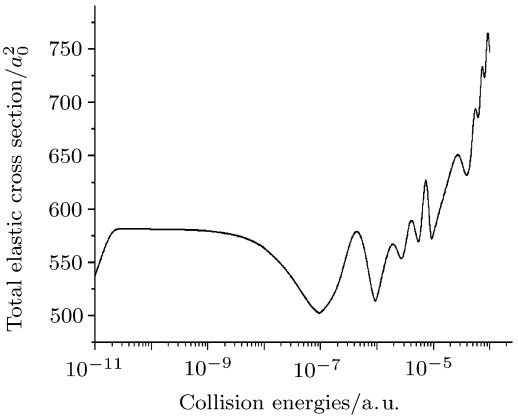


Fig.1. Total elastic cross sections versus scattering energies for collisions of H and S in the ground state approaching along the ground-state PEC of SH radical.

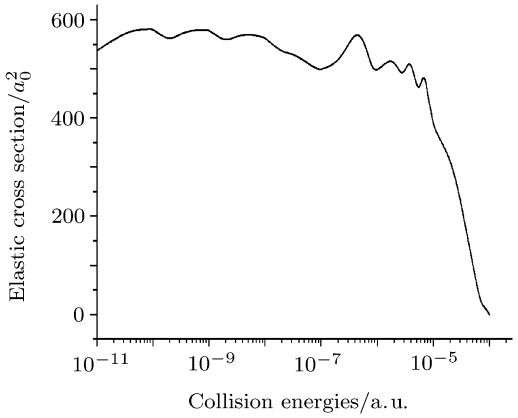


Fig.2. The l=0 partial-wave cross sections versus scattering energies for collisions between sulfur and hydrogen in the ground state approaching along the ground-state PEC of the SH radical.

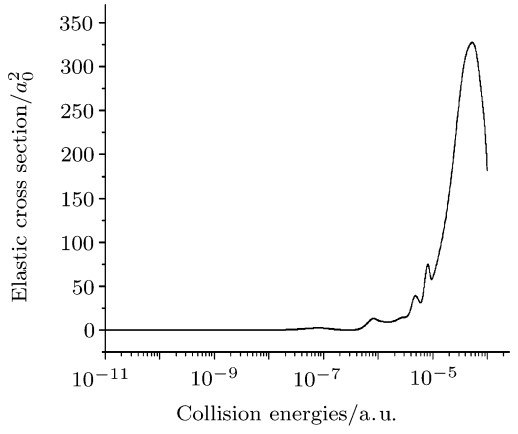


Fig.3. The l=1 partial-wave cross sections versus scattering energies for collisions between sulfur and hydrogen in the ground state approaching along the ground-state PEC of the SH radical.

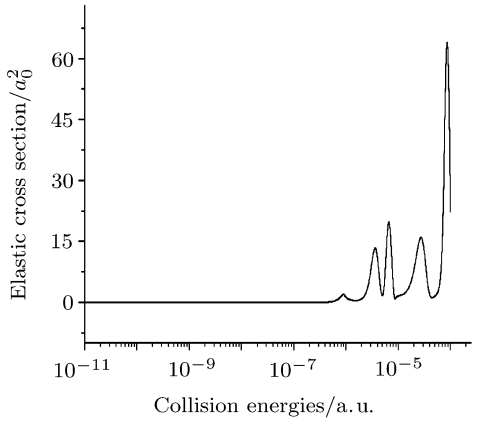


Fig.4. The l=5 partial-wave cross sections versus scattering energies for collisions between sulfur and hydrogen in the ground state approaching along the ground-state PEC of the SH radical.

