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On the *J*-Shift Approximation in Quantum Reaction Dynamics

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The validity of the *J*-shift or the energy-shift approximation is investigated numerically by taking the reaction $O(^3P) + HCl \rightarrow OH + Cl$ as an example. The approximation based only on the results of J (total angular momentum quantum number) $= 0$, which is the ordinary *J*-shift approximation, cannot reproduce the exact reaction dynamics well, especially when the initial rotational quantum number is high. The reaction rate constants for specified initial rovibrational states are over- or underestimated depending on the initial state and temperature. The good agreement with the accurate result of the thermal rate constant seems to be rather accidental because of the cancellations of these over- and underestimates. An extended *J*-shift approximation is proposed, in which accurate calculations should be carried out up to $J = j_i$ with $|\Omega| \leq \Omega_{max}$ when $j_i \leq \Omega_{max}$, or up to $J = \Omega_{max}$ when $j_i > \Omega_{max}$, where Ω_{max} is the maximum of the absolute values of the body-fixed projection quantum number Ω that give noticeable contributions to the reaction dynamics. When the maximum J required to have a well converged cross-section and rate constant is much larger than j_i, it is recommended to carry out accurate calculations at some representative J values and to use these values to estimate probabilities at other J values by an appropriate interpolation or extrapolation procedure.

1. Introduction

In the quantum mechanical studies of chemical reaction dynamics, a large number of the total angular momentum quantum number J should be taken into account in order to calculate accurate reaction cross-sections and rate constants. This still presents a big labor task, and thus the *J*-shift or the energy-shift approximation has been proposed to simplify the calculations. This enables us to evaluate cross-sections and rate constants using only the accurate results of $J = 0$.[1,2] An extended version of the energy-shift approximation (constant centrifugal potential approximation) has also been proposed, in which the accurate calculations are required for $J \leq j_i$, where j_i is the initial rotational quantum number.[3] The simple *J*-shift approximation based on the $J = 0$ results works relatively well when two or more atoms in triatomic reaction systems are light (thus the maximum J required for the convergence of cross-section is not large) and the initial rotational quantum number is equal to zero. When reactants are rotationally excited, however, the approximation becomes questionable.[4] This is true even for $j_i = 0$, when two or more heavy atoms are involved in the system and thus a large number of J are required.[5]

For the reaction system $O(^3P) + HCl$, Koizumi et al. applied the *J*-shift approximation and calculated the thermal rate constant.[6] Since their main purpose was to obtain an analytical potential energy surface (hereafter referred to as KSG-PES), they adjusted an analytical function so that the calculated thermal rate constant reproduces the experimental results. Therefore, we cannot judge the validity of the *J*-shift approximation from their results. After that, Nakamura and co-workers have carried out accurate calculations for $J \neq 0$ with use of the KSG−PES and claimed that the accurate calculations are necessary at least for $J \leq j_i$.[5,7] Their thermal rate constant is much larger than that of Koizumi et al. Recently, Thompson and Miller[8] and Aoiz et al.[9] calculated the thermal rate constant and obtained a good agreement among themselves, although their results are larger than that of Koizumi et al.[6] The former used the flux−flux autocorrelation function method,[10,11] and the latter carried out the quantum scattering calculations for $J = 0$ using the hyperspherical coordinate method. Both of them used the simple *J*-shift approximation. On the other hand, there has been found a simple error in the accurate calculations done in refs 5 and 7. (In the calculations of cross-sections and rate constants in references 5 and 7, the mass factor was erroneously taken to be the reduced mass of the reactant diatomic molecule HCl instead of the reduced mass of the system. Thus, the factors 1/11.35 and 1/38.22 should be multiplied to the cross-sections and rate constants in these references, respectively. All of the other calculations and results are all right.) The corrected values of thermal rate constant agree well with those of refs 8 and 9 over the temperature range of 300 ∼1000 K. Thus, the simple *J*-shift approximation seems very good at least for the thermal rate constant. However, as was already pointed out before, the *J*-shift approximation actually cannot reproduce the nonzero J results properly for transitions of specified initial states, especially for the probabilities and cross-sections. Thus, even the good agreement of thermal rate constant seems to be rather accidental. There is an example in which even the thermal rate constant cannot be well reproduced by the simple *J*-shift approximation, and the dynamics of the nonzero Ω (z-component of J in the body-fixed frame) should be treated properly to some extent.[12,13] In the present paper, the validity of the simple *J*-shift approximation is discussed in more detail and an extended version of the *J*-shift approximation is proposed.

