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CROSS SECTIONS FOR ION PRODUCTION IN REACTIONS OF H^+ WITH D_2. EFFECTS OF VIBRATIONAL AND ROTATIONAL EXCITED STATES OF D_2.

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Cross Sections for Ion Production in Reactions of H^+ with D_2. Effects of Vibrational and Rotational Excited States of D_2

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Cross sections for production of D_2^+, D^+, and HD^+ ions in the reaction of H^+ with D_2 were calculated in the center-of-mass collision energy range of 2.5 eV$\leqq$ E_{cm} $\leqq$ 8.0 eV by using a trajectory surface hopping (TSH) method with ab initio three-dimensional potential energy surfaces(3D-PES's). The calculations were carried out with D_2 reactants in the vibrational and rotational states with quantum numbers (v=0 to 3, j=1,5,10), and (v, j) dependence of each ion production was evaluated. It was found that the D_2^+ production is enhanced remarkably as the vibrational and rotational (v, j) state becomes high, where the vibrational excited state has the primary effect and the rotational excited state has the secondary effect. Compared with the D_2^+ production, the effect of vibrational excited state v on the D^+ and HD^+ production is small. The production of latter two ions is almost independent of the rotational excited state j.

Keywords : Ion Production Cross Section, State Selected Cross Section, Trajectory-surface-hopping, Ab Initio Potential Surfaces, H_3^+, H^+, D_2, D_2^+, HD^+, D^+

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$H^+ + D_2$反応におけるイオン生成の断面積.
D_2の振動回転励起状態がイオン生成に与える効果

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H^+とD_2の反応で生じるD_2^+、D^+、およびHD^+イオン生成の断面積を、重心衝突エネルギーE_{cm}= 2.5－8.0 eVの範囲内で、非経験的分子軌道計算で得られたH_3^+の3次元ポテンシャル面上でのトラジェクトリーサーフェスホッピング(TSH)法を用いることにより、評価した。反応物D_2の初期状態が各イオン生成に与える影響を調べるために、D_2の振動および回転の量子数をv= 0－3、j= 1, 5 , 10に設定して計算を行った。その結果、D_2^+イオンの生成は、D_2の振動回転状態(v, j)が高くなるに従って著しく増大することが分かった。D_2^+生成の飛躍的な増大には、D_2の振動励起が主要な役割を果たし、回転励起は補助的な効果を与えた。D_2^+生成と比較して、D_2の振動状態がD^+およびHD^+イオンの生成に与える効果は一桁小さく、D_2の回転状態に対する効果は殆ど無視しうる大きさであった。

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1. Introduction

Ion-molecule reactions occurring in the H_3^+ system and its isotopic variants have been studied theoretically as well as experimentally[1]. The absolute cross sections for ion production in the reactions $H^+ + D_2(v=0)$, $D^+ + H_2(v=0)$, and $D^+ + D_2(v=0)$ were measured by Ochs and Teloy[2] and by Schlier et al.[3] with an estimated error of ± 10 to 20% using a guided beam method, where v represents the vibrational quantum number. These cross sections were calculated theoretically by using a trajectory surface hopping (TSH) method with diatomics-in-molecules potential energy surfaces (DIM-PES's)[3-7]. The TSH calculations with DIM-PES's reproduce the D^+ and HD^+ production cross sections for the $H^+ + D_2$ reaction within the experimental uncertainty, but show systematic deviations from the experiments for other reactions[3]. Except for the region near the threshold energy, the disagreement with the experiment is attributed to the faulty repulsive wall of the ground state DIM-PES's[3,8].

In a recent paper[9] we also reported similar TSH calculations with ab initio three-dimensional (3D)-PES's, instead of DIM-PES's, which were calculated by the full configuration interaction method with a [8s6p2d1f] Gaussian-type basis set[10]. Compared with the TSH calculation with DIM-PES's, the energy dependence of experimental cross sections is reproduced better for the $D^+ + H_2$ and $D^+ + D_2$ systems by the use of the ab initio PES's. Although the TSH calculations with the ab initio PES's are systematically larger than the experiments for the $H^+ + D_2$ system, they almost coincide with each other within the corresponding uncertainties[2,9].

In this paper we present the cross sections for ion production from the reaction of H^+ with D_2 in vibrational and rotational excited states with quantum numbers (v=0 to 3, j=1,5,10). Three kinds of ions D_2^+, D^+, and HD^+ can be observed in the reaction of H^+ with D_2. These processes involving vibrationally and rotationally excited molecular species are of great importance for a plasma modeling of fusion reactor divertor[11], but there are no available data. So we undertook the TSH calculation with the ab initio 3D-PES's, and estimated how the vibrational and rotational excited states of D_2 affect each ion production in the collision energy range 2.5 eV $\leq E_{cm} \leq$ 8.0 eV.

2. Computational Method

The TSH calculation was carried out as before[9], except that the probability of surface hopping (nonadiabatic electronic transition) was evaluated by using the formula

established by Zhu and Nakamura (ZN)[12] instead of the Landau-Zener (LZ) formula[13-16]. All parameters in the ZN formula can be estimated directly from the ab initio PES's[12]. The hopping probability was calculated with the ZN formula when a surface hop was possible under the conventional TSH model[5].

3. Results and Discussion

Figures 1 to 3 show the cross sections for D_2^+ production by the electron transfer $H^+ + D_2 \rightarrow D_2^+ + H$. As the vibrational state v becomes high, the D_2^+ production is enhanced remarkably with the increase of energy E_{cm}. Fig.4 illustrates the section of ab initio PES's at R = 5.29 Å (10 bohr) in the C_{2v} geometry, where R is the distance between H^+ and D_2. In our TSH calculation, the surface hopping takes place on the avoided crossing point of two PES's. The avoided crossing between the $H^+ + D_2$ and $H + D_2^+$ electronic states arises in the region where the internuclear distance of D_2 (r) is about 1.32 Å (2.5 bohr) and R is larger than 2.65 Å (5 bohr)[10]. Thus the D_2^+ production is induced by such a $H^+ + D_2$ collision as D_2 is excited into the vibrational state with quantum number $v > 6$, because the vibration amplitude of D_2 in the $v > 6$ state is sufficient to reach the internuclear distance of r = 1.32 Å. If D_2 is in the vibrational excited state in advance, further vibrational excitation into the $v > 6$ state is brought about more easily by the collision with H^+, and that should cause the remarkable enhancement of the D_2^+ production.

The D_2^+ production cross section for $v \geqq 1$ also increases appreciably as the rotational state j becomes high. If D_2 is in the rotational excited state, the centrifugal force of the D_2 rotator contributes to the enlargement of D-D bond length, which should promote the D_2^+ production. From Figs.1 to 3, however, it is concluded that the vibrational excited state v has the primary effect on the D_2^+ production, and the rotational excited state j has the secondary effect.

Figs.5 to 7 show the cross sections for D^+ production. As v becomes larger, the D^+ production is reduced at E_{cm} below 4 eV, while it is enhanced above 5 eV. The D^+ ions are produced from reactions $H^+ + D_2 \rightarrow D^+ + HD$ (nuclear rearrangement) and $H^+ + D_2 \rightarrow D^+ + H + D$ (dissociation). Threshold energy of dissociation is 4.52 eV for the $H^+ + D_2(v=0, j=1)$ system and 3.11 eV for $H^+ + D_2(v=3, j=10)$. Thus, most of D^+ ions are produced by the nuclear rearrangement at E_{cm} below 4 eV. (The v dependence of D^+ production by the nuclear rearrangement is discussed later with the HD^+ production.) With the increase

of E_{cm}, the nuclear rearrangement decreases monotonically, while the dissociation increases[9]. Above 6 eV, the D^+ production from dissociation becomes more dominant than that from nuclear rearrangement. Figs.8 to 10 show contribution of the dissociation $H^+ + D_2 \rightarrow D^+ + H + D$ to the D^+ production. The dissociation is enhanced as the vibrational state v becomes high. From Figs.5 and 10 it is clearly demonstrated that the increase of D^+ production cross section with increasing v above 5 eV is due to the contribution of dissociation.

