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Importance of Different Multipole Interactions in Fast Reactions at Low Temperature

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For fast reactions dominated by long-range multipole interactions, the adiabatic capture model has been shown to work well for the calculation of rate constants. The contributions of different multipole interactions to the rate constants of fast diatom–diatom reactions at low temperatures have been studied by employing the rotational adiabatic second-order perturbation theory (RA2PT). It is found that at ultralow temperatures the weak dipole–induced dipole or quadrupole–quadrupole interactions will probably become significant and even tend to dominate the reaction rate due to the properties of the rotational adiabatic potentials. Calculations for the $\text{CN(X)} + \text{O}_2$ reaction and the $\text{CH(A)} + \text{CO}$ quenching process have been performed to demonstrate this behavior.

1. Introduction

Studies of fast diatom–diatom reactions play an important role in understanding the nature of chemical reactions and have been actively pursued in recent years. Several models^{1–5} have been developed, and these can be used for estimating the rates of such reactions. Many reactions involving radicals or electronic quenching processes fall into this class of collisional processes, and these are often of vital importance in the areas of interstellar chemistry,⁶ combustion,⁷ and atmospheric chemistry.⁸

In a recent paper, Stoecklin et al.² presented a new version of the adiabatic capture model, ACGCSA, for calculating rate constants of fast diatom–diatom reactions. It is an advance over previous versions of adiabatic capture theory,⁹ which invoke either the infinite-order sudden approximation (IOSA)¹⁰ for both reaction reagents or the IOSA for the molecule with the smaller rotational constant and the centrifugal sudden approximation (CSA)^{10,11} for the other molecule with the larger rotational constant. In the new ACGCSA model, the CSA is applied to both molecules, for a more accurate calculation of the rate constant.

The relative accuracy of ACGCSA comes at the cost of computation time needed for the diagonalization of the system Hamiltonian in a symmetrized basis set, which is formed from adiabatic rotational wave functions of both reagents. For large intermolecular distance, second-order perturbation theory can be used in place of the full diagonalization process to reduce the computation time without severely jeopardizing the accuracy. This approximation is known as the rotational adiabatic second-order perturbation theory (RA2PT). Since the effective potential barrier appears at very large intermolecular distance when the collision energy is small, RA2PT gives results in good agreement with ACGCSA results only at ultralow temperature.

It is relevant to the RA2PT model that for interactions involving odd-order electrical multipole moments such as the dipole–dipole or the dipole–quadrupole interaction, first-order perturbation theory yields no contribution to the energy. This suggests that the contribution to the adiabatic potential from these interactions will become quite small at large reagent separations. However, this is not the case for the interactions

involving two even-order electrical multipole moments. The two major terms of this kind are the quadrupole–quadrupole and dipole–induced dipole interaction. In first-order perturbation, their inverse fifth and inverse sixth power dependences, respectively, on the intermolecular distance are retained in the adiabatic potential. The contributions of the different multipole interactions to the adiabatic potential will thus change in importance to the reaction rate as the temperature is lowered. At ultralow temperatures, the contributions of the quadrupole–quadrupole and dipole–induced dipole interactions to the reaction rate may surpass those of the dipole–dipole and dipole–quadrupole interactions and thus tend to dominate the reactions.

We chose the radical–radical reaction $\text{CN} + \text{O}_2$ and electronic quenching reaction $\text{CH(A)} + \text{CO}$ as two examples to illustrate the variation in importance of the different multipole interactions at low temperatures. They are all entrance-channel-controlled fast reactions and have been studied in several previous theoretical and experimental investigations.^{2,9,12–14} Reliable kinetic data¹⁵ down to 13 K for the $\text{CN} + \text{O}_2$ reaction also make it possible to compare our calculations with the experimental data, thus providing a way to check the reliability of our model.

This paper has been organized as follows: Section 2 is devoted to supplementing the potential matrix elements of the quadrupole–quadrupole and the dipole–induced dipole interactions that have not been taken into account in the work of Stoecklin et al.² Section 3 presents numerical calculations, and section 4 presents a conclusion.

