Vol 11 No 10, October 2002
1009-1963/2002/11(10)/1013-05

Chinese Physics

© 2002 Chin. Phys. Soc.
and IOP Publishing Ltd

Cross sections for rotational excitation in He–H_2 collisions*

Yang Xiang-Dong(杨向东)[a)b)], Zhou Xiao-Lin(周晓林)[b)], Zhang Ji-Yan(张继彦)[b)], Sun Gui-Hua(孙桂华)[b)c)], and Zhu Jun(朱 俊)[d)†]

[a)] *Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621900, China*

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

[c)] *Department of Physics, Zhangye Teachers College, Zhangye 734000, China*

[d)] *College of Physics Science and Technology, Sichuan University, Chengdu 610065, China*

(Received 29 November 2001; revised manuscript received 10 June 2002)

Close coupling calculations have been carried out for rotational excitations in He–H_2 collisions with symmetric isotopic substitution (He–H_2, D_2, T_2) and asymmetric isotopic substitution (He–HD, HT, DT). Cross sections have been obtained at the incidence energy of 0.3eV. Based on the calculations, the effect of isotopic substitution on atom–diatom collisions is discussed.

Keywords: close coupling calculation, isotopic substitution, rotationally inelastic collision
PACC: 3450L

1. Introduction

Rotationally inelastic scattering of an atom by a diatomic molecule is of both theoretical and practical importance. It plays a very important role in practical processes, such as the cooling of interstellar matter, predicting the laser action,[1,2] resonance fluorescence[3] and gas phase relaxation[4] etc. Moreover, it can serve as a prototype for general molecular collisions.

The collisions between a helium atom and a hydrogen molecule is one of the simplest molecular scattering systems and it has received much attention.[5] Since hydrogen has three isotopes, the effect of isotopic substitution must be considered in practical problems. To obtain the magnitude of the isotope effect in practical systems and to determine the accuracy necessary in the measurement which is influenced by this effect, we need to study the isotope substitution effect in atom–molecule collisions.[6,7] However, little has been reported in this field and few data are available. In this paper, theoretical calculations and systematical studies of the cross sections for rotational excitation in He–H_2, D_2, T_2, HD, HT, DT collisions are presented.

2. Theoretical calculations

2.1. Close coupling calculations

The Hamiltonian of the scattering system between an atom and a diatomic molecule can be expressed as

$$H = -\frac{\hbar^2}{2\mu_{A,BC}}\nabla_R^2 - \frac{\hbar^2}{2\mu_{BC}}\nabla_r^2 + V(\hat{R},\hat{r},\cos\theta), \quad (1)$$

where $\mu_{A,BC}$ and μ_{BC} are the total reduced mass of the scattering system and the reduced mass of the diatom respectively, and $\cos\theta = \hat{R}\cdot\hat{r}$. The total wavefunction of the system has the following form

$$\Psi_\alpha(\boldsymbol{R},\boldsymbol{r}) = \frac{1}{K_{n_\alpha J_\alpha}} \sum_{n_\gamma}\sum_{J_\gamma}\sum_{l_\gamma}\sum_{J} g^J_{n_\gamma J_\gamma l_\gamma, n_\alpha J_\alpha M_\alpha}(R) \times \phi_{n_\gamma J_\gamma}(r) Y^{l_\gamma J_\gamma}_{J M_\alpha}(\hat{R},\hat{r}), \quad (2)$$

where $g(R)$ is the radial wavefunction of the relative motion between the atom and the diatom, $\phi(r)$ is the radial part of the ro-vibrational wavefunction for the diatomic molecule, α is the incidence channel and γ is other possible channel, n is the vibrational quantum number, J is the total angular momentum of the system, and l_γ and J_γ are the orbital quantum number of the incident atom and the rotational quantum number of the molecule in γ channel, respectively. The total

*Project supported by the National Natural Science Foundation of China (Grant No 19974028) and by the Doctoral Programme Foundation of Institutions of Higher Education, China. (Grant No 1999061015).

