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A Quasi-classical Trajectory Calculation for the Cesium Exchange Reaction of $^{133}\text{CsI} (\nu = 0, j = 0) + ^{135}\text{Cs} \rightarrow ^{133}\text{Cs} + \text{I}^{135}\text{Cs}$

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To investigate the reaction cross section of the cesium exchange reaction of $^{133}\text{CsI} (\nu = 0, j = 0) + ^{135}\text{Cs} \rightarrow ^{133}\text{Cs} + \text{I}^{135}\text{Cs}$, we performed quasi-classical trajectory calculations. The potential energy surface was constructed at the *ab initio* MP2/def2-QZVPPD level. The potential energy surface calculated implies that the title reaction is barrierless and that the Cs_2I intermediate, whose two Cs-I bonds are chemically equivalent, is easily formed. The reaction cross sections decrease monotonically with increasing collision energy. The rate constant $k (\nu = 0, j = 0)$ was estimated to be about $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at temperatures ranging from 500 to 1200 K and a slight negative temperature dependence was observed.

セシウム交換反応 $^{133}\text{CsI} (\nu = 0, j = 0) + ^{135}\text{Cs} \rightarrow ^{133}\text{Cs} + \text{I}^{135}\text{Cs}$ の反応断面積と速度定数を評価するため、準古典的トラジェクトリー計算を行った。トラジェクトリー計算は、MP2/def2-QZVPPD レベルの *ab initio* 電子状態理論計算より得たポテンシャルエネルギー曲面上で行った。得られたポテンシャルエネルギー曲面より、このセシウム交換反応では活性化障壁無く容易に Cs_2I 中間状態が形成されることが示唆された。この Cs_2I 中間状態の2つの Cs-I 結合長は同じであり、化学的に等価である。セシウム交換反応の反応断面積は、衝突エネルギーが高くなるにつれて小さくなる傾向を示した。反応速度定数は温度 500 K から 1200 K の間で約 $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ と計算され、わずかな負の温度依存性も確認された。

Key Words

Cs exchange reaction, Quasi-classical trajectory calculations, Chemical kinetics

1. Introduction

The cesium isotope of ^{135}Cs has an extremely long half-life ($\tau_{1/2} = 2.3 \times 10^6$ years) and is highly water soluble. Because of these properties, ^{135}Cs is one of the most important nuclear species for consideration for geological disposal¹⁾. It is known that ^{135}Cs can be converted to stable ^{136}Ba by neutron capture. Ultimately, ^{135}Cs becomes radioactively harmless. However, ^{133}Cs , which coexists in spent nuclear fuel, makes the transmutation ineffective. To avoid this problem, the isotopic separation of ^{135}Cs from ^{133}Cs is necessary²⁾.

For the efficient isotope-selective collection of Cs, we have suggested a laser-based isotope separation method, which uses the isotope-selective rotational excitation of

diatomic molecules by an optical frequency comb^{3)~5)}. The scheme consists of two steps. The first step is the induction of the isotope-selective photodissociation of cesium iodide (CsI) molecules. The second step is the induction of a preferential collecting reaction of the atomic Cs from the surrounding CsI molecules⁶⁾. In the procedure, however, the exchange reaction between CsI molecules and the dissociated Cs atoms,

is expected to prevent isotope selection. If the exchange reaction occurs between the first step and the second step, it would decrease the isotope selectivity significantly. The quantitative evaluation of the rate of reaction (1) is important for designing the isotope-selective collection of Cs atoms.

The quasi-classical trajectory (QCT) calculation is a classical means to compute the reaction rates^{7)~10)} and, to date, has proven a powerful tool. Moreover, concerning the title reaction of heavy atoms, quantum effects such as

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the tunneling effects should not affect the reaction. In this paper, using QCT calculations, we discuss the Cs exchange reaction in the temperature region of 500 to 1200 K such that,

where ν and j are the initial vibrational and rotational quantum number of ^{133}CsI , respectively. For ^{133}CsI , we have dealt with only the ground rovibrational state ($\nu = 0, j = 0$) for simplicity.

