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Conditional Monte Carlo Trajectory Calculation of Elementary Gas Reaction Rates

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A new Monte Carlo trajectory method is proposed to estimate the rate constants of elementary molecular reactions. In this study, we have introduced the conditional Monte Carlo technique and obtained the following advantages. First, the procedure of calculation has been simplified. That is, the trajectory data have been accumulated as only one data set, from which the rate constants at any temperature have been reduced easily. Secondly, the necessary number of trajectories has been decreased by employing appropriate conditional distribution functions. Lastly, the error estimation has become possible on a reasonable base. This method has been applied to the (H_2, H_2) direct exchange reaction as an example and the result is reported briefly.

Karplus, Porter, and Sharma have demonstrated the usefulness of the Monte Carlo trajectory method through the calculation of the rate constants of the (H, H_2) exchange reaction.[1] Since then, it has been frequently applied to the dynamics of various elementary molecular collisions.[2,3] In this procedure, the reaction cross sections are first estimated by the Monte Carlo trajectory calculation. Then, the rate constants are computed from the cross sections by the numerical integration method.

The cross sections are specified by the initial vibration-rotational quantum state and by the initial translational energy. Therefore, if we have to take account of many quantum states to estimate the rate constant, the necessary number of trajectory calculations becomes enormous. Some chemists have tried to get away from this trouble, but the results have been not so effective.[4,5]

The rate constant was originally defined as proportional to the expected value of the product of the relative velocity and the probability that a trajectory goes into the reaction channel. This aspect suggests that the calculation of cross sections can be bypassed and that the reaction rate may be computed directly from trajectory data. In this paper, the above idea is developed by introducing the conditional Monte Carlo method,[6] and the new technique is applied to the (H_2, H_2) direct exchange reaction[7] as an example.

Reaction Rate Calculation by the Conditional Monte Carlo Method

In this section, we discuss the development of the Monte Carlo trajectory method, using as an example the simplest exchange reaction **a**: A+BC→**b**: AB+C. Here, the collision system is identified by the vibration-rotational quantum state of the BC molecule, (v, j), and by the relative translational energy E_t. Other types of reactions can be treated in a similar way.

The overall thermal rate constant at temperature T is defined by

$$k_{a,b}(T) = N_A\left(\frac{8}{\pi\mu k_B^3T^3}\right)^{1/2} Q_{vib}^{-1}Q_{rot}^{-1}\sum_{v,j} g_j(2j+1) \times \exp\left(-\frac{E_v+E_j}{k_BT}\right)\int_0^\infty S_{a,b}(E_t, j, v) \times \exp\left(-\frac{E_t}{k_BT}\right)E_t\mathrm{d}E_t, \qquad (1)$$

where N_A is Avogadro's number, k_B is the Boltzmann constant, μ is the reduced mass of the A+BC system, Q_{vib} and Q_{rot} are the partition functions for the vibrational and the rotational motion, E_v and E_j are the vibrational and rotational energies of the BC molecule at the quantum states v and j, respectively, g_j is the statistical weight of the rotational state j, and $S_{a,b}(E_t, j, v)$ is the reaction cross section at the (E_t, j, v) state.[4] According to the quasiclassical trajectory theory, the cross section $S_{a,b}(E_t, j, v)$ is equal to the averaged probability that a trajectory with the (E_t, j, v) initial state goes into the reaction channel and is given by

$$S_{a,b}(E_t, j, v) = \frac{\pi\hbar^2}{\mu^2V_t^2}\sum_{l=0}^{\infty}(2l+1)\frac{1}{16\pi^3}\int_0^\pi \mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\int_0^{2\pi}\mathrm{d}\psi \times\int_0^{2\pi}\mathrm{d}\eta \sin\theta P_{a,b}(\theta, \phi, \psi, \eta, l, E_t, j, v), \qquad (2)$$

where l is the orbital quantum number of the initial collision system, V_t is the initial collision velocity, (θ, ϕ) and ψ are the orientation angles for the BC axis and the instantaneous rotational angular momentum, respectively, η is the vibrational phase angle,[8] and $P_{a,b}(\cdots\cdots)$ is the probability that a trajectory goes into the reaction channel, **a**→**b**.