†Author to whom correspondence should be addressed.

wavefunction $\Psi_\alpha(\boldsymbol{R},\boldsymbol{r})$ is given by the solution of the Schrödinger equation

$$(H-E)\,\Psi_\alpha(\boldsymbol{R},\boldsymbol{r})=0. \tag{3}$$

Substituting the corresponding parts of Eq.(3) by Eqs.(1) and (2), we have

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}R^2}-\frac{l_\beta(l_\beta+1)}{R^2}+k_\beta^2\right)g^J_{n_\beta J_\beta l_\beta,n_\alpha J_\alpha M_\alpha}(R) =\frac{2\mu_{A,BC}}{\hbar^2}\sum_{n_\gamma J_\gamma l_\gamma}V^J_{n_\beta J_\beta l_\beta,n_\gamma J_\gamma l_\gamma}(R)g^J_{n_\gamma J_\gamma l_\gamma,n_\alpha J_\alpha M_\alpha}(R). \tag{4}$$

Equation (4) is the close coupling equation in atom–diatom collisions.

2.2. Interaction potential between He–H_2, D_2, T_2 and He–HD, HT, DT

For the He–H_2 scattering system, we employ the Tang–Toennies model potential,[8] which can be written as

$$V(R,r,\theta)=\sum_\lambda V_\lambda(R,r)\mathrm{P}_\lambda(\cos\theta), \tag{5}$$

where R denotes the distance between He and the centre of mass (CM) of H_2, r represents the separation of H–H, and θ is the angle between R and r. Every coefficient in each term of the Legendre expansion (5) can be represented by a long-range dispersion attractive potential and a short-term self-consistent field (SCF) repulsive potential

$$V_\lambda(R,r)=A(r)\exp[-b(r)R] -\sum_{2n=0}^{\infty}\left[1-\sum_{k=0}^{2n}\frac{[b(r)R]^k}{k!} \times\exp[-b(r)R]\frac{C_{2n}(r)}{R^{2n}}\right]. \tag{6}$$

Within the Born–Oppenheimer approximation, isotopic substitution does not change the intermolecular potential. However, it may cause the CM of the diatom to shift a distance δ. For systems of symmetric isotopic substitution on He–H_2, that is, for He–D_2 and T_2 systems, the CM of the hydrogen molecule remains unshifted, and so the symmetric isotopic substitution does not change the intermolecular potential. For He–HD, HT and DT systems, the potential surface is still the same as that of He–H_2. However, the CM of the hydrogen molecule shifts a distance of δ and, since it is more convenient to treat this kind of scattering problem in a CM coordinate system, the potential must be reconstructed in the new coordinates. Substituting r by $\xi=(r-r_0)/r_0$, here $r_0(=1.449a_0)$ is the equilibrium separation of H–H, the original position O' in the old coordinates (R',ξ',θ') lies on the centre of BC, and the original position in the new coordinates (R,ξ,θ) shifts to O. The relation between the old and the new coordinates is shown in Fig.1. From Fig.1 we have

$$R'=R(1+t^2-2t\cos\theta)^{1/2}, \tag{7}$$

$$\cos\theta'=(\cos\theta-t)/(1+t^2-2t\cos\theta)^{1/2}, \tag{8}$$

where $t=\delta/R$.

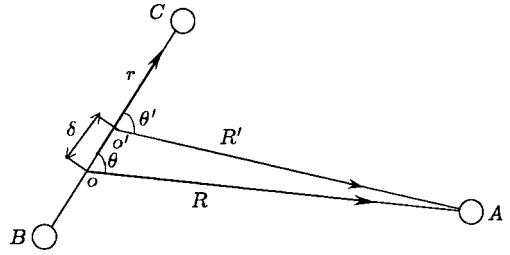


Fig.1. Collisions between an atom and a diatomic molecule. C is the lighter nuclei of the diatom BC and A is the atom. O and O' indicate the positions of the CM of the isotopically substituted and unsubstituted diatoms respectively.