2. Potential energy surface calculation

We calculated a full-dimensional potential energy surface (PES) for the $\text{CsI} + \text{Cs} \rightarrow \text{Cs} + \text{ICs}$ reaction. The PES is based on *ab initio* energies calculated with Møller-Plesset 2nd-order perturbation theory (MP2)¹¹ using the def2-QZVPPD basis set¹². The core electrons of both Cs and I were described by pseudopotentials, in which 46 and 28 core electrons, respectively, were replaced by effective core potentials (ECPs). Nine electrons in the 5s, 5p, and 6s orbitals of Cs and 25 electrons in the 4s, 4p, 4d, 5s, and 5p orbitals of I were included in the valence space and treated explicitly using the basis set mentioned. All electrons that were explicitly included in the valence orbitals were set to be correlated. All *ab initio* calculations were performed using MOLPRO (Version 2012.1)¹³.

The PES for the trajectory was obtained using a cubic spline interpolation along (d_1, d_2, θ) ¹⁴, where d_1 and d_2 are the bond lengths between Cs-I and θ is the Cs-I-Cs bond angle. The grid data for the interpolation were obtained from the *ab initio* electronic structure calculations. The energies were calculated every 5° from $\theta = 0^\circ$ to 25° , every 10° from $\theta = 30^\circ$ to 100° , and every 20° from $\theta = 100^\circ$ to 180° . The variables d_1 and d_2 were varied from 2.4 Å to 40 Å, and about 36,000 points of grid data were calculated. However, although the region in which the length between two Cs atoms is smaller than 2.3 Å is required for spline interpolation, *ab initio* calculations were not carried out because calculations in this region are challenging. Instead, the grid data for this region was inserted carefully to obtain a smooth PES in the region where the potential energy is less than +300 kJ mol⁻¹ from the $\text{CsI} + \text{Cs}$ asymptotic limit. Actually, the potential energies of the inserted region are over +400 kJ mol⁻¹ from the $\text{CsI} + \text{Cs}$ asymptotic limit and, thus, have no significant influence on this study because the collision energies we evaluated were less than 100 kJ mol⁻¹. Subsequently, to reduce computational cost, the number of grid data for the trajectory calculation was reduced. Finally, the number of the grids for (d_1, d_2, θ) were (64, 64, 22) for θ from -10° to 200° and d_1 and d_2 from 2.4 to 24.0 Å.

Fig. 1 shows the PES at $d_2 = 3.326$ Å, which is

Fig. 1 PES of $\text{CsI} + \text{Cs}$ at $d_2 = 3.326$ Å, which is the equilibrium length of the CsI molecule at the MP2/def2-QZVPPD level of theory. The contour lines are plotted every 4 kJ mol⁻¹. The nuclear position of Cs and I in the CsI molecule are also shown. The numbers on the PES are the potential energies in kJ mol⁻¹

the equilibrium length of CsI estimated at the same level of theory, as a function of x and z , where the z -axis is the direction of the molecular axis and the x -axis is perpendicular to the z -axis. The origin is set to the center of mass of CsI . Around the CsI molecules, no entrance barrier was observed, which indicates that there is no activation energy barrier on the reaction pathway to the Cs_2I intermediate. From this fact, we can predict that the Cs atom easily reacts to form the Cs_2I intermediate. Once the intermediate is generated, the Cs atom could be ejected (50% probability) because the excess energy should re-distribute to the vibrational degrees of freedom. Moreover, this exchange reaction is expected to be a collision-controlled reaction.

3. Quasi-classical trajectory calculation

The reaction cross sections for the collision energies (E_{col}) between 0.5 and 100 kJ mol⁻¹ and rate constants in the temperature range of 500 to 1200 K were calculated. The QCT calculations were performed using standard procedures and expressions¹⁵, employing the ANT 2015¹⁶ QCT code, but some parts of the code were modified.

We ran 10,000 trajectories. The maximum impact parameter, B , was the upper limit of the impact parameter that was generated for each trajectory and was set to values ranging from 16.0 Å to 9.0 Å. Initially, d_2 was set to be around the equilibrium length of the ^{133}CsI molecule and was varied according to the vibrational state of ^{133}CsI . The rovibrational quantum numbers of the ^{133}CsI molecule were set to ($\nu = 0, j = 0$). The ^{135}Cs atom was initially separated from the origin (center of mass of ^{133}CsI) by 20 Å. The trajectories were stopped if d_1 or d_2 became larger than 20 Å