Substituting the above expression for $S_{a,b}(E_t, j, v)$ in Eq. 1 yields a relation between the rate constant and $P_{a,b}$ of each trajectory. If we wish to estimate directly a rate constant by using the Monte Carlo trajectory method,[9] the dynamical equations of trajectories are numerically solved according to the initial conditions generated from the natural distribution functions G's. Then the expression of $k_{a,b}(T)$ takes the following Monte Carlo integration form:[10]

$$k_{a,b}(T) = \pi N_A b_m^2\frac{1}{N}\sum_{i=1}^{N} V_t(i)\cdot P_{a,b}(i), \qquad (3)$$

where b_m is the characteristic impact parameter that is large enough to include all reactive trajectories, i points out the i-th sample in an N-trajectories set, and the value of $P_{a,b}(i)$ becomes 1 for a case that i-th trajectory passes through the channel **a**→**b** and is 0 for the other cases. To estimate the rate constant

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at a temperature, we need only perform the Monte Carlo integration of Eq. 3. However, if the most of $V_t(i)P_{a,b}(i)$'s are expected to be zero and only a few samples with non-zero value contribute to $k_{a,b}(T)$, this method also requires numerous sample trajectories.

The conditional Monte Carlo method has been proposed to estimate the expected value of a given function of a random variable by a comparatively small number of samplings.[6,11] The values of random variables are generated not according to the natural distribution functions but to the conditional distribution functions. The initial state (l, E_t, j, v) of a trajectroy is determined by the conditional Monte Carlo choice, while all initial phases (θ, ϕ, ψ and η) of the BC molecule are determined by the analog Monte Carlo choice.[11,12] In the introduction of the conditional Monte Carlo method, we first have to set up adequate forms of the conditional distribution functions F's. Next, the calculations of trajectories with the above initial conditions are performed numerically and the necessary results are stored in one data set. This data set is independent of temperature. Then the rate constant at any temperature can be estimated by the following equation, which has been transformed from Eq. 3 according to the conditional Monte Carlo integration: (See Appendix I.)

$$k_{a,b}(T) = \pi N_A b_m^2 \frac{1}{N} \sum_{i=1}^{N} V_t(i) P_{a,b}(i) J_i(T), \tag{4}$$

where $J_i(T)$ is the Jacobian determinant of the G's with respect to the F's. If there are strong correlations among the random variables, we have to evaluate fully the terms of $J_i(T)$. However, in cases of no correlation, as is usually assumed, $J_i(T)$ is simply estimated by

$$J_i(T) = \frac{G^{\rm orb}_{l(i)} - G^{\rm orb}_{l(i)-1}}{F^{\rm orb}_{l(i)} - F^{\rm orb}_{l(i)-1}} \cdot \frac{G^{\rm vib}_{v(i)}(T) - G^{\rm vib}_{v(i)-1}(T)}{F^{\rm vib}_{v(i)} - F^{\rm vib}_{v(i)-1}} \cdot \frac{G^{\rm rot}_{j(i)}(T) - G^{\rm rot}_{j(i)-1}(T)}{F^{\rm rot}_{j(i)} - F^{\rm rot}_{j(i)-1}} \cdot \frac{\partial G(E_t(i), T)/\partial E_t(i)}{\partial F(E_t(i))/\partial E_t(i)}, \tag{5}$$

where ($G^{\rm orb}_l$, $G(E_t, T)$, $G^{\rm rot}_j(T)$, $G^{\rm vib}_v(T)$) and ($F^{\rm orb}_l$, $F(E_t)$, $F^{\rm rot}_j$, $F^{\rm vib}_v$) are the natural and conditional distribution functions for (l, E_t, j, v), respectively. In this procedure, it is expected that the necessary number of trajectories is greatly decreased, since the rate constant estimation at any temperature requires no additional trajectory data, and since the forms of the conditional distribution functions may be taken so as to decrease the number of samples within the limitation of the required accuracy.