Figs.11 to 13 show the HD^+ production cross sections from the reaction $H^+ + D_2 \rightarrow HD^+ + D$. As v becomes largr, the HD^+ production is enhanced at E_{cm} below about 5 eV. At low collision energies both the HD^+ and D^+ ions are produced via the H-D pair formation[6]. The HD^+ ion can be formed if the internal energy of the H-D pair is sufficient to reach the internuclear distance of 1.32 Å, where the avoided crossing of two PES's arises[17]. On the other hand, the D^+ ion (neutral HD molecule) is formed if the H-D pair is not in the vibrational excited state sufficient to reach the internuclear distance of 1.32 Å. In the present calculation the sum of cross sections for above two reactions $H^+ + D_2 \rightarrow D^+ + HD$ and $H^+ + D_2 \rightarrow HD^+ + D$ is almost independent of v. Figs.14 to 16 show the summed cross sections for the $H^+ + D_2$ system. It can be seen from Figs.5 to 7 and Figs.11 to 16 that the vibrational excited state v promotes the HD^+ production and reduces the D^+ production at the same time at E_{cm} below about 5 eV.

From Figs.5 to 7 and 11 to 13 it is known that both the HD^+ and D^+ production is almost independent of the rotational state j.

Compared with the HD^+ and D^+ production cross sections, the D_2^+ production cross section shows remarkable (v, j) dependence. The D_2^+ production cross section, which is less than 1.0 $Å^2$ for (v=0,j=1) at E_{cm}=8.0 eV, becomes more than 7.0 $Å^2$ for (v=3,j=10). In the D^+ and DH^+ production, the difference of cross sections between different rovibrational states is less than 0.5 $Å^2$ in the calculated energy range.

The (v, j) dependence is also observed in the maximum of impact parameter (b_{max}) selected to determine the D_2^+ production cross section. The value of b_{max} for the D_2^+ production, which is less than 1.5 Å for (v=0, j=1), increases as the rovibrational state (v, j) becomes high and exceeds 2.7 Å for (v=3, j=10) in the calculated energy range. The values of b_{max} for the HD^+ and D^+ production, which are not so sensitive to the rovibrational state (v, j), are less than 1.5 Å and 1.25 Å, respectively, for all (v, j) at $E_{cm} \geqq 3$ eV. When D_2 is in the vibrational excited state in advance, the D_2^+ production

takes place with less energy capture in the $H^+ + D_2$ collision with larger impact parameter. In the HD^+ and D^+ production, H^+ need to approach D_2 closely to create the H-D pair or to cut the D-D pair, so that the molecular size of D_2 and HD_2^+ should restrict b_{max} more rigidly.

Finally, we discuss the accuracy of the present calculation. In the previous study[9], ion production cross sections were calculated for the reaction of H^+ with $D_2(v=0,j=1)$ in the range of 2.5 eV$\leqq E_{cm} \leqq$ 8.0 eV, where the classical treatment for the nuclear motion was considered to be appropriate because the quantum effect such as tunneling is not significant[8,9]. In the present study, ion production cross sections were calculated for the reaction of H^+ with D_2 in the rovibrational excited states. The rovibrational energy level of D_2 (v=3,j=10) is 1.41 eV higher than that of $D_2(v=0,j=1)$. It is thought that the bundle of trajectories calculated for the $H^+ + D_2$ (v=3,j=10) system at E_{cm} = 6.59 eV covers the same area of PES's as the bundle for the $H^+ + D_2(v=0,j=1)$ system at E_{cm} = 8.0 eV with different density distribution. Since the ion production cross sections for $H^+ + D_2(v=0, j=1)$ are in agreement with the experiments within the uncertainty of about ±30 %[9] and the cross sections for other rovibrational states (v, j) are given by smooth curves in the calculated energy range, serious problem may not happen on our PES's.

In the present calculation the hopping probability was evaluated by the ZN formula[12], instead of the LZ formula[9]. The use of LZ formula is not appropriate when a trajectory crosses an avoided crossing point with energy near the threshold. The ZN formula used is applicable to the whole range of energies above threshold and more accurate than the LZ formula. Therefore, the present TSH calculation with the ZN formula is more reliable than the previous calculation with the LZ formula.

In order to evaluate the applicability of TSH calculation[18], experiments with excited D_2 molecule are strongly requested.

4. Summary and Concluding Remarks

The cross sections for the production of HD^+, D^+, and D_2^+ ions in the reaction of H^+ with D_2(v=0 to 3, j=1,5,10) were calculated in the energy range 2.5 eV$\leqq E_{cm} \leqq$ 8.0 eV by using the TSH method with ab initio 3D-PES's. As the rovibrational (v, j) state becomes high, the D_2^+ production is enhanced remarkably with the increase of E_{cm}. The vibrational excited state v has the primary effect on the D_2^+ production and the rotational

excited state j has the secondary effect. Although the HD^+ and D^+ production shows the v dependence, its effect is small compared with the case for D_2^+ production, and the production of these two ions is almost independent of the rotational state j. The D_2^+ ion production is induced when D_2 is excited into high rovibrational state by the collision with H^+ and the amplitude of this oscillation is sufficient to reach the avoided crossing point. On the other hand, the HD^+ and D^+ ion production is brought about via the particle rearrangement (H-D pair formation) or dissociation.

These cross sections are fundamental to accurate modeling of the plasma power exhaust by the neutral hydrogen gas in the fusion reactor divertor. It has been shown that the D_2^+ production, which is endothermic for the $H^+ + D_2(v \leqq 3)$ system, is the dominant reaction for $E_{cm} \leqq 8.0$eV. It is expected that the (v, j) dependence of each ion production obtained for the $H^+ + D_2$ system applies to the ion production occurring in other isotopic variants.

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References

[1] A. Ichihara, S. Hayakawa, M. Sataka, and T. Shirai, JAERI-Data/Code 94-015 (1994), and related references therein.

[2] G.Ochs and E.Teloy, J.Chem.Phys. **61**, 4930 (1974).

[3] Ch. Schlier, U. Nowotny, and E. Teloy, Chem.Phys. **111**, 401 (1987).

[4] M. Karplus, R.N. Porter, and R.D. Sharma, J.Chem.Phys. **43**, 3259 (1965).

[5] J.C. Tully and R.K. Preston, J.Chem.Phys. **55**, 562 (1971).

[6] J.R. Krenos, R.K. Preston, R. Wolfgang, and J.C. Tully, J.Chem.Phys. **60**, 1634 (1974).

[7] F.O. Ellison, J.Am.Chem.Soc. **85**, 3540, 3544 (1963).

[8] S. Chapman, Adv.Chem.Phys. **82**, 423 (1992).

[9] A. Ichihara, T.Shirai, and K. Yokoyama, J.Chem.Phys. **105**, 1857 (1996). It should be noted that the square root of the hopping coefficient E_c is given as a function of ΔE_0 in Fig.1 of this reference.

[10]A. Ichihara and K. Yokoyama, J.Chem.Phys. **103**, 2109 (1995).

[11]R.K.Janev, "Atomic, molecular and particle-surface interaction data for divertor physics design studies", INDC(NDS)-331(1995).

[12]C.Zhu and H.Nakamura, Comm.Atom.Mol.Phys.**32**, 249(1996). The hopping probability was calculated using Eq.(3.7) of the reference with parameters defined in Eqs.(3.3), (3.4), (3.5) and (3.10).