2. Theory

Since the methods of ACGCSA and RA2PT have been explained in full detail previously,² an introduction to the theory will not be presented. Instead, we supplement here the two interactions, quadrupole–quadrupole and dipole–induced dipole, that lead to significant contributions to the reaction rate at ultralow temperature but have not been included previously by Stoecklin et al.² For convenience, we adopt the same symbols as those used by these authors.

To obtain the rotationally adiabatic potential, the matrix elements of all terms of the interaction potential are first

calculated. In the body-fixed frame, the multipole interactions can be expanded in terms of spherical harmonics by employing the two-center expansion of the potential energy of interaction of two charge distributions:¹⁶

$$V(R, \hat{R}_1, \hat{R}_2) = \sum_{\mu, q_1, q_2} \alpha_{q_1, q_2}^{\mu}(R) Y_{q_1, q_2}^{\mu}(\hat{R}_1, \hat{R}_2) \quad (1)$$

where

$$Y_{q_1, q_2}^{\mu}(\hat{R}_1, \hat{R}_2) = \frac{4\pi[Y_{q_1}^{\mu}(\hat{R}_1)Y_{q_2}^{-\mu}(\hat{R}_2) + Y_{q_1}^{-\mu}(\hat{R}_1)Y_{q_2}^{\mu}(\hat{R}_2)]}{[2(1 + \delta_{\mu, 0})]^{1/2}} \quad (2)$$

R is the intermolecular distance, \hat{R}_i denotes the two azimuthal angles with respect to the intermolecular axis, and $Y_q^{\mu}(\hat{R})$ is the spherical harmonic. The quantities q_1 and q_2 are the orders of the electrical multipole moment of molecules 1 and 2, respectively. The allowed value of μ runs from zero to the minimum of q_1 and q_2 . For the quadrupole–quadrupole interaction, the coefficients $\alpha_{2,2}^{\mu}$ can be calculated as follows:

$$\alpha_{2,2}^0 = \frac{6}{5} \left[\frac{Q_1 Q_2}{R^5} \right] \quad (3)$$

$$\alpha_{2,2}^1 = \frac{4\sqrt{2}}{5} \left[\frac{Q_1 Q_2}{R^5} \right] \quad (4)$$

$$\alpha_{2,2}^2 = \frac{\sqrt{2}}{5} \left[\frac{Q_1 Q_2}{R^5} \right] \quad (5)$$

The dipole–induced dipole interaction is given by

$$V(R, \hat{R}_1, \hat{R}_2) = - \left(\frac{\mu_1^2 \alpha_2}{R^6} \right) \left[1 + \frac{1}{\sqrt{5}} Y_{2,0}^0(\hat{R}_1, \hat{R}_2) \right] - \left(\frac{\mu_2^2 \alpha_1}{R^6} \right) \left[1 + \frac{1}{\sqrt{5}} Y_{2,0}^0(\hat{R}_1, \hat{R}_2) \right] \quad (6)$$

where μ_i , q_i , and α_i denote dipole, scalar electrical quadrupole moment, and scalar polarizability of molecule i , respectively.

For convenience, we quote the potential matrix element given by Stoecklin et al. (eq 14 in ref 2):

$$V_{\gamma j \bar{\Omega}, \gamma' j' \bar{\Omega}'}(R) = \langle \gamma j \bar{\Omega} J M \epsilon | V(R, \theta_1, \theta_2, \phi) | \gamma' j' \bar{\Omega}' J M \epsilon \rangle = \sum_{\mu, q_1, q_2} \alpha_{q_1, q_2}^{\mu} \times (-1)^{j - \bar{\Omega} + j_1 + j_2 + q_1 + q_2} \left(\frac{2}{1 + \delta_{\mu, 0}} \right)^{1/2} \times \{ j, j', j_1, j_2, j'_1, j'_2, q_1, q_2 \}^{1/2} \delta_{\bar{\Omega} \bar{\Omega}'} \times \begin{pmatrix} j_1 & q_1 & j'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_2 & q_2 & j'_2 \\ 0 & 0 & 0 \end{pmatrix} \sum_k (2k+1) \times \begin{pmatrix} q_1 & q_2 & k \\ -\mu & \mu & 0 \end{pmatrix} \begin{pmatrix} j & k & j' \\ -\bar{\Omega} & 0 & \bar{\Omega}' \end{pmatrix} \begin{Bmatrix} j_1 & j'_1 & q_1 \\ k_2 & j'_2 & q_2 \\ j & j' & k \end{Bmatrix} \quad (7)$$