Reasonable error estimates of the calculated rate constants are readily possible in the conditional Monte Carlo method. If the variances of the sampled data set, $\sigma_{a,b}(T)^2$, are calculated, the relative errors of the calculated rate constant can be estimated in terms of the central limit theorem.[13] Then, the deviation at the α% confidence level is given by

$$|\pm \Delta k(T)| = \Phi^{-1}(\alpha/200)\, \sigma_{a,b}(T) N^{-1/2}, \tag{6}$$

where the function Φ^{-1} is the inverse function of the normal distribution function. Here, the sample variance $\sigma_{a,b}(T)^2$ is estimated by the following conditional Monte Carlo integration:

$$\sigma_{a,b}(T)^2 = (\pi N_A b_m^2)^2 \frac{1}{N-1} \left\{ \frac{1}{N} \sum_{i=1}^{N} [V_t(i) P_{a,b}(i) J_i(T)]^2 - \left[\frac{1}{N} \sum_{i=1}^{N} V_t(i) P_{a,b}(i) J_i(T) \right]^2 \right\}. \tag{7}$$

The conditional distribution functions should be formed so as to minimize the above variance.

Application to the (H_2, H_2) Exchange Reaction

We take up the (H_2, H_2) direct exchange reaction as a typical example among the AB+CD→AC+BD reactions. The determination of the conditional distribution functions F's for this reaction, the process of rate calculation, and the results will be briefly described below.

The Forms of ***F*****'s.** This exchange reaction happens with higher probability when the large energy present originates in vibrational and/or translational motions.[14] Now, if we adopt the thermal distribution functions at a representative temperature, there are few sample trajectories in the region where the reaction probability is comparatively high and the effect on the magnitude of rate constant is significant. On the other hand, the reaction probability is nearly zero where the density functions take large values and the samples are numerous. Therefore, we intend to adopt the conditional distribution functions so that the number of trajectories does not decrease in the high reactive conditions. The forms of F's for the various modes of motion are separately discussed as follows.

For Vibrational Quantum Number ***v*****:** Since large vibrational energy is favourable for a trajectory to go into the reaction channel, it is desirable to provide many samples in the high energy levels. The simplest treatment would be to assign an equal weight factor to each vibrational level. Then we construct the conditional distribution function in the following simple form:

$$F^{\rm vib}_v = (v+1)/(v_m+1) \qquad (0 \leq v \leq v_m \leq v_{\rm max}), \tag{8}$$

where v_m denotes the largest vibrational quantum number considered in the trajectory calculations and $v_{\rm max}$ means the dissociation limit of the hydrogen molecule, which has been assumed to be the Morse oscillator. We must choose the value of v_m carefully, because a too large v_m value gives many sample trajectories that are hardly expected in the thermal distribution, and because a too small v_m value neglects the samples necessary for the estimation of the rate constant.

For Rotational Quantum Number ***j*****:** The rotational effect on this reaction is expected to be weak. Therefore, the conditional distribution function $F^{\rm rot}_j$ is assumed to be the thermal equilibrium distribution function $G^{\rm rot}_j$ at a representative temperature T_0.

$$F^{\rm rot}_j = G^{\rm rot}_j(T_0). \tag{9}$$

Here, $G^{\rm rot}_j(T)$ is given by

$$G_j^{\mathrm{rot}}(T) = Q_{\mathrm{rot}}(T)^{-1}\sum_{j'=0}^{j} g_{j'}(2j'+1)\exp(-E_{j'}/k_{\mathrm{B}}T), \tag{10a}$$

$$Q_{\mathrm{rot}}(T) = \sum_{j'=0}^{\infty} g_{j'}(2j'+1)\exp(-E_{j'}/k_{\mathrm{B}}T), \tag{10b}$$

where the magnitude of statistical weight g_j is noted in Ref. 15. In the case of homonuclear diatomic molecule, the procedure to determine the j-value from the rotational distribution function F_j^{rot} is somewhat complex and is explained in Appendix II.