[13]L.D.Landau, Phys.Z.Sowjetunion **2**, 46 (1932).

[14]C. Zener, Proc.R.Soc. **A137**, 696 (1932).

[15]E.C.G. Stuckelberg, Helv.Phys.Acta **5**, 369 (1932).

[16]C.W. Bauschlicher, Jr., S.V. O'Neil, R.K. Preston, H.F. Schaefer III, and C.F. Bender, J.Chem.Phys. **59**, 1286 (1973).

[17]PES's are independent of the mass of nuclei.

[18]For an extended TSH method, see (i)J.C. Tully, J.Chem.Phys. **93**, 1061 (1990) and (ii) F.J.Webster, J. Schnitker, M.S. Friedrichs, R.A. Friesner, and P.J. Rossky, Phys.Rev.Lett.**66**, 3172(1991).

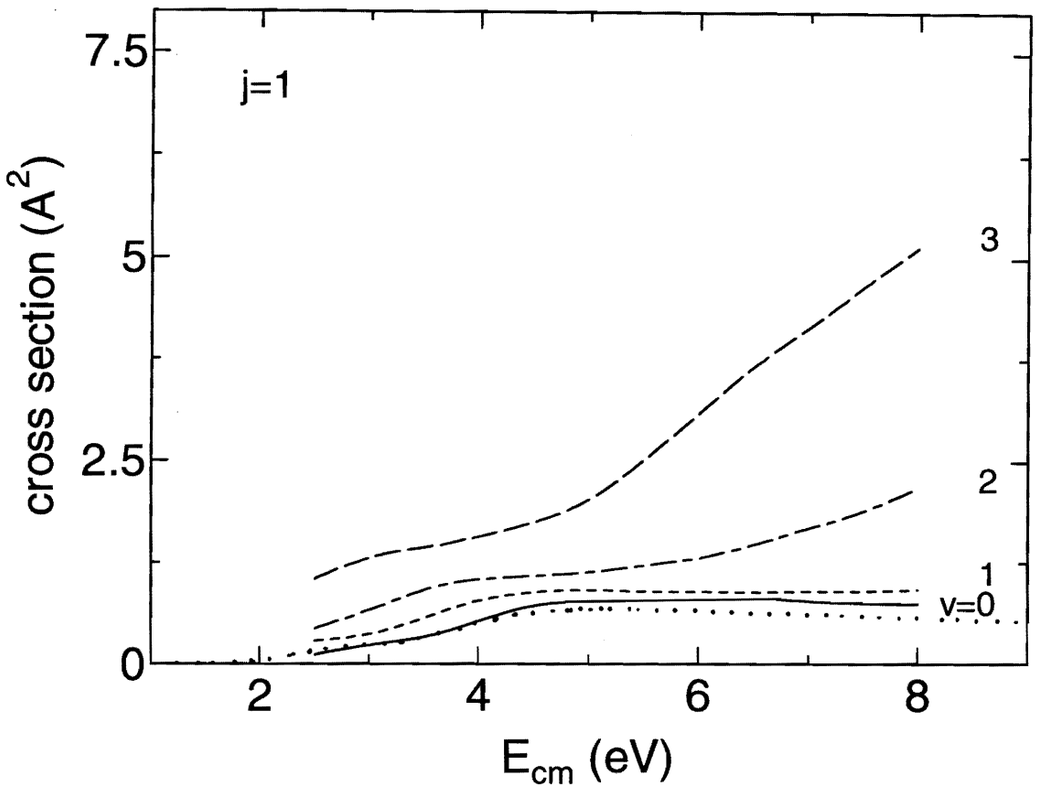

Fig.1 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=1) → $D_2^+ + H$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

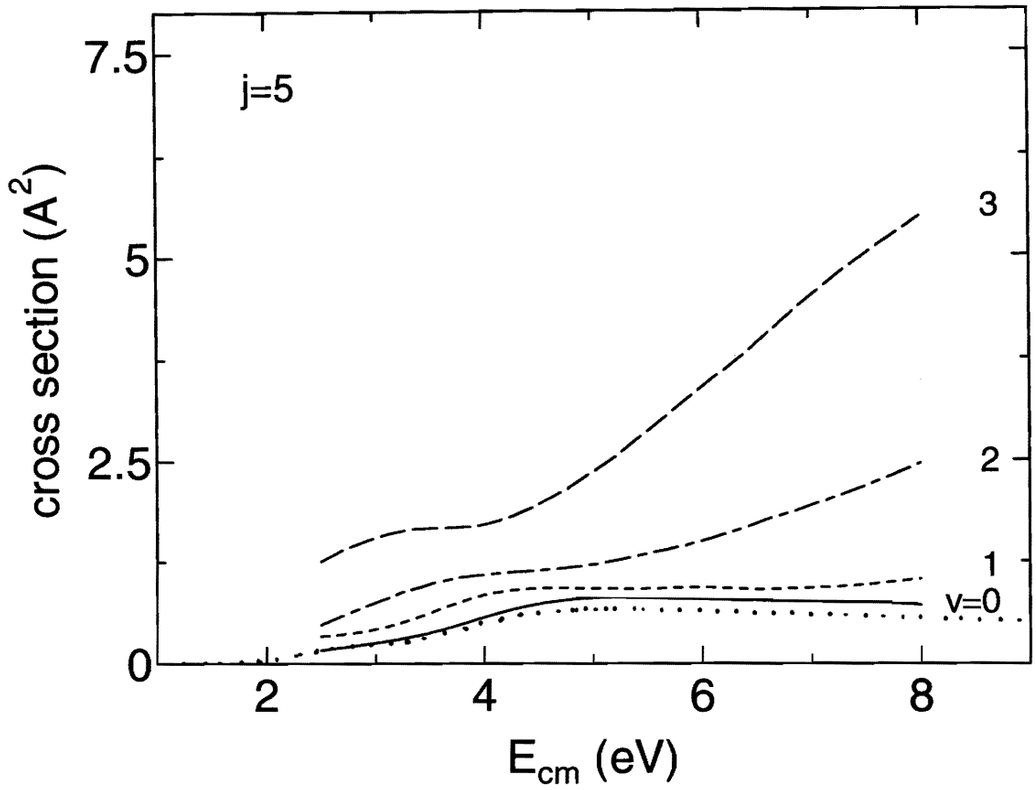

Fig.2 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=5) → $D_2^+ + H$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