This paper is organized as follows. In the next section the *J*-shift, or the energy-shift approximation, is briefly described

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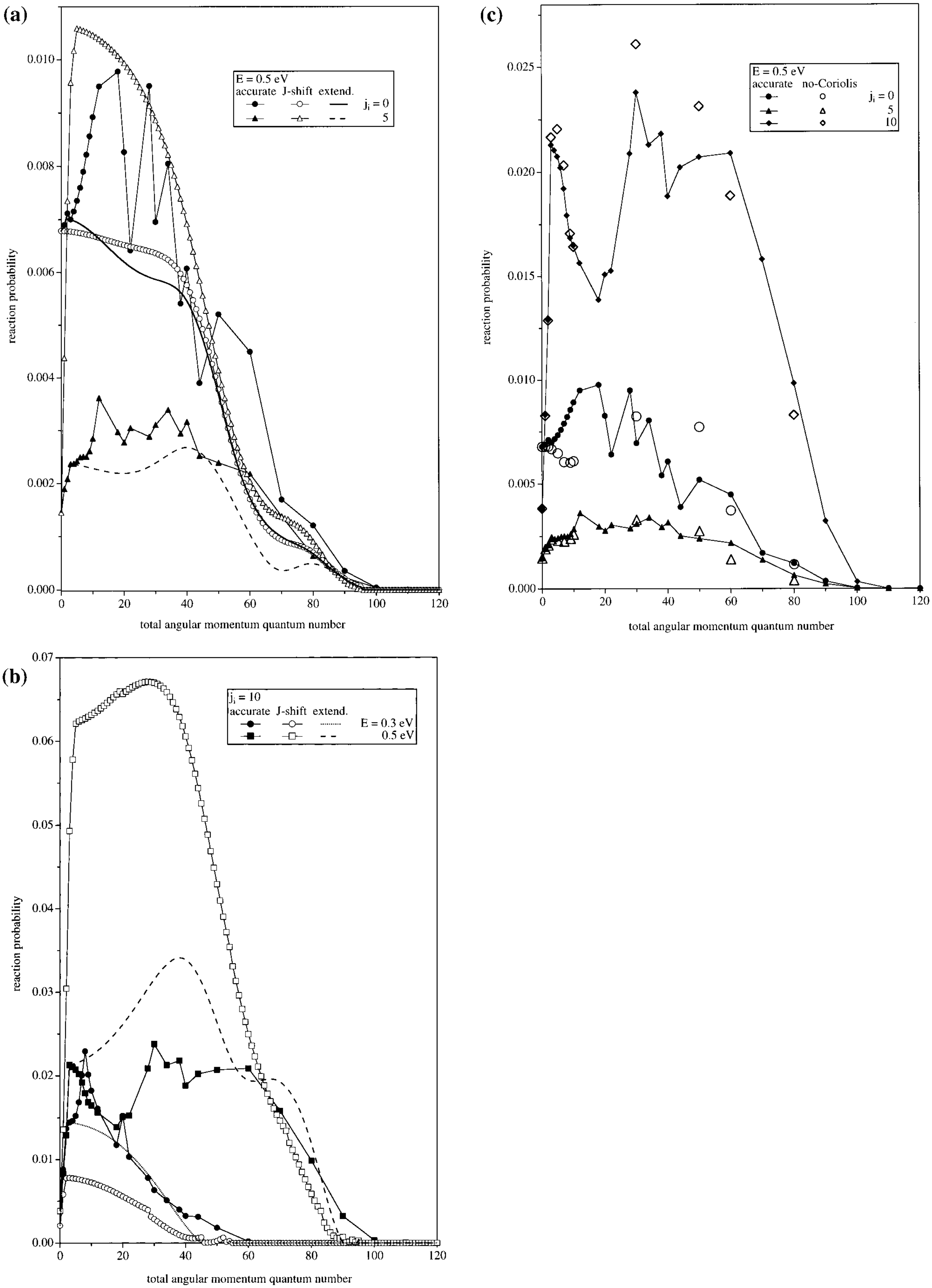

Figure 1. Accurate, simple *J*-shift and extended *J*-shift reaction probabilities (a) for $j_i = 0$ and 5 at $E = 0.5$ eV and (b) for $j_i = 10$ at $E = 0.3$ and 0.5 eV as a function of *J*. (c) Comparison of the reaction probabilities with and without Coriolis coupling.

