Erratum: ''On the 'direct' calculation of thermal rate constants. II. The flux-flux autocorrelation function with absorbing potentials, with application to the O+HCl→OH+Cl reaction'' [J. Chem. Phys. 106, 142 (1997)]

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After publication of our paper, we have discovered a programming error in the computer code for calculating the flux-flux autocorrelation function from which the thermal rate constants are obtained. None of the theoretical methodology is, of course, affected by this, nor any of the qualitative conclusions presented previously, but there are quantitative changes as described below.

Figures 1 and 2 show the flux-flux autocorrelation function for the O+HCl reaction at $T=300$ and 700 K (replacing Figs. 2 and 3 in the original paper). The correct correlation functions do indicate significant recrossing of the flux dividing surface by virtue of the presence of negative lobes as observed previously. However, the second positive lobes seen in the original correlation functions at longer times are not present.

An Arrhenius plot comparing experimental and theoretical rate constants is shown in Fig. 3 (replacing Fig. 7 in the original paper). The corrected rate constants are lower by a factor of 1.5–3.2 over the temperature range 200–700 K. However, the new values are still larger than experiment[1,2] for all temperatures and are larger than those obtained by Koizumi et al.[3] by a factor of about 2–3. Thus, the conclusion that the barrier height on the Koizumi–Schatz–Gordon potential energy surface[4,3] may be too low remains unchanged. Table I reports the numerical values for the rate

FIG. 2. The flux-flux autocorrelation function for the O+HCl reaction at $T=700$ K.
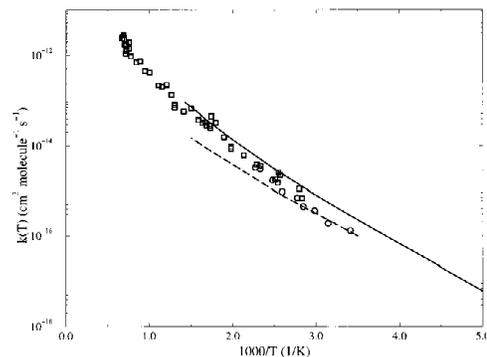
FIG. 3. Arrhenius plot of calculated and experimental thermal rate constants. The present J-shifted calculations are shown as a solid line and the results of Koizumi et al. as a dashed line. The experimental results of Brown and Smith (Ref. 1) are shown as filled circles and that of Mahamud et al. (Ref. 2) as open squares. (The results of Koizumi et al. were measured from their Fig. 2 and hence may be considered approximate.)
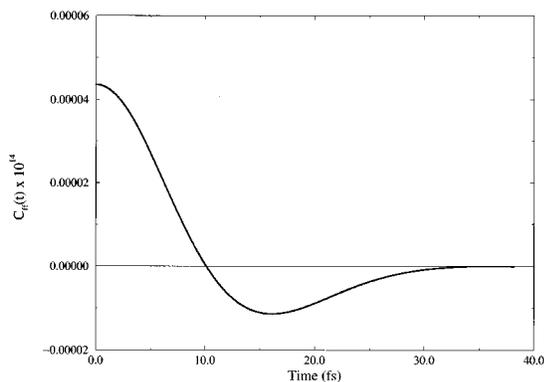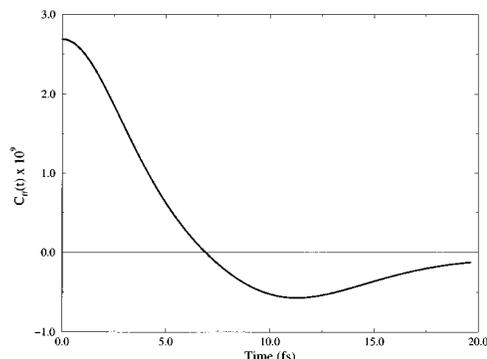

FIG. 1. The flux-flux autocorrelation function for the O+HCl reaction at $T=300$ K. The units of the correlation function are (atomic units of time)$^{-2}$.

TABLE I. Total thermal rate constants within the J-shifting approximation compared for the three-dimensional O+HCl reaction in units of cm^3 molecule^{-1} s^{-1}.

Temp. (K)	$k(T)$ J shifting
200	6.1(−18)[a]
250	6.7(−17)
300	3.4(−16)
350	1.2(−15)
400	3.0(−15)
500	1.3(−14)
600	4.0(−14)
700	8.9(−14)

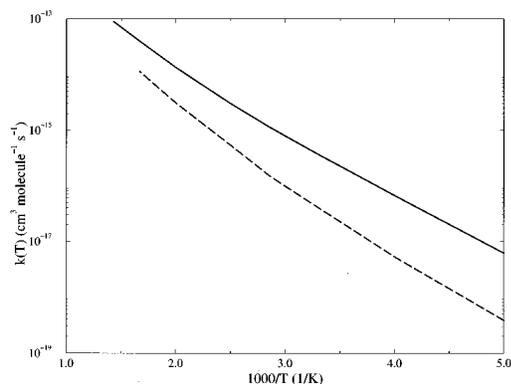[a]The number in parentheses is the power of 10.

FIG. 4. Calculated thermal rate constants, $k(T)$ vs $1000/T$ for the O+HCl (solid line) and O+DCl (dashed line) reactions.

obtained with the J-shifting approximation[5] (replacing Table I of the original paper).

Finally, Fig. 4 presents the corrected rate constants for the O+HCl and O+DCl reactions (replacing Fig. 8 of the original paper). The non-Arrhenius behavior observed for O+HCl compared with the Arrhenius rate constants for O+DCl indicated tunneling is important at low temperatures (as concluded before).

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