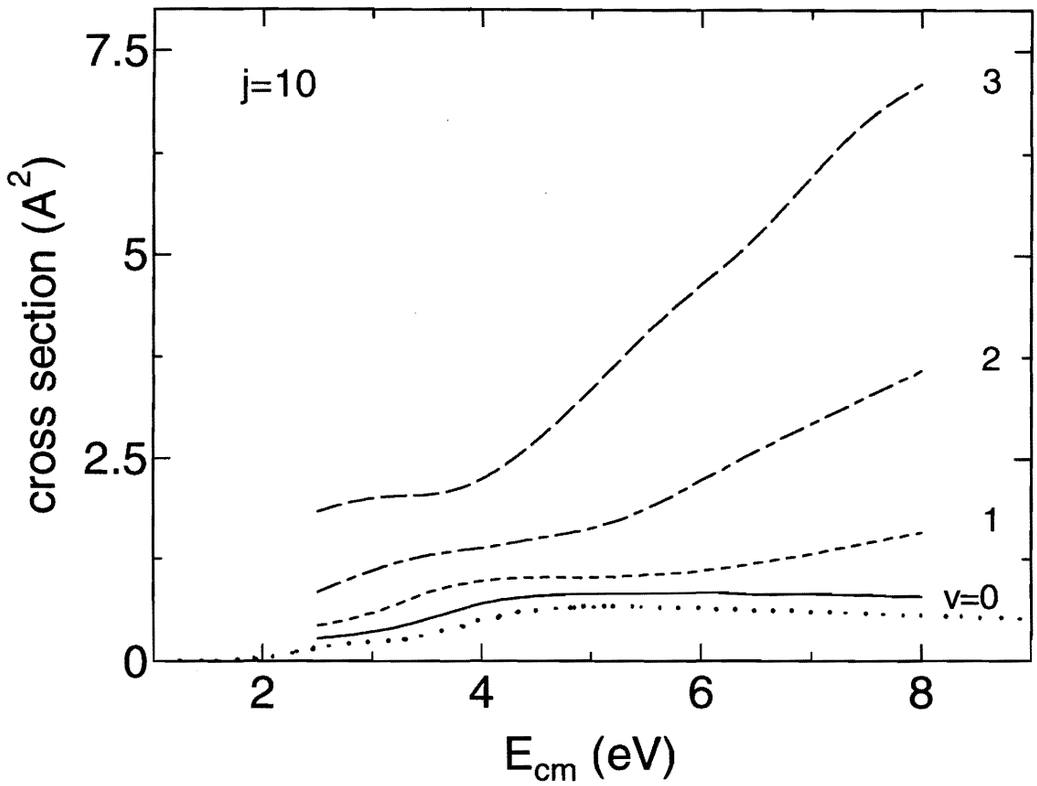

Fig.3 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=10) → $D_2^+ + H$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

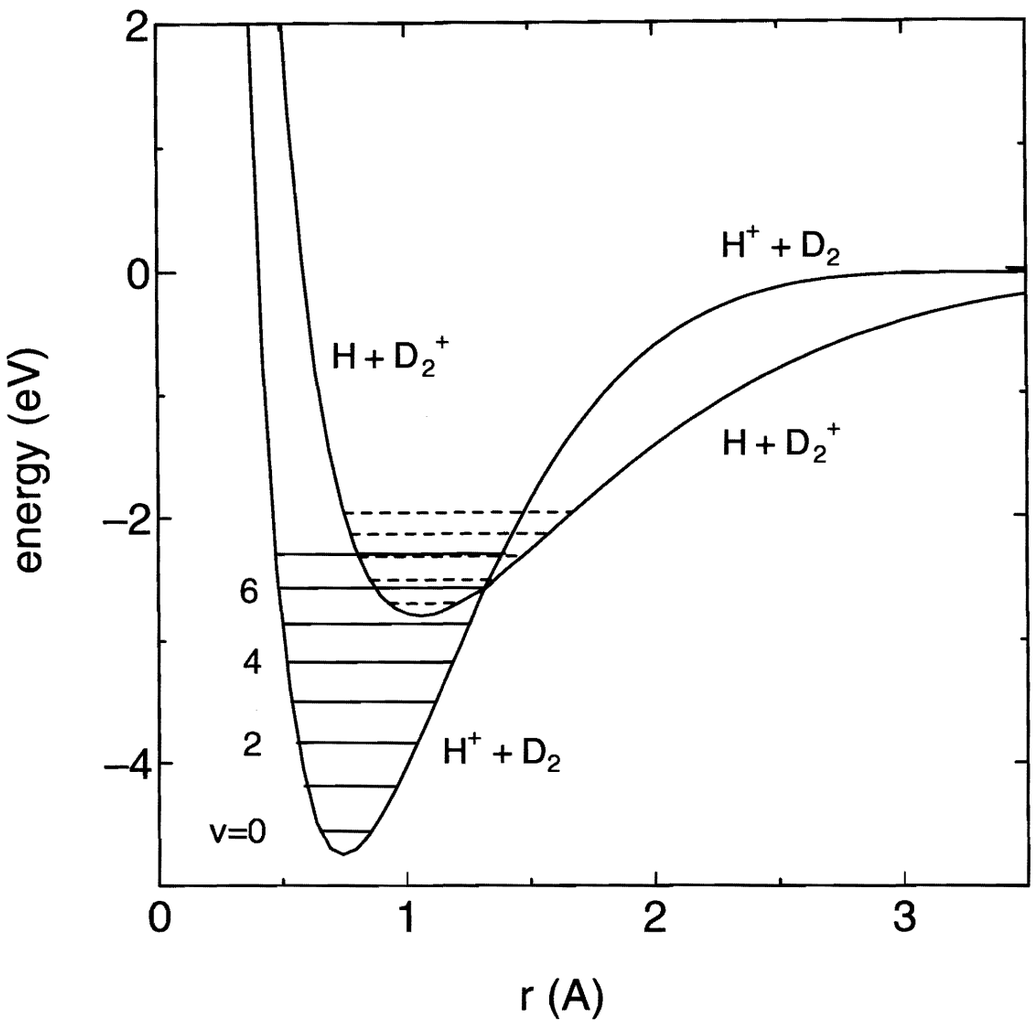

Fig.4 Section of potential energy surfaces for R=5.29 Å in the C_{2v} geometry. r is the distance between two deuterons. The vibrational energy levels of D_2 and D_2^+ are shown by solid and dotted lines, respectively.

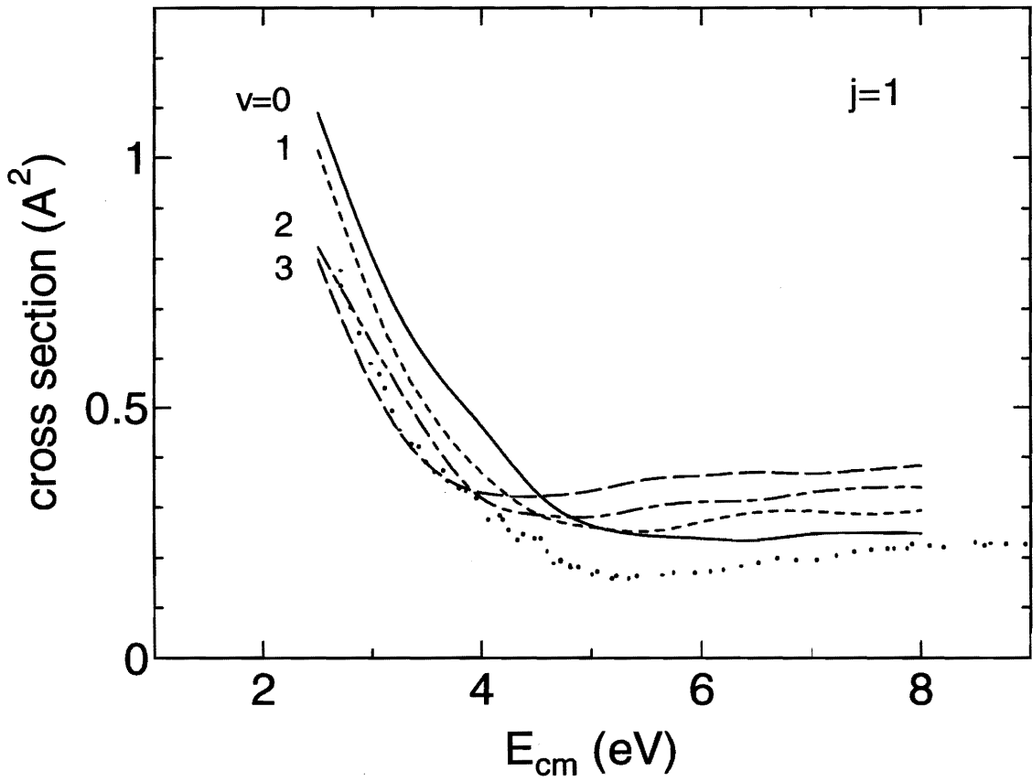

Fig.5 Absolute cross sections for the D^+ production from the reactions $H^+ + D_2$(v=0 to 3, j=1). The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