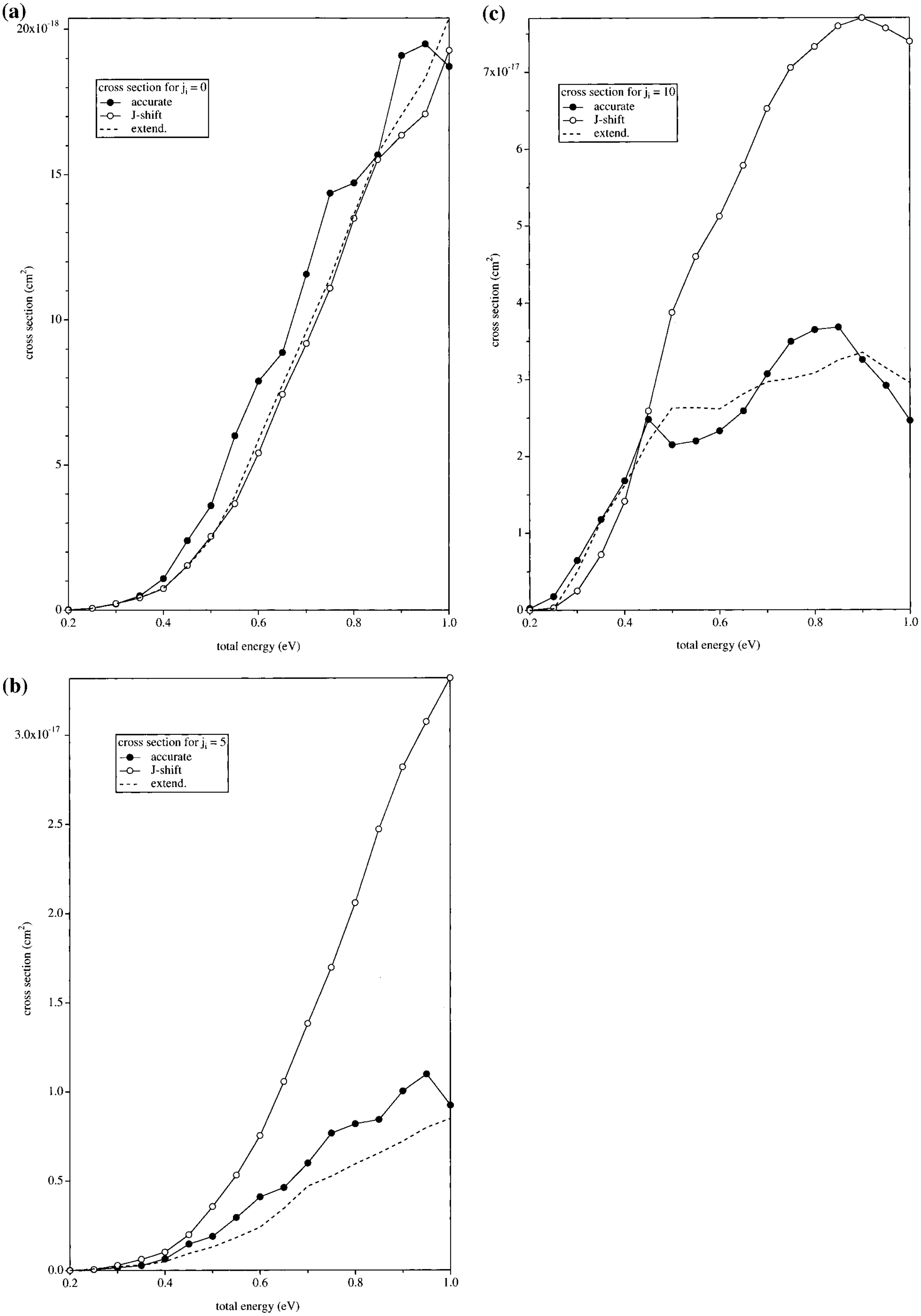

Figure 2. Accurate, simple *J*-shift and extended *J*-shift reaction cross-sections for j_i = (a) 0, (b) 5, and (c) 10 as a function of *E*.

and the extended *J*-shift approximation is proposed. In section 3, various numerical data are presented to demonstrate the inaccuracy of the simple *J*-shift approximation with respect to probability, cross-section, and rate constant. Section 4 provides concluding remarks.