For Translational Energy $\boldsymbol{E}_{\mathrm{t}}$: For the same reason as for the vibrational motion, we have employed the following conditional distribution function:

$$F(E_{\mathrm{t}}) = \begin{cases} E_{\mathrm{t}}/E_{\mathrm{t,m}} & : \ 0 \leq E_{\mathrm{t}} \leq E_{\mathrm{t,m}} \\ 1 & : \ E_{\mathrm{t,m}} \leq E_{\mathrm{t}} \end{cases} \tag{11}$$

where $E_{\mathrm{t,m}}$ is a sufficiently large value of E_{t}, similarly to v_{m}.

For Orbital Quantum Number $\boldsymbol{l}$: The following form is assumed as in the vibrational case, because the smaller value of l is expected to give the higher reaction probability:

$$F_l^{\mathrm{orb}} = (l+1)/(l_{\mathrm{m}}+1) \quad (0 \leq l \leq l_{\mathrm{m}}). \tag{12}$$

Here l_{m} denotes the maximum orbital quantum number for a given translational energy and is calculated by the following equation if the characteristic impact parameter b_{m} is fixed:

$$l_{\mathrm{m}} = \left[\frac{\{1+b_{\mathrm{m}}(8\mu E_{\mathrm{t}})^{1/2}/\hbar\}^{1/2}-1}{2}\right]_{\mathrm{int}}. \tag{13}$$

Here $[\ \ ]_{\mathrm{int}}$ means to omit the decimal part. Once l is chosen, the impact parameter b, which is necessary for trajectory calculation, is estimated by

$$b = \hbar\{l(l+1)/2\mu E_{\mathrm{t}}\}^{1/2}. \tag{14}$$

We add the remark that a similar technique has already been applied for the orbital motion.[4,16)

Calculating Procedure. Two FORTRAN IV programs were written to estimate the rate constants. The first program initializes the trajectories according to the given conditional distribution functions, integrates the Hamilton equation numerically, and then writes out the results into a data file. The second program reads the trajectory data in the file, and then estimates the rate constant at an optional temperature by use of Eq. 4.

The parameter values of the conditional distribution functions are set to those shown in Table 1. T_0 shows a representative value in the range of 500 to 5000 K. The values of v_{m}, $E_{\mathrm{t,m}}$, and b_{m} have been determined by analyzing the results of the 4000 trajectories test run which has employed sufficiently large values for them. The LEPS type potential surface devised by Raff *et al.*[17) and the parameter values by Porter *et al.*[4) are used to specify the Hamilton equation of the system. Numerical integration has been performed by the Adams-Moulton fifth-order predictor, sixth-order corrector method, and the time increment is set to 2×10^{-16} s. More details of trajectory calculation can be found elsewhere.[2,8)

TABLE 1. PARAMETERS ADOPTED IN THE CONDITIONAL DISTRIBUTION FUNCTIONS FOR THE (H_2, H_2) DIRECT EXCHANGE REACTION

$v_{\mathrm{m}}=4$
$T_0=1000$ K
$E_{\mathrm{t,m}}=125$ kcal mol^{-1}
$b_{\mathrm{m}}=2.25$ au

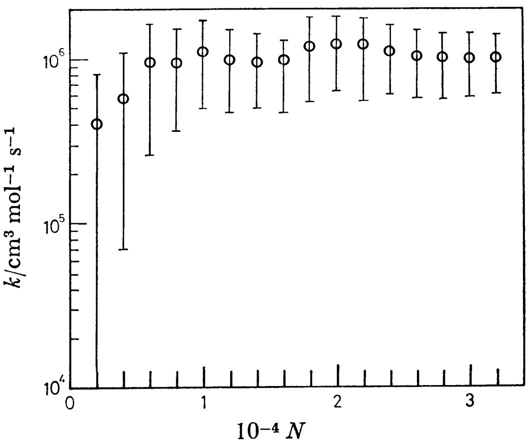

Fig. 1. The calculated rate constant of (H_2, H_2) direct exchange reaction at 2000 K *vs.* the number of sample trajectories, N. The error bars depict the 90% confidence limits.