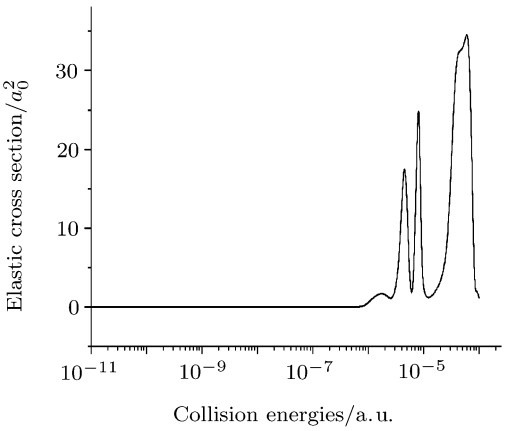


Fig.5. The l=6 partial-wave cross sections versus scattering energies for collisions between sulfur and hydrogen in the ground state approaching along the ground-state PEC of the SH radical.

Abundant resonant structures exist in Fig.1. Obviously, these sharp peaks come from the shape resonances. For the low-energy atom-atom scattering, because the collision energy is lower than the centrifugal barrier, the shape resonance that is associated with the quasi-bound state trapped by the centrifugal barrier is important. At very low temperatures, with the increase of the collision energy, the first obvious resonant peak appears. Careful calculations have proved that it results from the s-wave contributions and the resonant energy is of 4.6×10^{-7}a.u.. Subsequently, the second peak arrives. The peak is consistent with the resonant position of f partial wave and the resonant energy is of 1.9×10^{-6}a.u.. For the third resonance, investigations have shown that its most prominent composition comes from the $l = 3$ and 6 partial-wave contributions. Eight sharp resonances can be found in Fig.1. Their resonant energies and main contributors are all summarized in Table 7.

Table 7. Shape resonance energies (in units of a.u.) of two ground-state sulfur and hydrogen collisions when approaching along the PEC of the SH($X^2\Pi$) radical.

l	0	4	3, 6	3, 6, 8	3, 8	1, 6, 7	4, 8	2, 3
E	4.6×10^{-7}	1.9×10^{-6}	3.7×10^{-6}	7.3×10^{-6}	2.8×10^{-5}	5.5×10^{-5}	7.3×10^{-5}	9.1×10^{-5}

We have investigated the elastic collisions between two Li atoms and between H and N atoms in their ground states at low temperatures using the present theoretical method.[22,38] And the results are in excellent agreement with those obtained from the experiments. Thus, the present method should be reliable. Since the interaction potential attained here is accurate and reliable, therefore, though no experimental and theoretical results have been found about the elastic collisions between two sulfur and hydrogen atoms at low temperatures, we have reasons to believe that various elastic cross sections calculated in this paper are reliable and accurate. These results are expected to be detected experimentally and to be examined theoretically in the near future.

5. Conclusions

The accurate interaction potential has been constructed at the CCSD(T)/aug-cc-pV5Z level of theory, and consequently, the spectroscopic parameters and the vibrational manifolds have been calculated. Excellent agreement is found when they are compared with the available measurements. In contrast with the experiments and other theories, the conclusions can be gained that the present investigations are more complete and accurate as a whole. The total and various elastic cross sections of two sulfur and hydrogen collisions are investigated for the first time by using the present interaction potential. It has been found that the abundant resonant structures exist in the total elastic cross sections. The pronounced shape resonances in the total elastic cross sections come from the $l = 0, 1, 2, 3, 4, 6, 7, 8$ partial-wave contributions. The positions of these sharp resonances are calculated, and the corresponding contributors are determined.

Acknowledgment

We heartily thank Professor Zhu Zheng-He of Sichuan University, for helpful discussion about the arithmetic of vibrational manifolds during the planning stages of this work.