2. Energy-Shift Approximation

2.1. *J*-Shift Approximation. Since the simple *J*-shift approximation has been well described elsewhere, here we give only a brief outline. The essence of this approximation consists of the following replacement:

$$P^J_{j_i j_f}(E_{\mathrm{tr}}) \approx \tilde{P}^J_{j_i j_f} \equiv \sum_{\Omega=-J}^{J} P^{J=\Omega=0}_{j_i j_f}(E_{\mathrm{tr}} - E_{J\Omega}) \qquad (1)$$

where $P^J_{j_i j_f}$ is the reaction probability for the specified initial and final rotational states j_i and j_f at each J, E_{tr} is the translational energy, and $E_{J\Omega}$ is the rotational or centrifugal potential energy at a certain representative configuration such as a saddle point. In the case of a heavy−light−heavy system, it is appropriate to take the rotational energy of a symmetric top at the saddle point and then $E_{J\Omega}$ is given by[6]

$$E_{J\Omega} = \frac{J(J+1)\hbar^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)\Omega^2\hbar^2 \qquad (2)$$

where I_B and I_A are effectively the moment of inertia of O−Cl and that of H about the O−Cl axis, respectively. Equation 1 clearly shows that not only nonzero J but also nonzero Ω dynamics are approximated by the simple energy shift using only the $J = 0$ results. As will be described later in detail, this inaccurate treatment of nonzero Ω dynamics sometimes causes a big error.

2.2. Extended *J*-Shift Approximation. As was demonstrated before[5,7] and will also be shown in the next section, the nonzero Ω dynamics in the case of $j_i > 0$ cannot be simply estimated by the energy-shift approximation from the results of $J = 0$. In fact, previously we have claimed that the accurate calculations should be carried out up to $J = j_i$ for $|\Omega| \le \Omega_{\max}$, where $\Omega_{\max}$ is the maximum of the absolute values of Ω that give noticeable contributions to the dynamics. Although it is necessary to find $\Omega_{\max}$ by carrying out accurate calculations, $\Omega_{\max} = 3 \sim 5$ would practically be quite enough if the body-fixed z -axis is chosen properly. Here, we propose the alternative energy-shift approximation named as the extended *J*-shift approximation given by

$$P^{J>j_i}_{j_i j_f}(E_{\mathrm{tr}}) \approx P^{J=j_i}_{j_i j_f}\left(E_{\mathrm{tr}} - \frac{J(J+1)\hbar^2}{2I_B} + \frac{j_i(j_i+1)\hbar^2}{2I_B}\right) \qquad (3)$$

This approximation is essentially the same as the constant centrifugal potential approximation.[5] A more convenient, yet quite accurate, version of $j_i > \Omega_{\max}$ is

$$P^{J>\Omega_{\max}}_{j_i j_f}(E_{\mathrm{tr}}) \approx \mathrm{P}^{J=\Omega_{\max}}_{j_i j_f}\left(E_{\mathrm{tr}} - \frac{J(J+1)\hbar^2}{2I_B} + \frac{\Omega_{\max}(\Omega_{\max}+1)\hbar^2}{2I_B}\right) \qquad (4)$$

This simplification can save a lot of computational effort for a large j_i since $\Omega_{\max} = 3 \sim 5$ would usually be large enough. The similar notion about the significance of nonzero Ω dynamics has been pointed out in connection with the OH + H_2 reaction in ref 12. When two or more heavy atoms are involved in a system such as in the present O(^{3}P) + HCl system, the maximum J required to have cross-sections well converged extends to a large number. In this case, it is recommended to carry out accurate calculations at some representative large J values, and the results may be interpolated or extrapolated to obtain cross-section and rate constant.