In the old coordinate system, the potential function is expanded as

$$V(R',\xi,\theta')=\sum_{i=0}^{n}V_i(R',\xi)\mathrm{P}_i(\cos\theta') \qquad l=0,2,4,\cdots \tag{9}$$

In the new coordinate system it is written as

$$U(R,\xi,\theta)=\sum_{k=0}^{m}U_k(R,\xi)\mathrm{P}_k(\cos\theta), \tag{10}$$

with $\xi=\dfrac{r-r_0}{r+r_0}$. Since isotopic substitution does not change the potential surface of the atom–diatom system, we have

$$U(R',\xi,\theta')=U(R,\xi,\theta)=\sum_{k=0}^{m}U_k(R,\xi)\mathrm{P}_k(\cos\theta). \tag{11}$$

From Eq.(11) and by using of the normal property of the Legendre polynomial, the components U_k of the expansion given in Eq.(10) are obtained as

$$U_k(R,\xi)=\left(k+\frac{1}{2}\right)\int_0^\pi V(R',\xi,\theta')\mathrm{P}_k(\cos\theta)\mathrm{d}(\cos\theta) =\left(k+\frac{1}{2}\right)\sum_{i=0}^{n}\int_0^\pi V_i(R',\xi)\mathrm{P}_i(\cos\theta') \times\mathrm{P}_k(\cos\theta)\mathrm{d}(\cos\theta). \tag{12}$$

Treating t as an expansion parameter and employing a Taylor series expansion of $V_l(R',\xi)$ about t=0, Liu *et al*[9] obtained analytical expressions for the $U_k(R)$ functions of Eq.(7) in terms of functions $V_l(R,\xi)$ and their derivatives. The first eight terms are as follows

$$U_0(R,\xi) = V_0 + t^2\left[\frac{1}{3}RV_0^{(1)} + \frac{1}{6}R^2V_0^{(2)} + \frac{1}{5}V_2 + \frac{1}{3}RV_2^{(1)} + \frac{1}{15}R^2V_2^{(2)}\right] + O(t^4),$$

$$U_1(R,\xi) = t\left[-RV_0^{(1)} - \frac{6}{5}V_2 - \frac{2}{5}RV_2^{(1)}\right] + O(t^3),$$

$$U_2(R,\xi) = V_2 + t^2\left[-\frac{1}{3}RV_0^{(1)} + \frac{1}{3}R^2V_0^{(2)} - \frac{11}{7}V_2 + \frac{11}{21}RV_2^{(1)} + \frac{11}{42}R^2V_2^{(2)} + \frac{10}{7}V_4 + \frac{6}{7}V_4^{(1)} + \frac{2}{21}R^2V_4^{(2)}\right] + O(t^4),$$

$$U_3(R,\xi) = t\left[\frac{6}{5}V_2 - \frac{3}{5}RV_2^{(1)} - \frac{20}{9}V_4 - \frac{4}{9}RV_4^{(1)}\right] + O(t^3),$$

$$U_4(R,\xi) = V_4 + t^2\left[\frac{48}{35}V_2 - \frac{6}{7}RV_0^{(1)} + \frac{6}{35}R^2V_2^{(2)} - \frac{390}{77}V_4 + \frac{39}{77}RV_4^{(1)} + \frac{39}{154}R^2V_4^{(2)}\right] + O(t^4),$$

$$U_5(R,\xi) = t\left[\frac{20}{9}V_4 - \frac{5}{9}RV_4^{(1)}\right] + O(t^3),$$

$$U_6(R,\xi) = t^2\left[\frac{40}{11}V_4 - \frac{15}{11}RV_4^{(1)} + \frac{5}{35}R^2V_4^{(2)}\right] + O(t^3),$$

$$U_7(R,\xi) = t^3\left[\frac{2240}{42}V_4 - \frac{1015}{429}RV_4^{(1)} + \frac{175}{429}R^2V_4^{(2)} - \frac{35}{1287}R^3V_4^{(3)}\right] + O(t^5).$$