or the simulation times became longer than 200,000 fs for $E_{\text{col}} = 0.5 \text{ kJ mol}^{-1}$, 100,000 fs for $E_{\text{col}} = 1.0 \text{ kJ mol}^{-1}$, and 50,000 fs for the other E_{col} cases. The number of reactive trajectories were defined as the summation of (i) the number of trajectories where d_2 reached 20 Å and (ii) half the number of trajectories that reached the upper limit of the simulation time. For the given set of initial parameters, the reactive cross section, using Monte Carlo sampling of the impact parameter, is given by

$$\sigma(E_{\text{col}}) = \pi B^2 \frac{N_{\text{react}}}{N_{\text{total}}}, \quad (3)$$

where N_{react} is the number of reactive trajectories, and N_{total} is the total number of trajectories¹⁵⁾. For a convergence check with respect to the number of trajectories, the cross sections of a few E_{col} values were calculated by running 20,000 trajectories to reduce statistical errors. The differences in the cross sections of 20,000 and 10,000 trajectories were within 1% for almost all E_{col} .

Once the cross sections as a function of E_{col} were obtained, we computed the rate constants. By assuming a Maxwell-Boltzmann distribution over E_{col} , we obtained the rate constant k at temperature T from eq. (4).

$$k(T, \nu = 0, j = 0) = \sqrt{\frac{8}{\pi\mu}} (k_{\text{B}}T)^{-\frac{3}{2}} \int_0^{\infty} E_{\text{col}} \sigma(E_{\text{col}}) \exp\left(-\frac{E_{\text{col}}}{k_{\text{B}}T}\right) dE_{\text{col}} \quad (4)$$

Here, μ is the ^{133}CsI - ^{135}Cs reduced mass and k_{B} is the Boltzmann constant. The integral in eq. (4) was calculated by cubic spline interpolation, while $\sigma(E_{\text{col}} < 0.5 \text{ kJ mol}^{-1})$ was linearly extrapolated.

$\sigma(E_{\text{col}})$ as a function of E_{col} is shown in Fig. 2(a). $\sigma(E_{\text{col}})$ decreases with increasing E_{col} . The behavior is consistent with a barrierless reaction. This is because a higher initial translational energy makes it more difficult for the Cs atom to be captured in the potential well. $\sigma(E_{\text{col}})$ is the $E_{\text{col}}^{-0.62}$

dependence at energies ranging from 5.0 to 100.0 kJ mol^{-1} . In the low E_{col} region, $\sigma(E_{\text{col}})$ is the $E_{\text{col}}^{-0.41}$ dependence. The cross section is much larger than those of the known fast reactions of light and electrically neutral species, i.e., $\text{C}_2\text{H}_2 + \text{C}(^3\text{P})$, etc.¹⁷⁾ This large cross section might originate from the larger electron correlation of heavier species. If so, the strong induced-dipole and the long-range attractive forces may result in the large cross section.

The thermal rate constant in the temperature range of 500-1200 K is shown in Fig. 2(b). A slightly negative temperature dependence was observed. The rate constant is over $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the whole temperature range; this is as high as the ordinal rate of the collision-control reaction.

The calculations show that reaction (2) is very fast. There are two means to suppress the Cs exchange reaction. One is to suppress the density of CsI molecules in the reaction system. This would decrease the collision probability, suppressing the reaction and reducing the efficiency of the collection. The other is to generate Cs atoms with high translational energies at the photodissociation step because, as shown in Fig. 2(a), σ decreases as E_{col} increases.

4. Summary

Quasi-classical trajectory calculations for the Cs exchange reaction of $\text{CsI}(\nu = 0, j = 0) + \text{Cs} \rightarrow \text{Cs} + \text{ICs}$ were performed to investigate the reaction cross section and thermal rate constant in the temperature range of 500-1200 K as a simple case. The reaction cross section decreases with increasing collision energy. This tendency is one of the characteristics of a barrierless reaction. The rate constant is about $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range investigated. This indicates that ^{135}Cs must be collected

Fig. 2 (a) Reaction cross section of reaction (2) as a function of collision energy plotted on the log-log scale. The filled circles show the computational results. The dotted line is the cross section for the integration of eq. (4). The function shows the $E_{\text{col}}^{-0.62}$ dependence between 5.0 and 100.0 kJ mol^{-1} (blue line) and the $E_{\text{col}}^{-0.41}$ dependence between 0.5 and 5.0 kJ mol^{-1} (red line). (b) The rate constant of reaction (2) as a function of temperature. The rate constant shows the negative temperature dependence and is greater than $3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

as soon as possible after the isotope-selective dissociation. Otherwise, ^{135}Cs and ^{133}CsI would collide with each other, exchanging Cs isotopes and resulting in a decrease in the isotope selectivity. To suppress the exchange reaction before the preferential collection, a reduction in the collision frequency of $\text{CsI} + \text{Cs}$ is necessary.