where $\{j, j', \dots\} = (2j+1)(2j'+1)\dots$ In eq 7, γ stands for the rotational angular momentum quantum numbers j_1 and j_2 of molecules 1 and 2, respectively. The quantity j is the vector sum of the angular momentum j_1 and j_2 , while J is the total angular momentum. The term $\bar{\Omega}$ is the absolute value of the projection of the angular momentum j on the body-fixed intermolecular axis, and M is the laboratory-fixed z -axis

projection of angular momentum J . The parity of the basis function is labeled by ϵ .

Substitution of eqs 3–5 into eq 7 yields the potential matrix element of the quadrupole–quadrupole interaction. Also, by factorization of eq 6 into the symmetrized basis set, we obtain the potential matrix element of dipole–induced dipole interaction:

$$V_{\gamma j \bar{\Omega}, \gamma' j' \bar{\Omega}'}^{D-ID}(R) = \langle \gamma j \bar{\Omega} J M \epsilon | V^{D-ID}(R, \theta_1, \theta_2, \phi) | \gamma' j' \bar{\Omega}' J M \epsilon \rangle = - \left[\frac{\mu_1 \alpha_2}{R^6} \right] \times \delta_{\gamma \gamma'} \delta_{jj'} \delta_{\bar{\Omega} \bar{\Omega}'} - \left[\frac{\mu_1 \alpha_2}{R^6} \right] \times \delta_{\bar{\Omega} \bar{\Omega}'} \times (-1)^{j - \bar{\Omega} + j_1 + j_2} \begin{pmatrix} j_1 & 2 & j'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_2 & 2 & j'_2 \\ 0 & 0 & 0 \end{pmatrix} \times \{ j, j', j_1, j_2, j'_1, j'_2 \}^{1/2} \sum_k (2k+1) \begin{pmatrix} 2 & 0 & k \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} j & k & j' \\ -\bar{\Omega} & 0 & \bar{\Omega}' \end{pmatrix} \begin{Bmatrix} j_1 & j'_1 & 2 \\ j_2 & j'_2 & 0 \\ j & j' & k \end{Bmatrix} \quad (8)$$

In eq 8 we only give the matrix element of the interaction between the dipole of molecule 1 and the polarizability of molecule 2. The other term, involving the interaction between the dipole of molecule 2 and the polarizability of molecule 1, can be readily obtained by a simple permutation of subscript 1 and 2.

From eq 7 one can see that if either q_1 or q_2 is odd, the sum of q_i , j_i , and j'_i will yield a odd integer in first-order perturbation since j_i equals j'_i . This will yield a zero value for the potential matrix element in the first-order perturbation formula, due to the symmetry properties of $3 - j$ symbol. Therefore, dipole–dipole and dipole–quadrupole interaction have only second-order but no first-order contributions. These terms will have a higher power dependence on the intermolecular distance and will become smaller at large intermolecular distances. Although these two terms are generally considered to be the most dominant in neutral molecule–molecule reactions, they are not as important as expected for fast diatom–diatom reactions at ultralow temperatures, which are dominated by very large intermolecular interactions. In this case, the generally considered weak interactions, namely, the quadrupole–quadrupole and dipole–induced dipole interactions, become significant and can even dominate the rate constant since their dependence on the intermolecular distance in first-order perturbation theory is the same as for the corresponding matrix element.