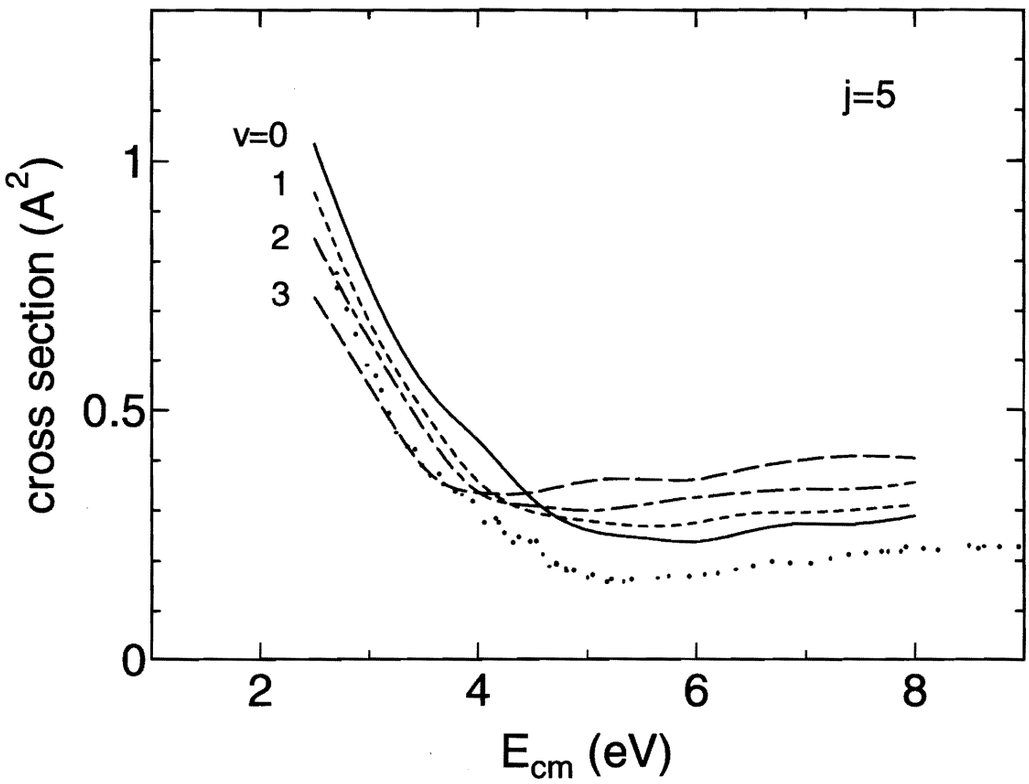

Fig.6 Absolute cross sections for the D^+ production from the reactions $H^+ + D_2$(v=0 to 3, j=5). The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

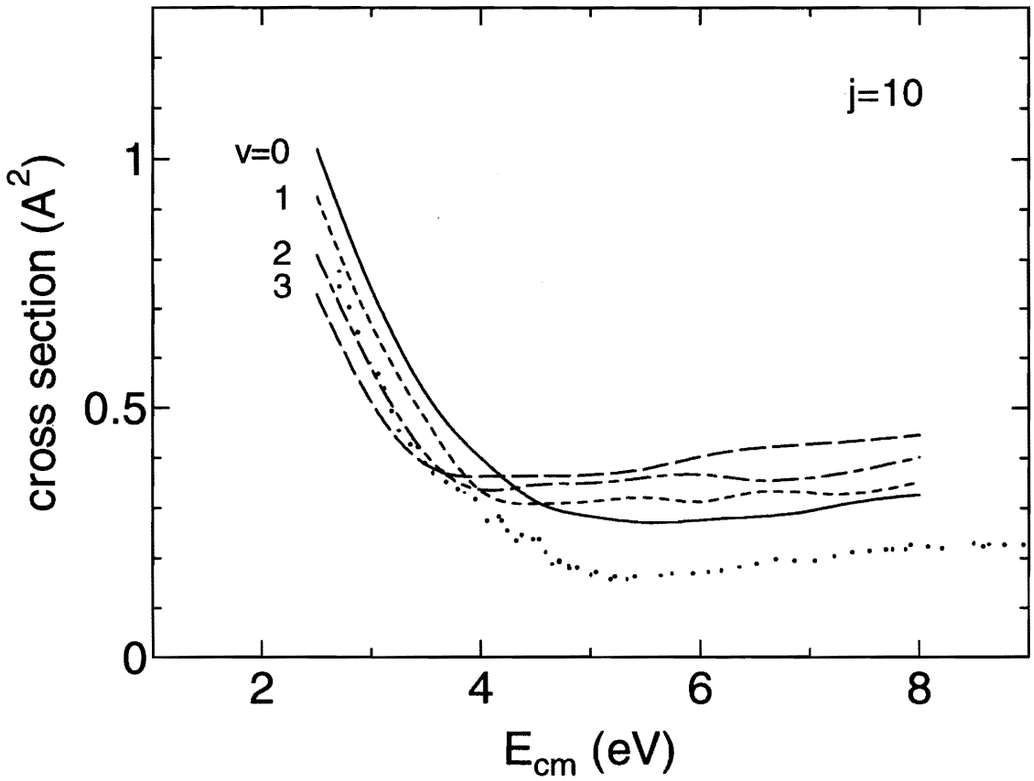

Fig.7 Absolute cross sections for the D^+ production from the reactions $H^+ + D_2$(v=0 to 3, j=10). The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

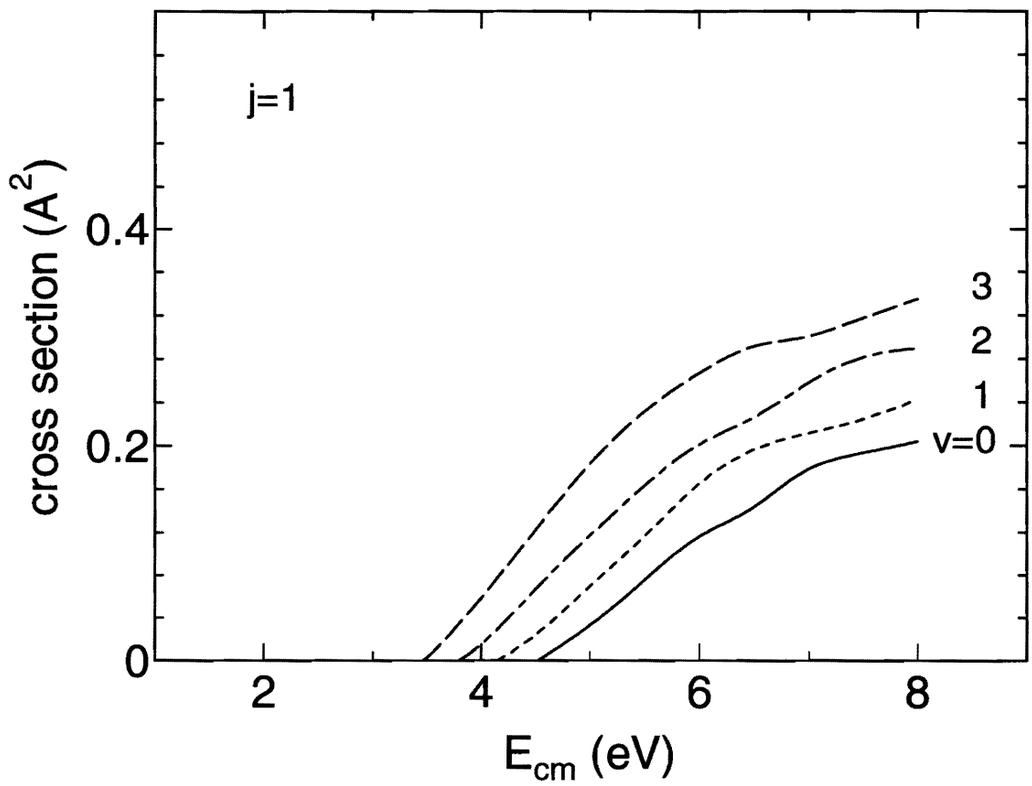

Fig.8 Contribution of the dissociation $H^+ + D_2(v, j=1) \rightarrow D^+ + H + D$ to the D^+ production.