Results. The calculated rate constants at a temperature of 2000 K are plotted as a function of the number of sample trajectories in Fig. 1. The confidence intervals at the 90% level are also depicted by the error bars, the lengths of which tend to decrease with the increase of N.

Here, we will estimate the necessary number of trajectories to attain accuracy within an order of magnitude:

$$\frac{\Delta k(T)}{k(T)} \leq 0.9\ . \tag{15}$$

Since the relative error at the α% confidence level inherent in the N-samplings is evaluated by Eq. 6, the relative standard deviation $\sigma(T)/k(T)$ can be related to Eq. 15 as follows:

$$\sigma(T)/k(T) \leq 0.9N^{1/2}/\Phi^{-1}(\alpha/200). \tag{16}$$

Therefore, we will seek the number N which satisfies the above relation. The procedure can be traced in Fig. 2, where the calculated $\sigma(T)/k(T)$'s at $T=$ 1000 K and 2000 K are plotted against $N^{1/2}$, and three straight lines are drawn to show the equality of Eq. 16 for α=90, 95, and 99(%). If a calculated point of $\sigma(T)/k(T)$ lies below each line, the $k(T)$ value is regarded to have the desired accuracy at the corresponding degree of confidence. For instance, it can be seen from this figure that 4000 and 18000 trajectories are enough to reach the 90% level at T=2000 and 1000 K, respectively.

The Arrhenius plot of the calculated rate constants and their 90% confidence limits at 32000 trajectories are shown in Fig. 3. This plot tends to be slightly concave and an activation energy of *ca.* 67 kcal/mol has been evaluated by fitting the Arrhenius equation to this slope. We also note the tendency that the

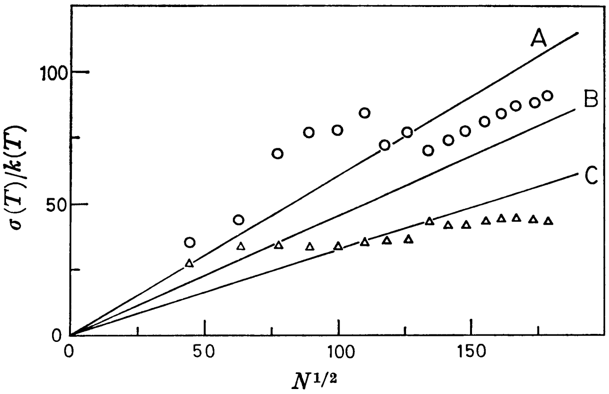

Fig. 2. Plot of $\sigma(T)/k(T)$ *vs.* $N^{1/2}$.
The marks ○ and △ represent the points of $\sigma(T)/k(T)$ at $T=1000$ and 2000 K, respectively. The straight lines A, B, and C mean the limits which satisfy the equality of Eq. 16 for $\alpha=90$, 95, and 99 (%), respectively.

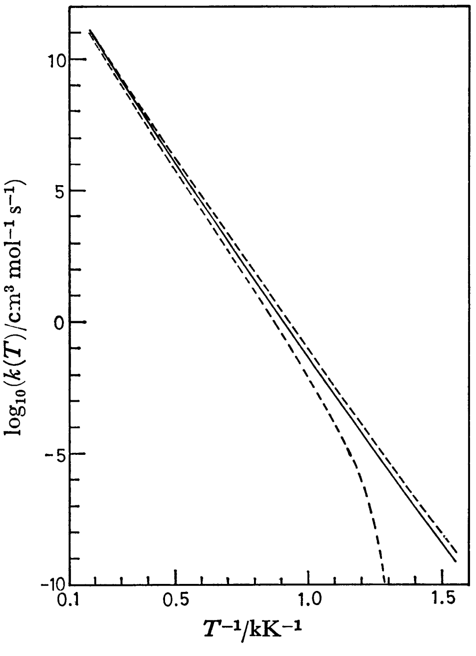

Fig. 3. Arrhenius plot for the (H_2, H_2) direct exchange reaction. The full line represents the Arrhenius plot calculated from 32000 trajectories. Two dotted lines show the 90% confidence limits.

accuracies attained at lower temperatures are poorer than those at higher ones. However, such results simply come from our choice of conditional distribution functions. Different tendencies are expected for other functional forms.