3. Numerical Calculations

RA2PT and collision-complex^{13,17,18} calculations for the CN(X) + O₂(X) reaction and the CH(A) + CO(X) electronic quenching process have been performed. In the collision-complex calculation, the most favorable orientation is used. The collision-complex theory is the classical equivalent of the adiabatic capture theory. The reaction section formulas in these two theories are similar to each other. In adiabatic capture theory, the maximal angular momentum quantum number J_{\max} , below which reaction collisions can occur, replaces the quantity b_0 in collision-complex theory, which denotes the maximal collision parameter. Because of this analogy and the fact that the classical intermolecular potential is used in collision-complex theory to construct the effective potential, the contributions of the different multipole interactions calculated with the collision-

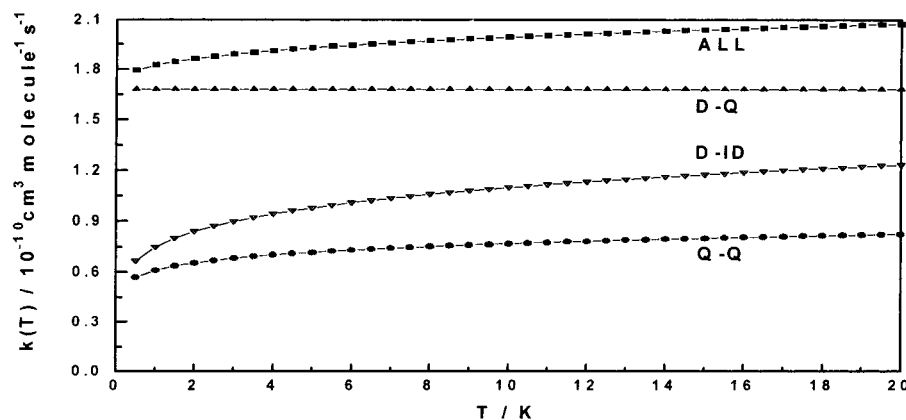


Figure 1. Thermal rate constants calculated for the CN(X) + O₂ reaction by the collision-complex theory. The interactions are specified for each of the calculated curves.

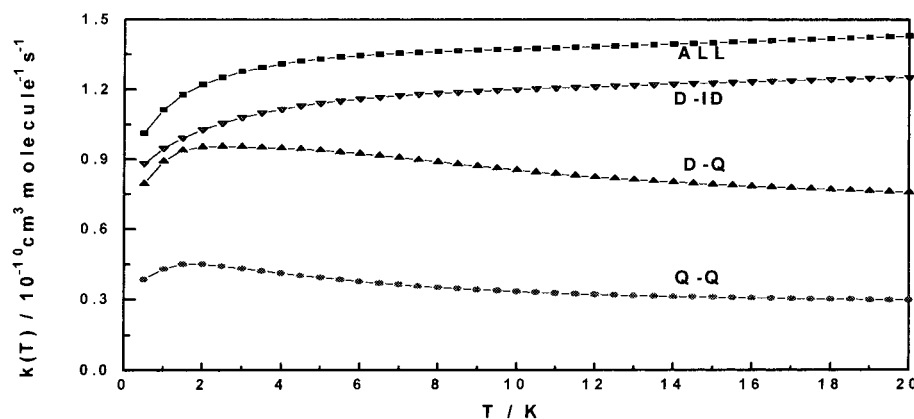


Figure 2. Thermal rate constants calculated for the CN(X) + O₂ reaction by the RA2PT model using the rotational basis $j(\text{CN}) = 0-8$, $j(\text{O}_2) = 1, 3, 5, 7$, and 9 . The interactions are specified for each of the calculated curves.

TABLE 1: Multipole Moments, Polarizability, and Rotational Constants Used in the Calculation

molecule	μ (D)	Q (10^{-26} esu cm ²)	α (\AA^3)	B (cm ⁻¹)
CN(X)	1.45 ^a	0.53 ^b	2.26 ^a	1.8997 ^d
O ₂ (X)	0	0.39 ^c	1.58 ^c	1.445 63 ^d
CH(A)	0.78 ^c	2.287 ^c	3.3 ^c	14.93 ^d
CO(X)	0.11 ^c	2.50 ^c	1.95 ^c	1.931 28 ^d

^a From ref 2. ^b Estimated by method reported in ref 19. ^c From ref 14. ^d From ref 20.

complex theory can be used as the classical standard by which we can observe the variation in the importance of different multipole interactions at low temperature.