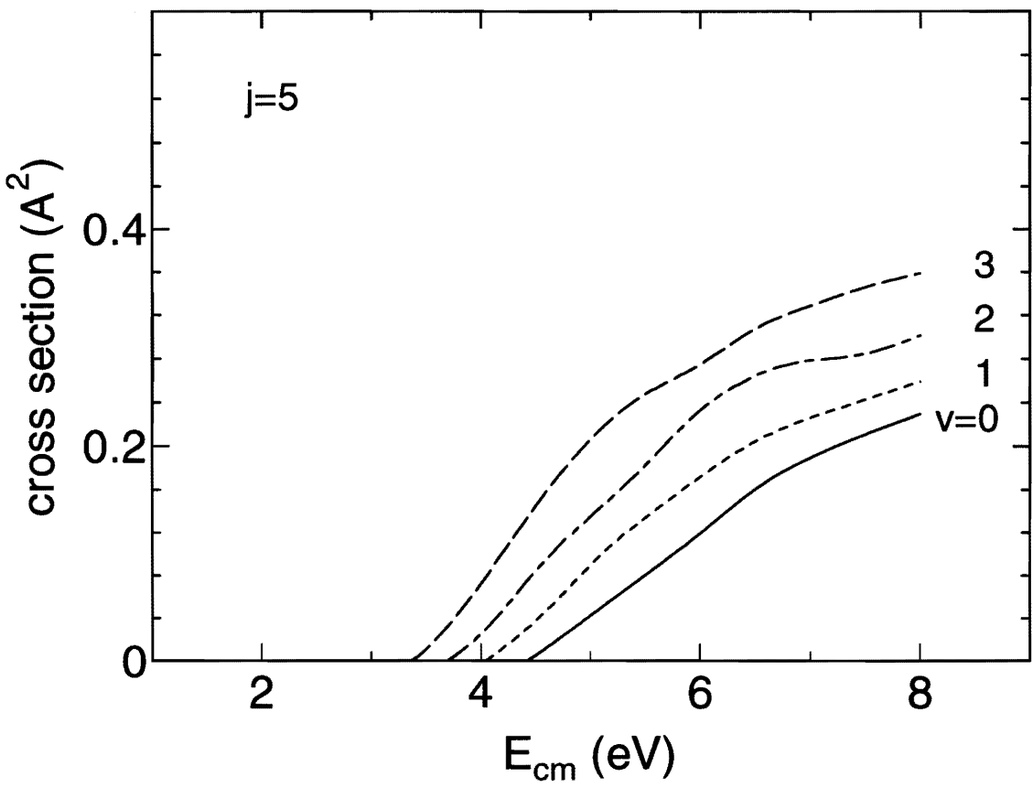

Fig.9 Contribution of the dissociation $H^+ + D_2(v, j=5) \rightarrow D^+ + H + D$ to the D^+ production.

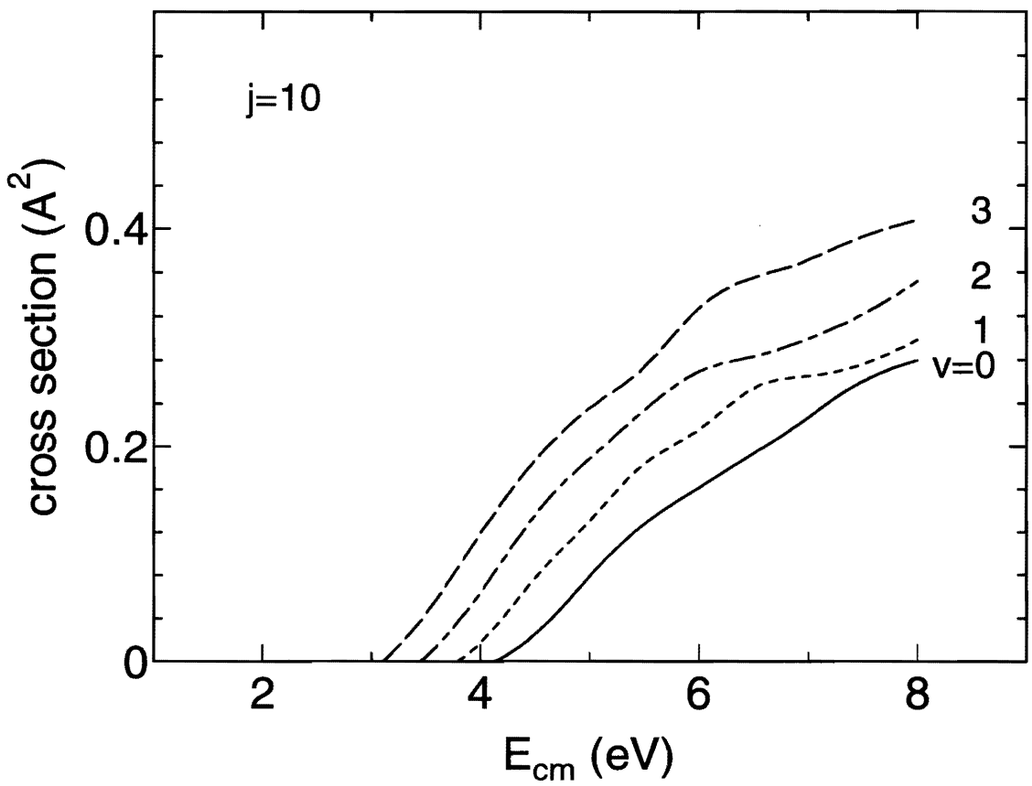

Fig.10 Contribution of the dissociation $H^+ + D_2(v, j=10) \rightarrow D^+ + H + D$ to the D^+ production.