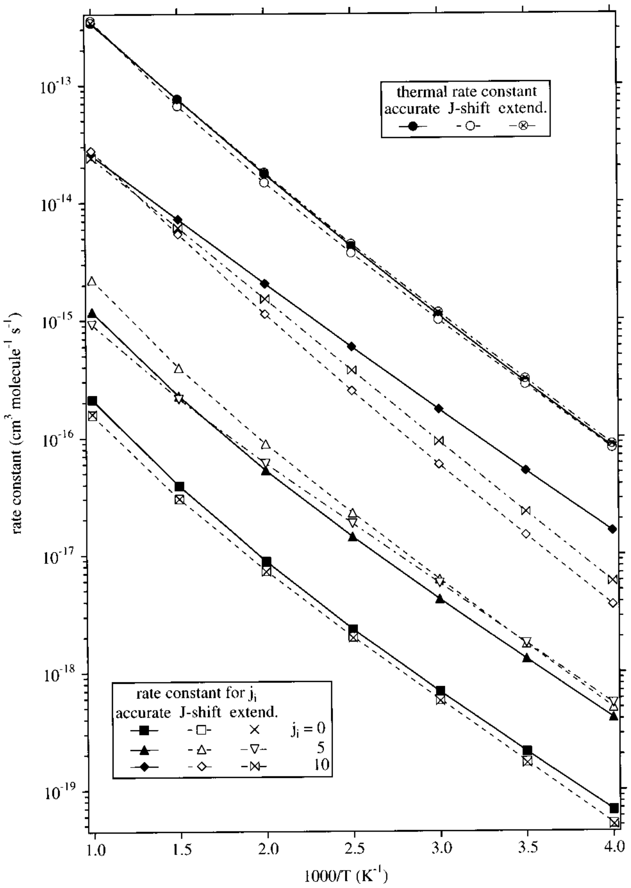

Figure 3. Accurate, simple *J*-shift and extended *J*-shift thermal rate constants and initially specified rate constants for $j_i = 0$, 5, and 10 as a function of 1000/*T*.

Recently, Zhang and Zhang proposed a uniform *J*-shift approach to evaluate thermal rate constants.[14] They proposed to use a temperature-dependent shifting constant to produce the best possible thermal rate constant, but not trying to accurately reproduce the individual dynamics at $J \neq 0$. In the present extended *J*-shift approximation, we do not vary the shifting constant, but we can well reproduce not only the thermal rate constant but also the individual reaction probabilities at $J \neq 0$ for a specified initial state by carrying out the accurate dynamics calculations up to $J = \min(j_i, \Omega_{\max})$.

3. Validity of the Approximation

3.1. Reaction Probability for Specified Initial States. Figures 1 (a) and (b) show reaction probabilities for some representative j_i and E as a function of J. Not only the results of the accurate and the simple *J*-shift calculations but also those of the extended *J*-shift approximation are shown. The accurate ones are the calculations of the same level as those in ref 7. As a whole, the simple *J*-shift approximation cannot reproduce the accurate results well. Discrepancy in the cases of $j_i = 3$ and 5 in Figure 1(a) and of $j_i = 10$ at $E = 0.5$ eV in Figure 1(b) is quite noticeable. This is obviously due to the inaccurate