However, the case of CsI ($v = 0, j = 0$) is a limited case in the temperature region of interest. At $T = 1000\text{ K}$, for example, the distribution of the CsI rotation has its maximum at $j \sim 120$. It has often been reported that a higher initial rotational quantum number makes the formation of an intermediate complex more difficult, thus reducing the reaction cross section¹⁸⁾. We plan to calculate the reaction cross sections for several initial v and j and rotation-vibration averaged rate constants.

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References

- 1) Chaltikyan, V.; Papoyan, A.; Oshita, H.; Shiotani, H.; Ono, K.; Ishikawa, M.; Ozawa, M., *J. Radioanal. Nucl. Chem.*, **280**, 343-352 (2009)
- 2) Arie, K.; Kawashima, M.; Araki, Y.; Sato, M.; Mori, K.; Nakayama, Y.; Ishiguma, K.; Fuji-ie, Y., Proceedings of the 7th International Conference on Advanced Nuclear Fuel Cycles and Systems (GLOBAL 2007), Sept. 9-13, 2007, Boise (ID): American Nuclear Society Compiler, 2007, 310-317
- 3) Yokoyama, K.; Matsuoka, L.; Kasajima, T.; Tsubouchi, M.; Yokoyama, A., *In Advances in Intense Laser Science & Photonics*, J. Lee et al. (ed.), Publishing House for Science and Technology, Hanoi, p. 113-119, (2010)
- 4) Ichihara, A.; Matsuoka, L.; Kurosaki, Y.; Yokoyama, K., *Opt. Rev.*, **22**, 153-156 (2015)
- 5) Ichihara, A.; Matsuoka, L.; Segawa, E.; Yokoyama, K., *Phys. Rev. A*, **91**, 043404 (2015)
- 6) Kobayashi, T.; Yokoyama, K., *J. Nucl. Sci. Tech.*, **53**, 1489-1493 (2016)
- 7) Mayne, H. R., *Chem. Phys. Lett.*, **66**, 487-492 (1979)
- 8) Varandas, A. J. C.; Brandão, J.; Pastrana, M. R., *J. Chem. Phys.*, **96**, 5137-5150 (1992)
- 9) de Oliveira-Filho, A. G. S.; Ornellas, F. R.; Bowman, J. M., *J. Phys. Chem. Lett.*, **5**, 706-712 (2014)
- 10) Martínez, R.; Enríquez, P. A.; Puyuelo, M. P.; González, M., *Chem. Phys.*, **461**, 98-105 (2015)
- 11) Møller, C.; Plesset, M. S., *Phys. Rev.*, **46**, 618-622 (1934)
- 12) Rappoport, D.; Furche, F., *J. Chem. Phys.*, **133**, 134105 (2010)
- 13) MOLPRO, version 2012.1, A Package of *Ab Initio* Programs, Werner, H.-J. *et al.*, <http://www.molpro.net>
- 14) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T., Numerical Recipes in C, Japanese Edition from Nihon Kogyo Sha, (1993)
- 15) Truhlar, D. G.; Wang, H.; Hase, W. L., *In Atom-Molecule Collision Theory: A Guide for the Experimentalist*, Bernstein, R. B. (Ed.), Plenum Press: New York, (1979)
- 16) Zheng, J. *et al.*, ANT, version 2015, University of Minnesota, Minneapolis, 2015, <http://comp.chem.umn.edu/ant>
- 17) Clary, D. C.; Buonomo, E.; Sims, I. R.; Smith, I. W. M.; Geppert, W. D.; Naulin, C.; Costes, M.; Cartechini, L.; Casavecchia, P., *J. Phys. Chem. A*, **106**, 5541-5552 (2002)
- 18) Clary, D. C., *J. Chem. Soc. Faraday Trans. 2*, **83**, 139-148 (1987)