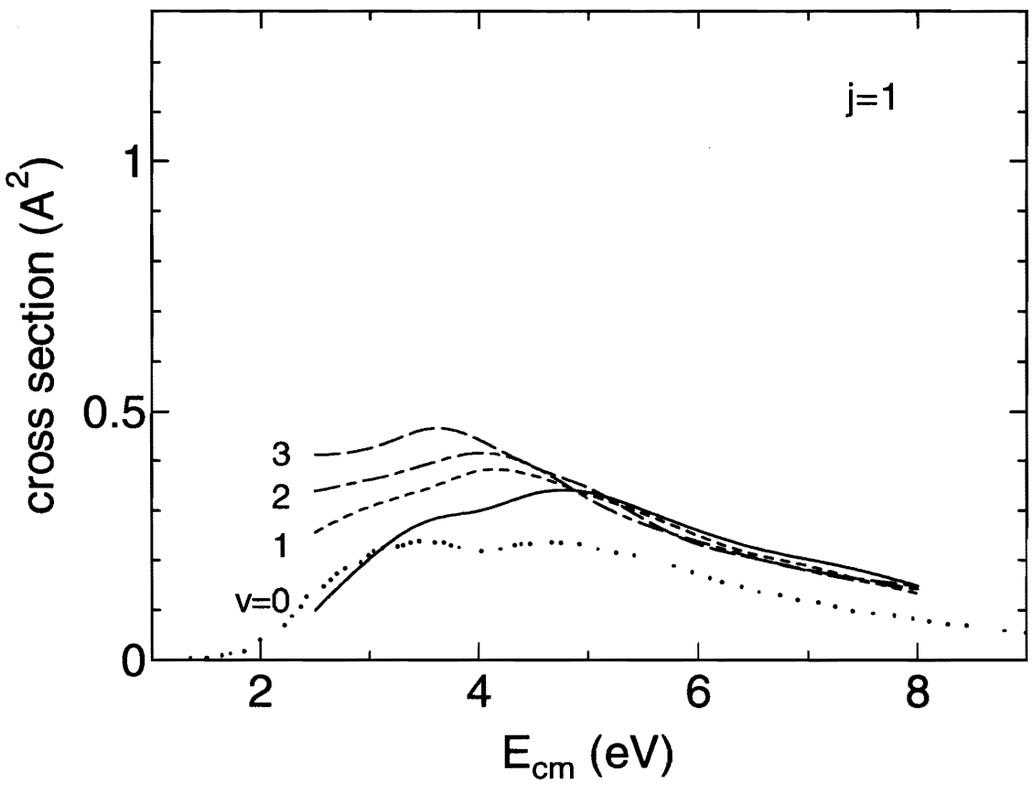

Fig.11 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=1) → $HD^+ + D$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

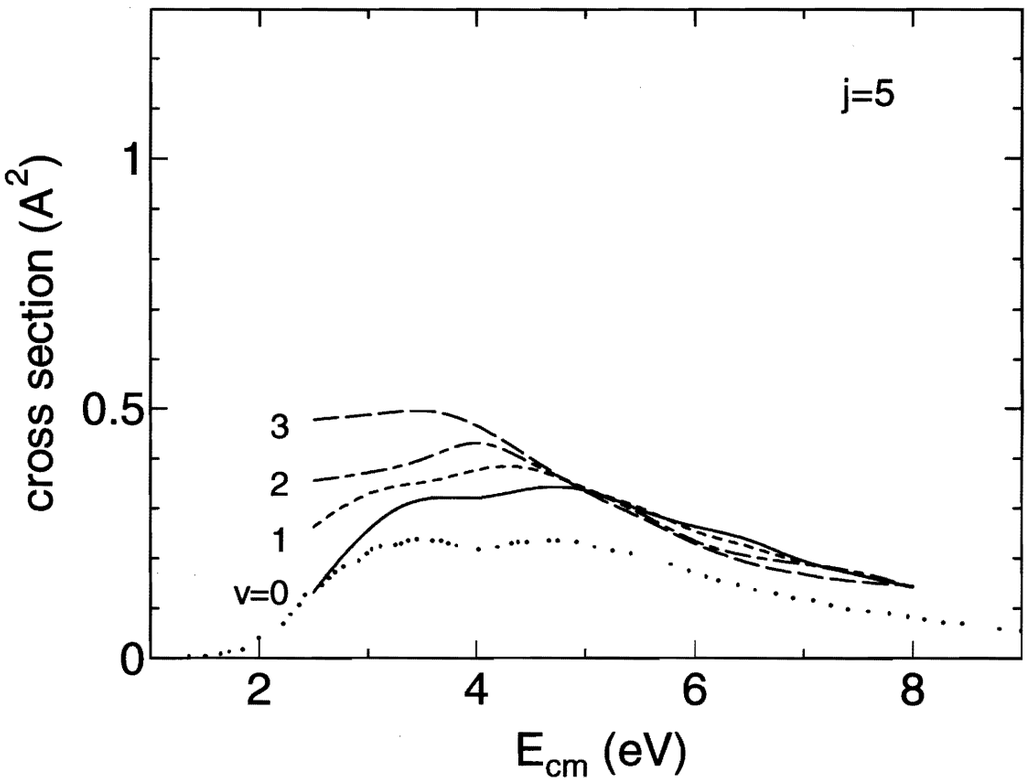

Fig.12 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=5) → $HD^+ + D$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

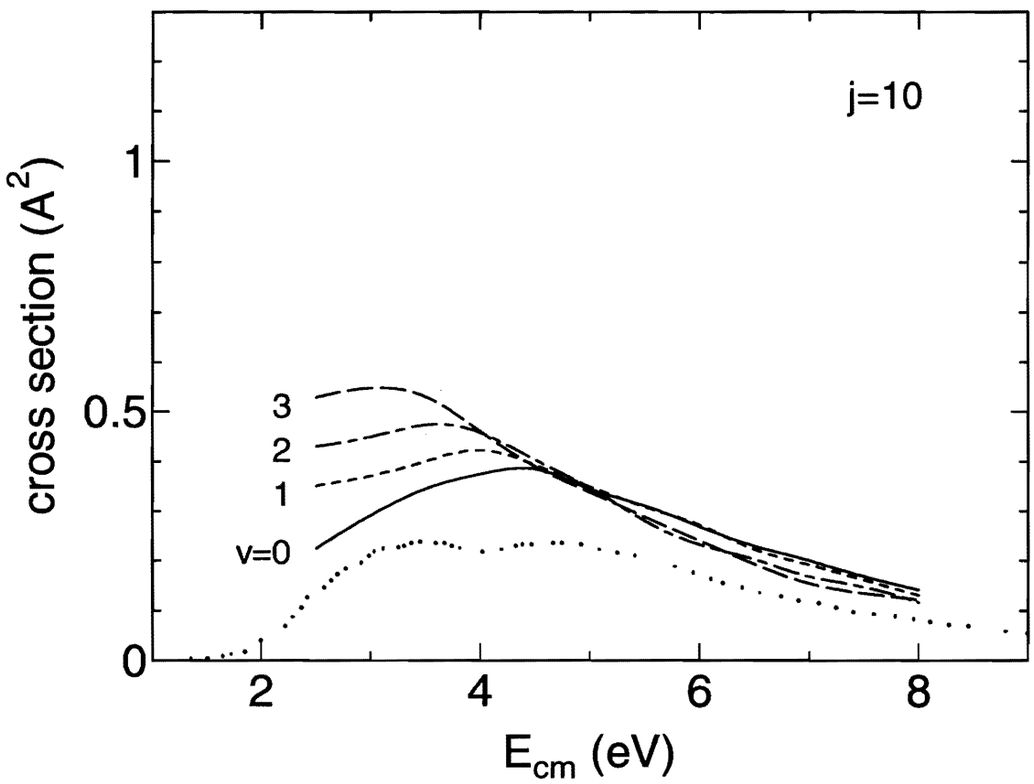

Fig.13 Absolute cross sections for the reactions $H^+ + D_2$(v=0 to 3, j=10) → $HD^+ + D$. The cross section is given as a function of center-of-mass collision energy E_{cm}. The experimental data for v=0 (Ref.2) are plotted by dots in the figure.