It should be noted here that δ is relevant to the masses of atoms B and C in the molecule, and r is the separation between B and C,

$$\delta = \frac{1}{2}\frac{m_B - m_C}{m_B + m_C}r, \tag{13}$$

$$t = \frac{\delta}{r}\frac{r}{R} = \frac{1}{2}\frac{m_B - m_C}{m_B + m_C}\frac{r}{R}. \tag{14}$$

For DT, HD and HT molecules, t is $\frac{r}{10R}$, $\frac{r}{6R}$ and $\frac{r}{4R}$ respectively, and because $r \le R$ is considered valid in our calculations only, $t < 1$ is always valid.

In our calculation, only the first five terms of Eq.(10) are taken, and for each of these terms the expression is expanded as a power series and only includes terms up to $O(t^4)$. The convergence of the expansion in powers of t has been discussed in Ref.[9]. It was shown that such a treatment of the potential function in an asymmetric isotopic substitution system is not very accurate,[9] but it is accurate enough in general calculations and evaluations of cross sections.

3. Results and conclusion

By solving the close coupling differential equation, we have obtained the cross sections for the rotational excitation at E=0.3eV. The results are given in Tables 1 and 2. The partial cross sections for the systems of symmetric isotopic substitutions are shown in Figs.2–5, and their angular distributions are given in Figs.6–9.

Table 1. State-to-state cross sections of He–H_2, D_2 and T_2 at E=0.3eV.

j	$\longrightarrow$	j'	He–H_2	He–D_2	He–T_2
0		0	0.1263(+3)	0.1235(+3)	0.1217(+3)
0		2	0.1165(+2)	0.1746(+2)	0.1928(+2)
0		4	0.2231	0.1835(+1)	0.3154(+1)
0		6	0.1696(−6)	0.2758(−1)	0.1470
0		8		0.6834(−5)	0.1105(−2)
0		10			0.1457(−6)
Total cross section σ/arb.units			0.1383(+3)	0.1429(+3)	0.1443(+3)

Table 2. State-to-state cross sections of He–HD, HT and DT at E=0.3eV.

j	$\longrightarrow$	j'	He–HD	He–HT	He–DT
0		0	0.1090(+3)	0.9941(+2)	0.1155(+3)
0		1	0.1710(+2)	0.2115(+2)	0.1108(+2)
0		2	0.5958(+1)	0.7498(+1)	0.7336(+1)
0		3	0.6352(+1)	0.7154(+1)	0.6692(+1)
0		4	0.2112(+1)	0.5052(+1)	0.1806(+1)
0		5	0.4231	0.2034(+1)	0.1049(+1)
0		6	0.1675(−1)	0.2749	0.1707
0		7	0.2068(−6)	0.3413(−2)	0.2403(−1)
Total cross sections σ/arb.units			0.1410(+3)	0.1426(+3)	0.1437(+3)

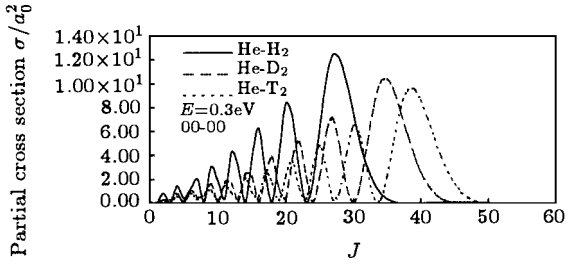


Fig.2. Partial cross sections as functions of total angular momentum J.