The CN + O₂ reaction has long been used as a model system for radical-radical reactions. Previous adiabatic capture calculations^{2,9} have employed the dipole-quadrupole interaction. To compare the contributions of different multipole potentials to these two reactions, the calculations have been performed with inclusion of only the dipole-quadrupole, dipole-induced dipole, and quadrupole-quadrupole interactions in turn for both reactions and additionally the dipole-dipole interaction for the CH(A) + CO quenching reaction. The total rate constant, combined by combining all the contributions to the interaction potential, has also been included for both reactions. The multipole moments, polarizability, and rotational constants used in the calculation are listed in Table 1.

Figure 1 presents the rate constants calculated with the collision-complex model for the CN(X) + O₂ reaction from 0.5 to 20 K. It can be seen that dipole-quadrupole interaction has

the largest contribution, followed by the dipole-induced dipole interaction and quadrupole-quadrupole interaction in decreasing order.

In contrast with the collision-complex calculation, the RA2PT calculation gives a very different result, which is shown in Figure 2. The calculation used a rotational basis set with $j(\text{CN})$ from 0 to 8 and $j(\text{O}_2) = 1, 3, 5, 7$, and 9 . It clearly shows that the dipole-induced dipole interaction now becomes the dominant interaction, and the total rate constants calculated with all the interactions included resemble those calculated solely with the dipole-induced dipole interaction, within the calculation temperature range considered.

It can be seen from Figure 2 that if the dipole-quadrupole interaction is taken as the major term and other terms are neglected, the calculated rate constants for the CN + O₂ reaction at low temperatures will greatly deviate from those calculated with inclusion of the all multipole interaction terms. This is the case for the ACGCSA calculations performed by Stoecklin et al.² on the CN + O₂ reaction in which only the dipole-quadrupole interaction was included. They obtained an expression for the rate constant in the low-temperature limit as $(5.64 \times 10^{-11})T^{1/4}$ cm³ molecule⁻¹ s⁻¹ by postulating that the CN radical is populated only in the $j = 0$ state and the O₂ molecule in the $j = 1$ state. Their calculated rate constant at 13 K is 10.7×10^{-11} cm³ molecule⁻¹ s⁻¹, smaller than the experimental rate constant of $(13.4 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ reported by Sims et al.¹⁵ Although the difference in the calculated and experimental rate constants is small, this deviation can provide us with some useful information about the importance of the various interaction terms for this reaction at

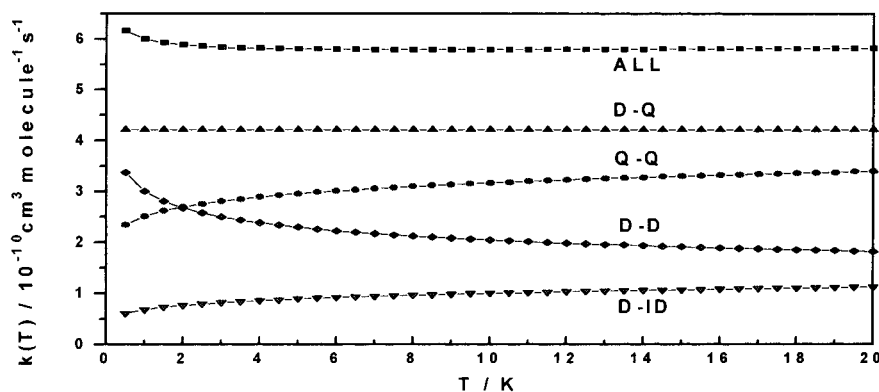


Figure 3. Thermal rate constants calculated for the CH(A) + CO quenching process by the collision-complex theory. The interactions are specified for each of the calculated curves.