In this trial calculation, we have not determined the optimum functional forms of F's. Generally, a great number of test runs would be required to carry it out.[12] Therefore, we adopted appropriate forms of F's and performed a reasonable error estimation to determine the necessary number of trajectories.

Conclusion

We have presented a new technique for the numerical trajectory calculation of the rate constant for the elementary gas phase reaction. The conditional Monte Carlo method employed here has provided the following advantages. First, the dependence of the accuracy of the calculated rate constant on the number of sample trajectories has become clearer than that found in the conventional way. Next, the estimating procedure has become simpler. That is, the trajectory data are put into only one data set, from which the rate constant at any temperature can be calculated immediately. Lastly, even the smaller number of trajectories can give a fairly good estimation of rate constants, if the conditional distribution functions are formed well. Hence, the analysis of the collision process of complex molecules may be possible in the present method, while the necessary number of cross sections grows prohibitively with the increase of the intramolecular freedom of reactants in the conventional method.

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Appendix I. Conditional Monte Carlo Integration

The derivations of Eqs. 4 and 5 are inferred from analogy with the expected value of a function $P(x,n)$ of two random variables (x, n) which are generated according to natural distribution functions $G(x)$ and G_n, where x and n stand for continuous and integral values, respectively. The expected value of $P(x,n)$ is given by

$$\langle P(x,n)\rangle = \sum_{n=0}^{n(\max)} \int_0^1 P(x,n)\,\mathrm{d}G(x)\,(G_n-G_{n-1}), \tag{A1}$$

where the integral is a Rieman-Stieltjes type and G_{-1} and $G_{n(\max)}$ are defined by 0 and 1, respectively. If we want the values of random variables to be generated according to conditional distribution functions $(F(x), F_n)$, Eq. A1 should be reformulated as follows:

$$\langle P(x,n)\rangle = \sum_{n=0}^{n(\max)} \int_0^1 P(x,n)J(x,n)\,\mathrm{d}F(x)\,(F_n-F_{n-1}), \tag{A2}$$

where $J(x,n)$ is the Jacobian:

$$J(x,n) = \frac{\mathrm{d}G(x)}{\mathrm{d}F(x)}\cdot\frac{G_n-G_{n-1}}{F_n-F_{n-1}}. \tag{A3}$$

Employing the analog Monte Carlo method,[12] we can choose an N-samples set $((x_i, n(i)),\ i=1,\ldots., N)$ from the distribution according to the $(F(x), F_n)$-functions and can simultaneously establish the corresponding set $(P(x_i,n(i))\ J(x_i,n(i)),\ i=1,\ldots., N)$. Then, Eq. A2 is approximated by

$$\langle P(x,n)\rangle = \frac{1}{N}\sum_{i=1}^{N} P(x_i, n(i))J(x_i, n(i)), \tag{A4}$$

where i-th sample values $(x_i, n(i))$ are derived from two uniform random numbers ξ_i and η_i using the following equations:

$$\begin{cases} x_i = F^{-1}(\xi_i) & (0\le\xi_i<1), \\ F_{n(i)-1}\le\eta_i<F_{n(i)} & (0\le\eta_i<1). \end{cases} \tag{A5}$$

Appendix II. Monte Carlo Choice of the Rotational State for Homonuclear Diatomic Molecule