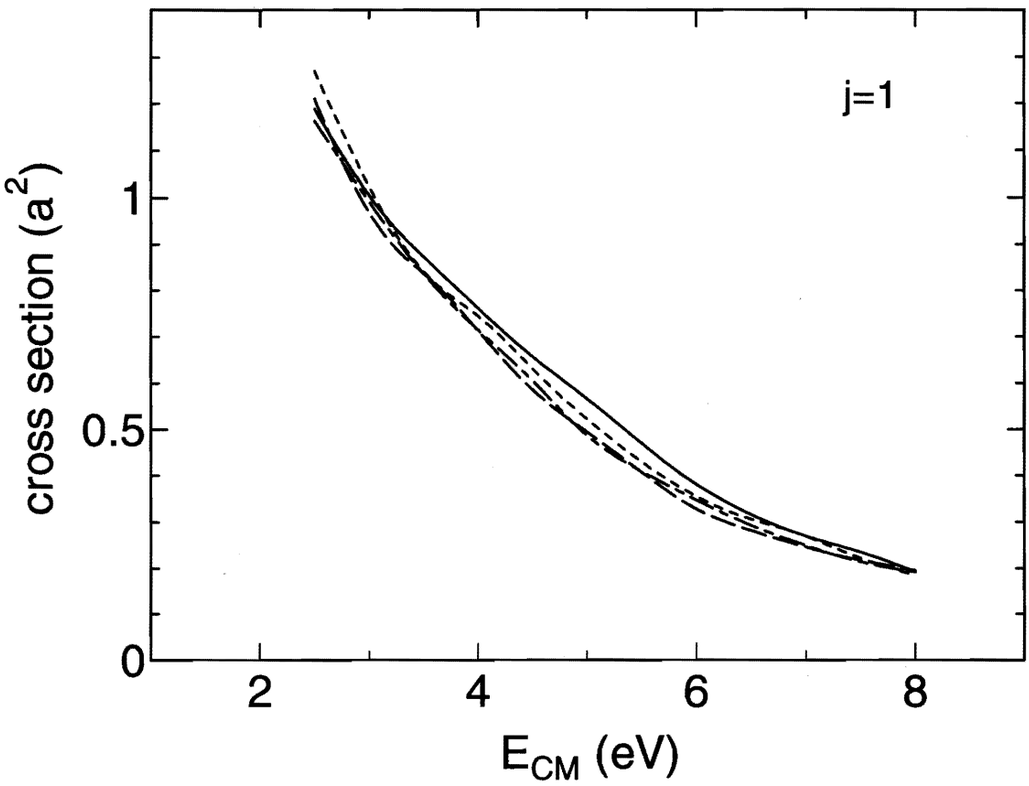

Fig.14 The sum of cross sections for the reactions $H^+ + D_2(v,j=1) \rightarrow D^+ + HD$ and $H^+ + D_2(v, j=1) \rightarrow HD^+ + D$.

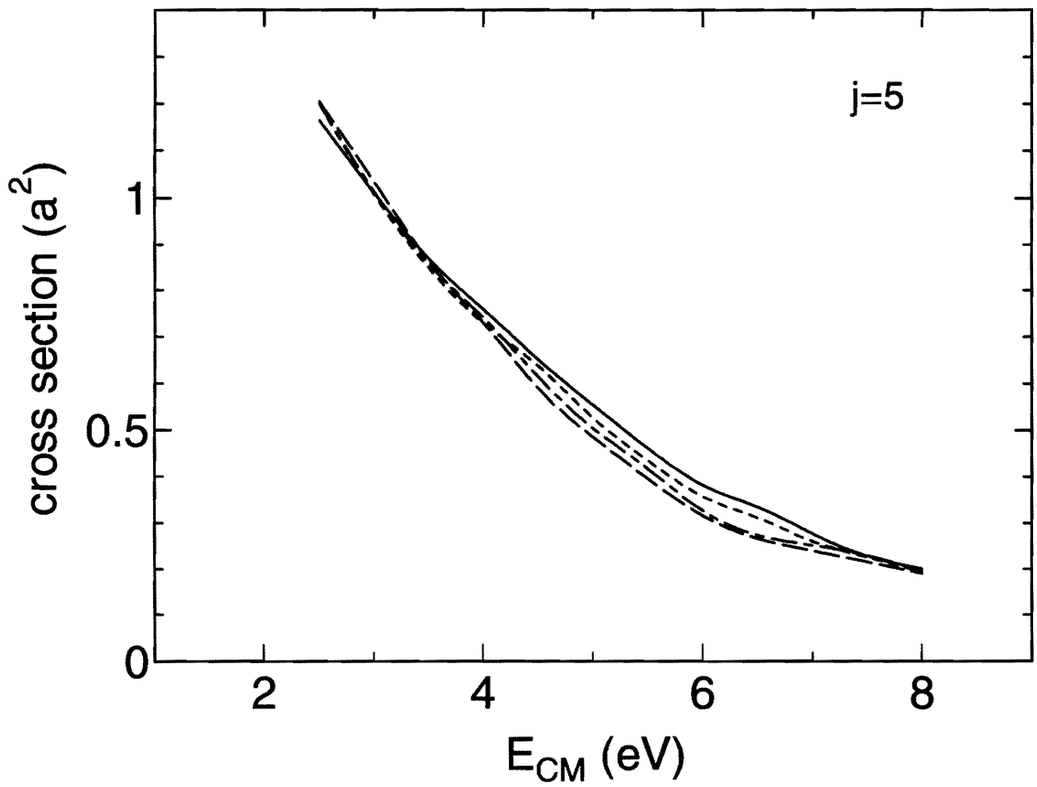

Fig.15 The sum of cross sections for the reactions $H^+ + D_2(v,j=5) \rightarrow D^+ + HD$ and $H^+ + D_2(v, j=5) \rightarrow HD^+ + D$.

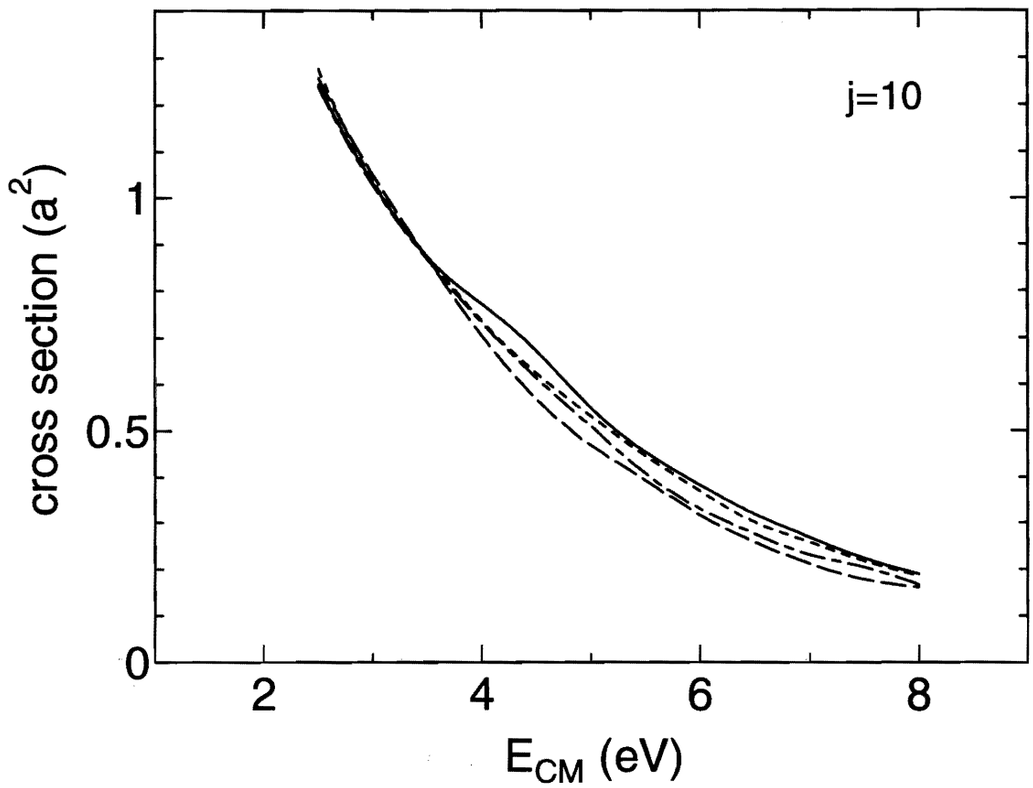

Fig.16 The sum of cross sections for the reactions $H^+ + D_2(v,j=10) \rightarrow D^+ + HD$ and $H^+ + D_2(v, j=10) \rightarrow HD^+ + D$.