References

[1] Sinha K 1991 *Proc. Astron. Soc. Austr.* **9** 32
[2] Walker C K, Lada C J, Young E T, Maloney P R and Wilking B A 1986 *Astrophys. J.* **309** L47
[3] Saito S, Kawaguchi K, Yamamoto S, Ohishi M, Suzuki H and Kaifu N 1987 *Astrophys. J.* **317** L115
[4] Yamamoto S, Saito S, Kawaguchi K, Kaifu N, Suzuki H and Ohishi M 1987 *Astrophys. J.* **317** L119
[5] Ram R S, Bernath P F, Engleman R and Brault J W 1995 *J. Mol. Spectrosc.* **172** 34
[6] Continetti R E, Balko B A and Lee Y T 1991 *Chem. Phys. Lett.* **182** 400
[7] Bernath P F, Amano T and Wong M 1983 *J. Mol. Spectrosc.* **98** 20
[8] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure*. Vol.4 *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold) p590
[9] Pathak C M and Palmer H B 1969 *J. Mol. Spectrosc.* **32** 157
[10] Ramsay D A 1952 *J. Chem. Phys.* **20** 1920
[11] Cade P E and Huo W M 1967 *J. Chem. Phys.* **47** 649
[12] Senekowitsch J, Werner H J, Rosmus P, Reinsch E A and Oneil S V 1985 *J. Chem. Phys.* **83** 4661
[13] Bruna P J and Hirsch G 1987 *Mol. Phys.* **61** 1359
[14] Park J K and Sun H 1992 *Chem. Phys. Lett.* **194** 485
[15] Resende S M and Ornellas F R 2001 *J. Chem. Phys.* **115** 2178
[16] Woon D E and Dunning T H 1993 *J. Chem. Phys.* **99** 1914
[17] Hirata S, Yanai T, de Jong W A, Nakajima T and Hirao K 2004 *J. Chem. Phys.* **120** 3297
[18] Raghavachari K, Trucks G W, Pople J A and Head-Gordon M 1989 *Chem. Phys. Lett.* **157** 479
[19] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
[20] Peterson K A, Woon D E and Dunning T H 1994 *J. Chem. Phys.* **100** 7410
[21] Peterson K A, Kendall R A and Dunning T H 1993 *J. Phys. Chem.* **99** 1930
[22] Sun J F, Zhang J C and Wang J M 2006 *Chin. Phys.* **15** 531
[23] Côté R, Dalgarno A and Jamieson M J 1994 *Phys. Rev.* A **50** 399
[24] Jamieson M J, Dalgarno A and Yukich J N 1992 *Phys. Rev.* A **46** 6956
[25] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Jr Montgomery J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M,

Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2004 Gaussian 03 Revision D.01 (Wallingford CT: Gaussian Inc.)

[26] Pawlowski F, Jørgensen P, Olsen J, Hegelund F, Helgaker T, Gauss J, Bak K L and Stanton J F 2002 *J. Chem. Phys.* **116** 6482

[27] Ruden T A, Taylor P R and Helgaker T 2003 *J. Chem. Phys.* **119** 1951

[28] Ruden T A, Helgaker T, Jørgensen P and Olsen J 2004 *J. Chem. Phys.* **121** 5874

[29] Bak K L, Gauss J, Jørgensen P, Olsen J, Helgaker T and Stanton J F 2001 *J. Chem. Phys.* **114** 6548

[30] Shi D H, Zhang J P, Sun J F, Zhu Z L, Yu B H and Liu Y F 2008 *J. Mol. Struct.* (*Themchem*) **851** 30

[31] Aguado A and Paniagua M 1992 *J. Chem. Phys.* **96** 1265

[32] Shi D H, Sun J F, Ma H and Zhu Z L 2007 *Acta Phys. Sin.* **56** 2085 (in Chinese)

[33] Yan S Y and Bao W S 2007 *Chin. Phys.* **16** 3765

[34] Shi D H, Sun J F, Liu Y F, Ma H, Zhu Z L and Yang X D 2007 *Acta Phys. Sin.* **56** 4454 (in Chinese)

[35] Veillard A 1968 *Theor. Chim. Acta* **12** 405

[36] Shi D H, Sun J F, Zhu Z L and Liu Y F 2007 *Chin. Phys.* **16** 2701

[37] González J L M Q and Thompson D 1997 *Comput. Phys.* **11** 514

[38] Shi D H, Zhang J P, Sun J F, Zhu Z L, Liu Y F and Yang X D 2008 *Chin. Phys.* B **17** 2090