The summation in Eq. 10 is first divided into two series with even and odd j-number, and these troublesome summations are carried out in the approximations of integral expression[8] as follows:

$$\begin{aligned} F_j^{\text{rot}} &= Q_{\text{rot}}^{-1}\left\{g_{\text{even}} \sum_{\text{even } j'} (2j'+1)\exp\left(-\frac{\hbar^2 j'(j'+1)}{2Ik_{\text{B}}T_{\text{o}}}\right) + g_{\text{odd}} \sum_{\text{odd } j'} (2j'+1)\exp\left(-\frac{\hbar^2 j'(j'+1)}{2Ik_{\text{B}}T_{\text{o}}}\right)\right\} \\ &= Q_{\text{rot}}^{-1}\left\{g_{\text{even}}\int_0 (8x+2)\exp\left(-\frac{\hbar^2 x(2x+1)}{Ik_{\text{B}}T_{\text{o}}}\right)\text{d}x + g_{\text{odd}}\int_0 (8x+6)\exp\left(-\frac{\hbar^2 (x+1)(2x+1)}{Ik_{\text{B}}T_{\text{o}}}\right)\text{d}x\right\}, \end{aligned} \quad \text{(A6)}$$

where I is the moment of inertia and the upper bounds of summations and integrals are limited by j-value. By calculating the above integrals between the interval $(0,\infty]$, Q_{rot} is expressed as

$$Q_{\text{rot}} = Q_{\text{rot}}(\text{even}) + Q_{\text{rot}}(\text{odd}), \quad \text{(A7)}$$

$$Q_{\text{rot}}(\text{even}) = g_{\text{even}}(2Ik_{\text{B}}T_{\text{o}}/\hbar^2), \quad \text{(A8a)}$$

$$Q_{\text{rot}}(\text{odd}) = g_{\text{odd}}(2Ik_{\text{B}}T_{\text{o}}/\hbar^2)\exp(-\hbar^2/Ik_{\text{B}}T_{\text{o}}). \quad \text{(A8b)}$$

Then, F_j^{rot} is represented by the following formulae:

$$F_j^{\text{rot}} = Q_{\text{rot}}^{-1}\{Q_{\text{rot}}(\text{even})F_j^{\text{rot}}(\text{even}) + Q_{\text{rot}}(\text{odd})F_j^{\text{rot}}(\text{odd})\}, \quad \text{(A9)}$$

$$F_j^{\text{rot}}(\text{even}) = 1 - \exp\left(-\frac{\hbar^2 j(j+1)}{2Ik_{\text{B}}T_{\text{o}}}\right), \quad \text{(A10a)}$$

$$F_j^{\text{rot}}(\text{odd}) = 1 - \exp\left(-\frac{\hbar^2 (j-1)(j+2)}{2Ik_{\text{B}}T_{\text{o}}}\right), \quad \text{(A10b)}$$

where $F_j^{\text{rot}}(\text{even})$ and $F_j^{\text{rot}}(\text{odd})$ are considered to be distribution functions for even and odd rotational states alone, respectively.

In order to determine the quantum number j, we first distinguish whether it belongs to the even or the odd j-series by introducing a uniform random number η. Then, by use of another uniform random number ξ, the value of j in the respective series can be assigned as follows:

if $0 \leq \eta < Q_{\text{rot}}(\text{even})/Q_{\text{rot}}$, even j-series:

$$j = \left[\frac{-1+(1-A)^{1/2}}{2}\right]_{\text{even}}, \quad \text{(A11a)}$$

if $Q_{\text{rot}}(\text{even})/Q_{\text{rot}} \leq \eta < 1$, odd j-series:

$$j = \left[\frac{-1+(9-A)^{1/2}}{2}\right]_{\text{odd}}, \quad \text{(A11b)}$$

where A is given by

$$A = (8Ik_{\text{B}}T_{\text{o}}/\hbar^2)\ln\xi, \quad \text{(A12)}$$

and $[\ ]_{\text{even}}$ and $[\ ]_{\text{odd}}$ mean to adopt the maximum number in the even and the odd integer sequence below the given value, respectively.

The case of heteronuclear diatomic molecule has already been treated in Ref. 8.

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