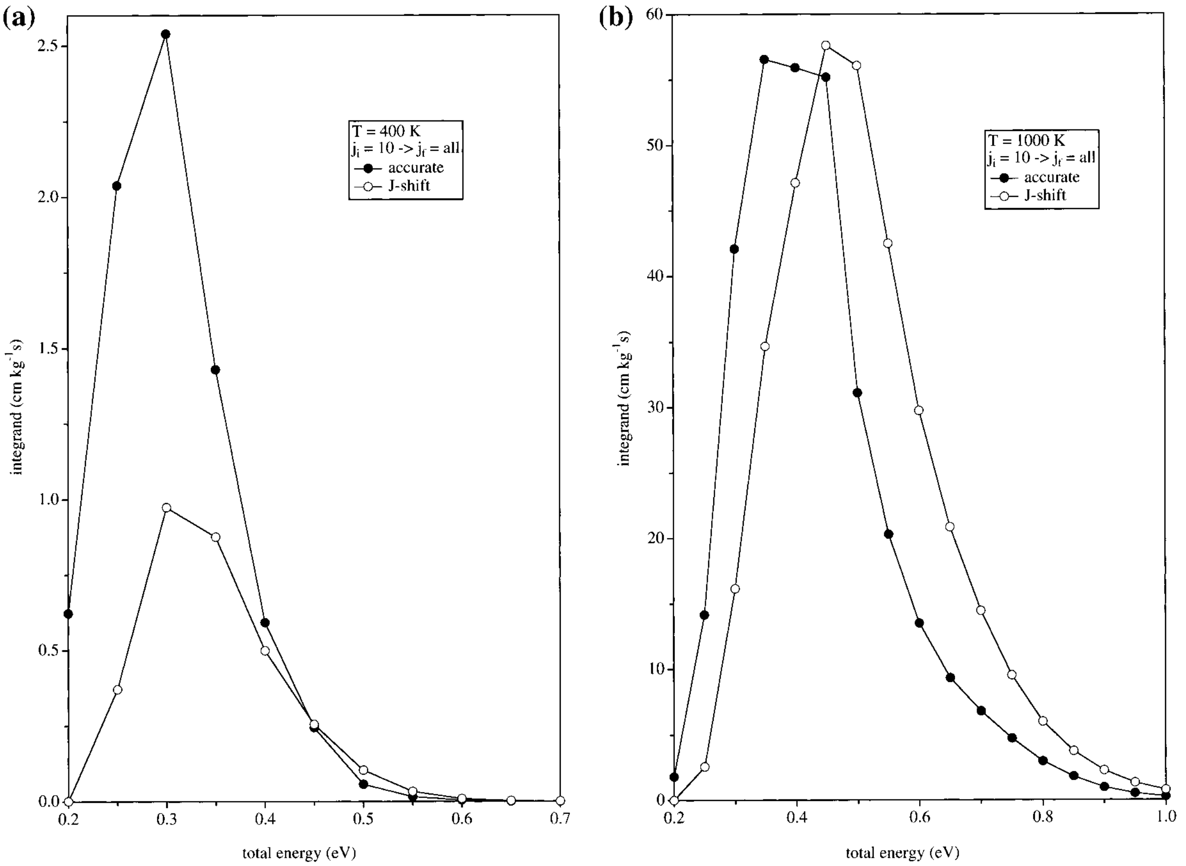

Figure 4. Integrands of the rate constant for $j_i = 10$ as a function of E at $T =$ (a) 400 K and (b) 1000 K. The closed circles are the accurate results and open circles the simple J-shift approximation.

treatment of the nonzero Ω dynamics within the simple J-shift approximation. Since $E_{J\Omega}$ is relatively small at small J, the approximate probability for $J > 0$ is nearly equal to the accurate one at $J = 0$ multiplied by $2J + 1$ (see, eq 1). As a result, the overestimate or underestimate occurs depending on j_i and E, which we cannot predict a priori. Actually, the accurate results deviate quite a lot from those values. Since there is no nonzero Ω component when $j_i = 0$, the approximate J-shift probability decreases monotonically as a function of J. The accurate results for $j_i = 0$, however, depict rather sharp changes at $J > 0$ in the similar way as in $j_i \neq 0$ cases. This is due to the effect of the Coriolis coupling, which is, obviously, not taken into account within the energy-shift approximation. Figure 1(c) shows the effect of the Coriolis coupling for certain j_i and J at $E = 0.5$ eV. There is a relatively large discrepancy especially when $j_i = 0$. However, rather good agreement between the probabilities with and without the Coriolis coupling has been found for $j_i =$ 3, 5, and 10. Since the probabilities for large j_i ($\sim$10) give a dominant contribution to the thermal rate constant in the present system, the Coriolis coupling does not seem to give a large effect as a whole.

Figures 1(a) and (b) also depict results of the extended J-shift approximation. This approximation reproduces relatively well the accurate results. In this approximation, the exact calculations were carried out for $J \leq \Omega_{\max} = 3$ including all $|\Omega| \leq \Omega_{\max}$ components. The approximation improves the simple J-shift approximation very much but is still not enough to reproduce fine structures of the accurate results. This is not due to the neglect of the components of $|\Omega| > \Omega_{\max}$ but is rather ascribed to the intrinsic defect of the simple energy shift.