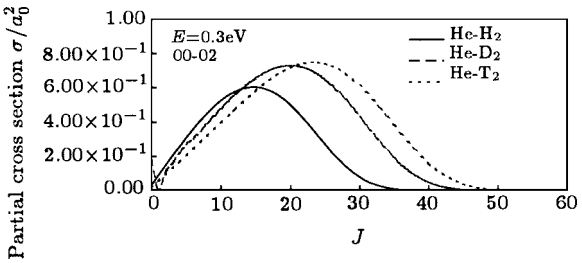


Fig.3. Partial cross sections as functions of total angular momentum J.

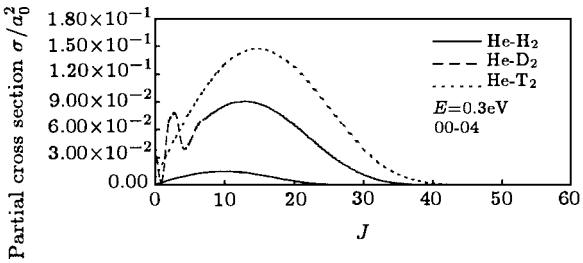


Fig.4. Partial cross sections as functions of total angular momentum J.

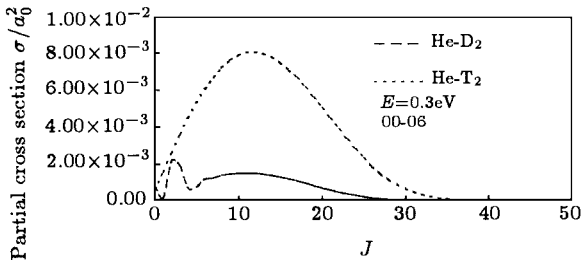


Fig.5. Partial cross sections as functions of total angular momentum J.

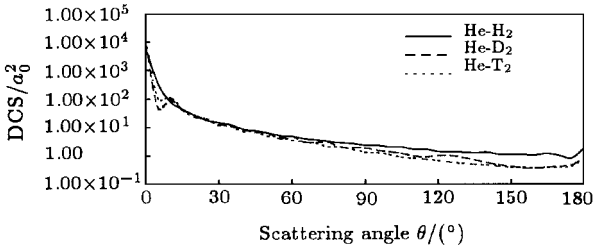


Fig.6. Differential cross sections for 0–0 rotational excitation at E=0.3eV.

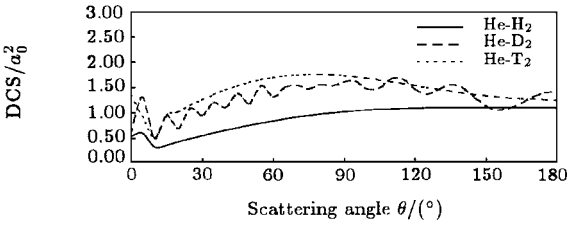


Fig.7. Differential cross sections for 0–2 rotational excitation at E=0.3eV.

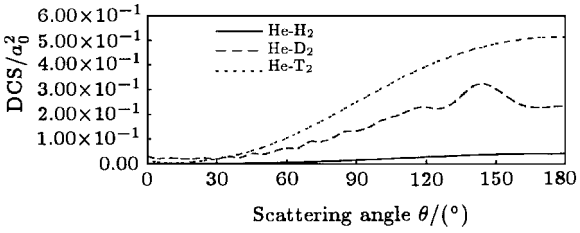


Fig.8. Differential cross sections for 0–4 rotational excitation at E=0.3eV.

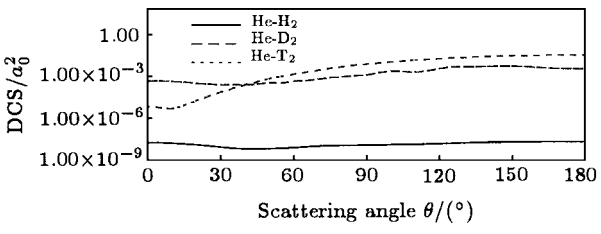


Fig.9. Differential cross sections for 0–6 rotational excitation at E=0.3eV.