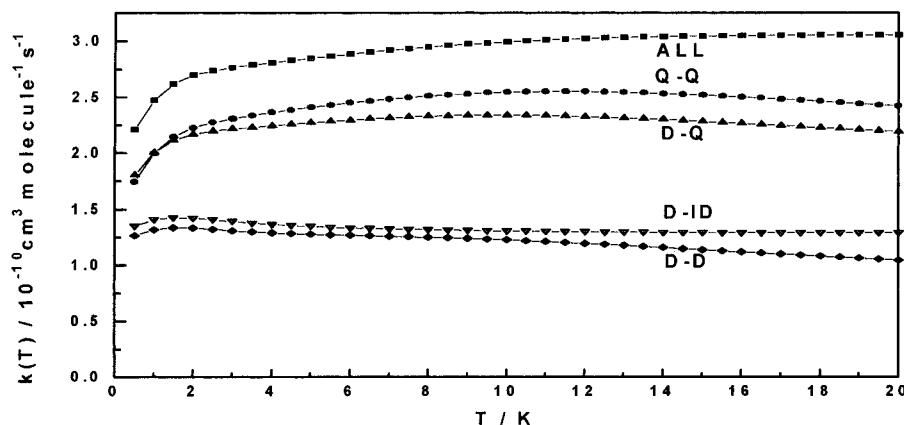


Figure 4. Thermal rate constants calculated for the CH(A) + CO quenching process by the RA2PT model using the rotational basis $j(\text{CH}) = 0-7$, $j(\text{CO}) = 0-9$. The interactions are specified for each of the calculated curves.

low temperatures if the following two facts are taken into account. First, the calculated rate constant for the CN + O₂ reaction with consideration of the dipole–quadrupole interaction only decreases when rotations of both molecules are allowed to be excited. In particular, the contribution of excited rotational states reduces the calculated rate constant at 13 K to $8.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, as shown by the calculations presented in Figure 2. Second, in adiabatic capture theory, it is assumed that the reaction probability equals unity if the collision energy is larger than the effective potential barrier. Therefore, the calculated rate constants should be an upper limit to the true rate constant. This is also the case for collision-complex theory. Figure 1 shows that the calculated rate constants are larger than the experimental data even though only the dipole–quadrupole interaction is included. With inclusion of all the multipole interactions, our RA2PT calculation yields a rate constant of $13.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 13 K, in good agreement with the experimental measurement.

The same types of calculations have been performed for the CH(A) + CO system. Unlike CN(X) + O₂, this system has a very strong quadrupole–quadrupole interaction since the electrical quadrupole moments of both reagents are large. The system provides a good example to observe the variation in importance of the different multipole interactions. The collision-complex calculation, presented in Figure 3, shows that the contribution of the dipole–quadrupole interaction is dominant, while that of the dipole–induced dipole is the weakest. The contribution of the quadrupole–quadrupole interaction is significant and surpasses that of dipole–dipole term above 2 K.

The RA2PT calculation for the CH(A) + CO quenching process, presented in Figure 4, clearly displays the variation in

importance of the different multipole interactions as a function of temperature. The contribution of the dipole–dipole term is surpassed by that of the dipole–induced dipole term within the whole temperature range from 0.5 to 20 K, while the contribution of the quadrupole–quadrupole term surpasses that of the dipole–quadrupole term above 1 K and becomes the dominant term for the quenching reaction.

4. Conclusion

It may be a deficiency that the more accurate ACGCSA model was not used in our calculations since it is much more time-consuming. Previous work² has shown that the perturbation theory approach gives results in good agreement with those of ACGCSA below 4 K for the CN + O₂ reaction. Above this temperature, the perturbation theory will yield rate constants larger than those of the ACGCSA model. This suggests that an ACGCSA calculation for this reaction will probably yield a rate constant smaller than the experimental data at 13 K. However, inclusion of the dispersion term and higher-order multipole interactions will increase the calculated rate constant. It is also unfortunate that our calculations for the reaction CN + O₂ could not be used to investigate theoretically the temperature range studied experimentally by Sims et al.¹⁵ The second-lowest temperature studied by this group was 25 K, which highly exceeds the temperature range for which RA2PT calculations are deemed to be reliable. For the CH(A) + CO quenching process, the rotational constant of CH is much larger than those of CN and O₂, and the perturbation theory approach should work over a broader temperature range.

Despite the above limitations, it still can be seen from our calculations that within the framework of adiabatic capture

theory the commonly considered small or even negligible terms, such as the quadrupole–quadrupole and the dipole–induced dipole interactions, may play an important role in determining the rate constant for fast diatom–diatom reactions at ultralow temperatures. Since different multipole interactions lead to different temperature dependences in the thermal rate constant, the quadrupole–quadrupole and the dipole–induced dipole interactions may strongly influence the rate constant calculated with inclusion of all the multipole terms. Also, care should be taken to include the correct major interactions at low temperature if it is necessary to reduce the computation time.

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