3.2. Cross-Section for Specified Initial States. Figure 2 shows the similar comparisons between the accurate and approximate results of cross-sections for $j_i = 0$, 5, and 10. It is clearly seen that the simple J-shift approximation does not work well for large j_i and at high energies, although the $j_i = 0$ case is acceptable. Besides, deviation from the accurate results is not simple. The approximation overestimates the results at all energies when $j_i = 5$, but under- and overestimates interchange at around $E \sim 0.42$ eV when $j_i = 10$. These under- and overestimates actually cancel with each other and lead to a good agreement in the final result of the rate constant, as will be demonstrated in the next section. As is expected, the extended J-shift approximation works much better than the simple J-shift approximation and reproduces the overall feature relatively well.

3.3. Rate Constant. Figure 3 shows the accurate and approximate thermal rate constants as a function of temperature. The simple J-shift approximation reproduces the accurate one quite well, especially at high temperature $T \sim 1000$ K. This good agreement is rather surprising, considering the inaccuracies of the approximation shown so far. The rate constants for the specified initial rotational states, $j_i = 0$, 5, and 10, are also shown in the same figure. As is expected, the overestimate (underestimate) occurs in the case of $j_i = 5$ (0 and 10). This kind of cancellation makes the thermal rate constant closer to the accurate one. More significantly, the cancellation of the under- and overestimates seen in Figure 2(c) in the case of $j_i = 10$ makes the thermal rate constant in the simple J-shift approximation to be in very good agreement with the accurate one, because $j_i = 10$ gives a large contribution to the thermal rate constant. To see this more directly, the integrand of the rate constant for $j_i = 10$ as a function of energy is shown in Figure 4(a) and (b) for $T = 400$ K and 1000 K. The underestimate of the integrand is apparently expected at $T = 400$ K, and the cancellation is anticipated at $T = 1000$ K in agreement with Figure 3. From these results one can guess that the very good agreement of the thermal rate constant at $T = 1000$ K would be rather accidental. Actually, the deviation seems to grow again to some extent at temperatures higher than 1000 K, as is conjectured from Figure 3. This could not be confirmed numerically, however, because of the difficulty of carrying out well converged calculations at such high temperatures. It should be noted that there is an example that the simple *J*-shift approximation cannot reproduce the thermal rate constant well.[12]

Figure 3 also depicts the results of the extended *J*-shift approximation. As is seen, the approximation improves the results and is expected to provide a much more reliable method than the simple *J*-shift approximation, in general.

Concluding Remarks

The validity of the *J*-shift or the energy-shift approximation has been investigated by taking the O(^{3}P) + HCl reaction as an example in comparison with the quantum mechanically accurate calculations. The reaction probabilities, cross-sections, and rate constants for specified initial states could not be well reproduced by the simple *J*-shift approximation. The approximation becomes worse at high j_i and high energies. Nevertheless, the thermal rate constant was found to be reproduced well by the approximation. It is true that various cancellations occur generally in a highly averaged quantity such as thermal rate constant, and such quantity might be relatively well estimated by even a rough approximation. The agreement in the present case, however, seems to be too good for the quality of the approximation. Besides, the agreement becomes better at high temperatures around 1000 K than at lower temperatures. This should be other way around, in principle, and we think that this good agreement is actually accidental. The analysis carried out in the present work indicates that the dynamics of nonzero *J* should be properly treated, as was claimed before.[5,7] In view of this analysis, the extended *J*-shift approximation has been proposed. Exact calculations are carried out up to $J = j_\mathrm{i}$ with $|\Omega| \leq \Omega_\mathrm{max}$ when $j_i \leq \Omega_\mathrm{max}$, or up to $J = \Omega_\mathrm{max}$ when $j_i > \Omega_\mathrm{max}$, where Ω_max is the maximum of the absolute values of Ω that give noticeable contributions to dynamics. This Ω_max should be found from numerical calculations, but usually $\Omega_\mathrm{max} = 3 \sim 5$ would be enough if the body-fixed *z*-axis is chosen properly. In some cases, such as in the present heavy−light−heavy system, the required maximum *J* extends to 100 or more, while the maximum j_i necessary for the thermal rate constant for 1000 K is around ∼15. In such cases, additional accurate calculations are required at some representative J ($> j_\mathrm{i}$) to obtain the well converged cross-sections and rate constants. The probabilities at other *J* can be either interpolated or extrapolated using these results. Although the effects of Coriolis coupling were not investigated in much detail, that does not seem to give large effects.

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