According to the theoretical calculation, the following conclusions can be drawn:

(i) For both the systems with symmetric and asymmetric isotopic substitutions, the total cross sections in the He–H_2 collisions are not changed significantly. The physical significance of this fact is clear: the total cross sections of the collisions are dominated by the potentials of the systems, while they are not significantly changed by isotopic substitution.

(ii) For the scattering systems He–H_2, He–D_2 and He–T_2, their inelastic partial cross sections show the following regular changes:

$$\sigma_{0\to2}(H_2) < \sigma_{0\to2}(D_2) < \sigma_{0\to2}(T_2),$$

$$\sigma_{0\to4}(H_2) < \sigma_{0\to4}(D_2) < \sigma_{0\to4}(T_2),$$

$$\sigma_{0\to6}(H_2) < \sigma_{0\to6}(D_2) < \sigma_{0\to6}(T_2),$$

$$\sigma_{0\to8}(H_2) < \sigma_{0\to8}(D_2) < \sigma_{0\to8}(T_2).$$

While the changes of the elastic partial cross sections show the opposite trend, that is $\sigma_{0\to0}(H_2) > \sigma_{0\to0}(D_2) > \sigma_{0\to0}(T_2)$. The physical significance of such a fact is not difficult to understand when we notice that the rotationally excited energy levels become closer in the order H_2, D_2 and T_2. This means that the possibilities of being excited to higher levels in a collision become larger in the above order, and when the probabilities of inelastic transitions become larger, the probabilities of elastic transitions will correspondingly be smaller. So the elastic cross section, which is in fact another expression of the probability of elastic transitions, will become smaller.

(iii) From Fig.2 we can see that for He–H_2, D_2 and T_2 systems, as the incident energy is determined, the elastic partial cross sections $\sigma^J_{0\to0}$ continue to oscillate with the increase of J, and the oscillation enlarges until the final maximum is reached, and then it tends toward zero rapidly. For the three systems concerned, with the increase of reduced mass, the value of the maximum decreases, and the converging speed slows down. For He–H_2, D_2 and T_2 systems the cross sections converge at J=38, 44 and 48, respectively. From Figs.3–5 we can also see that for a definite scattering system, the cross sections for higher excitation converge more rapidly.

(iv) From Figs.6–9 we can see that for each scattering system the elastic differential cross section has a maximum at $\theta = 0°$, and with the increase of scattering angle, the elastic differential cross section tends toward zero rapidly. While the differential cross section for rotational excitation is smaller at a small angle, and becomes larger with the increase of the scattering angle.

Finally, it must be noted that the method used in this paper to treat the potential function is not very accurate, but from our calculations, it is proved to be reasonable. A more accurate method, which has been developed by Liu *et al*[9] will be applied in our calculations and the results will be reported later.

References

[1] Collins C B and Johnson B W 1972 *J. Chem. Phys.* **37** 5317

[2] Peterson L M, Lindgulst G H and Arnold C B 1974 *J. Chem. Phys.* **61** 3480

[3] Alkins D L, Fink E H and Moore C B 1970 *J. Chem. Phys.* **52** 1604

[4] Gordon R G and Klemperer W 1968 *Ann. Rev. Phys. Chem.* **19** 215

[5] Yang X D 1990 *Sci. Chin.* A **8** 833

[6] Yang X D, Zhang J Y and Jing F Q 1998 *Chin. Phys. Lett.* **15** 14

[7] Manson J T 1999 *Acta. Phys. Sin.* (Overseas Edition) **8** 313

[8] Tang K T and Toennies J P 1982 *J. Chem. Phys.* **76** 2524

[9] Liu W, Grabenstetter J E and Le Roy R J 1978 *J. Chem. Phys.* **68** 11