Supplements to:
Influence of Distortion and Duschinsky Effects on Marcus-Type Theories of Electron Transfer Rate

Kuo Kan Liang *et al.*.

The numerical results similar to Figure 1 of the article are shown in this supplement. In the following figures, thee kinds of calculations are shown. The blue lines show the results of exact TCF method calculations. The thick red dashed lines show the calculations with short-time CE method for a single DDHO, that is, Eq. (1) combined with Eqs. (58) and (59). The thin black lines show the calcualtions using the Marcus equation like Eq. (56). The λ value in Eq. (56) is calculated with Eq. (59) using the same parameters. The x-coordinates of the figures are the electronic energy gap $\hbar\omega_{ba}$, therefore, when using Eq. (56), the difference between ΔG_{ab} and the electronic energy gap should be compensated for. This is done by calculating the entropy difference between the initial and final electronic levels according to Eq. (62). Notice that in our model, the FC-weighted DOS is equivalent to the EGL.

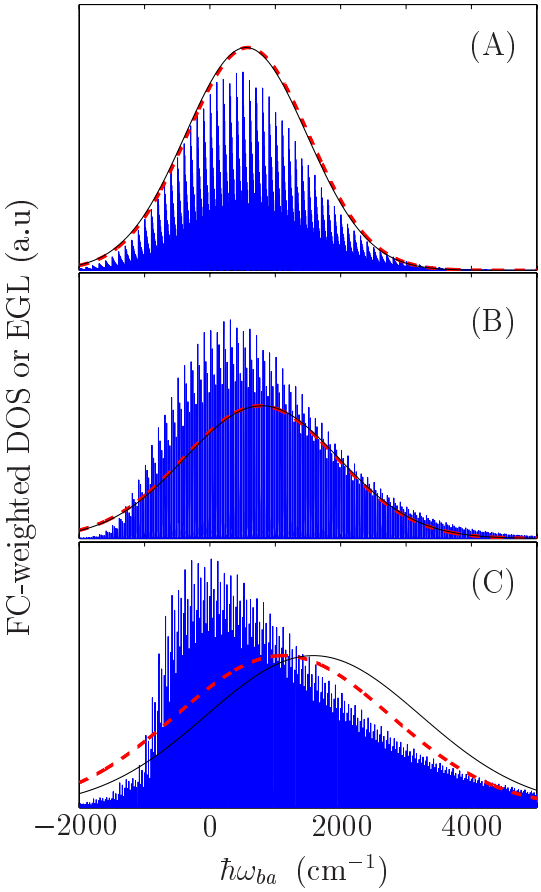
Two tables are shown under each figure. In the first one, the temperature under which the calculations are done is shown. Also shown is the frequency of the mode we considered in the final (lower) electronic level, that is, ω. In the three panels of each figure, the conditions are different in the degree of distortion: (A) $\omega' = 0.9\omega$;

(B) $\omega' = 0.75\omega$; (C) $\omega' = 0.6\omega$. An S value is also shown. This S value is determined by assuming $\omega' = \omega$, that is, when there is no distortion. The displacement which results in this S value is used in all three calculations in each figure.

The second table summarizes the important properties of the results. The λ values are shown for each case. According to the calculated FC-weighted DOS or the EGL, we calculate the mean energy gap of each result. The standard deviation (std) is also shown. Notice that the std of the CE method and the Marcus theory are the same in our calculations.

In all cases, we can see that when the distortion is more significant, the EGL calculated with the exact TCF method deviates from the Gaussian form. However, when the magnitude of λ is large, this deviation is significant but seemingly not so obvious. Notice that the λ value will be large if the frequency of the mode considered is high, or if the coupling constant is large. When λ is large, then, the calculation with CE method seems to always reflect the average properties of the exact EGL to a good extend. However, if the temperature is not high enough, the calculations with the Marcus theory may estimate the peak position of the EGL significantly wrongly, especially when there is a large distortion.

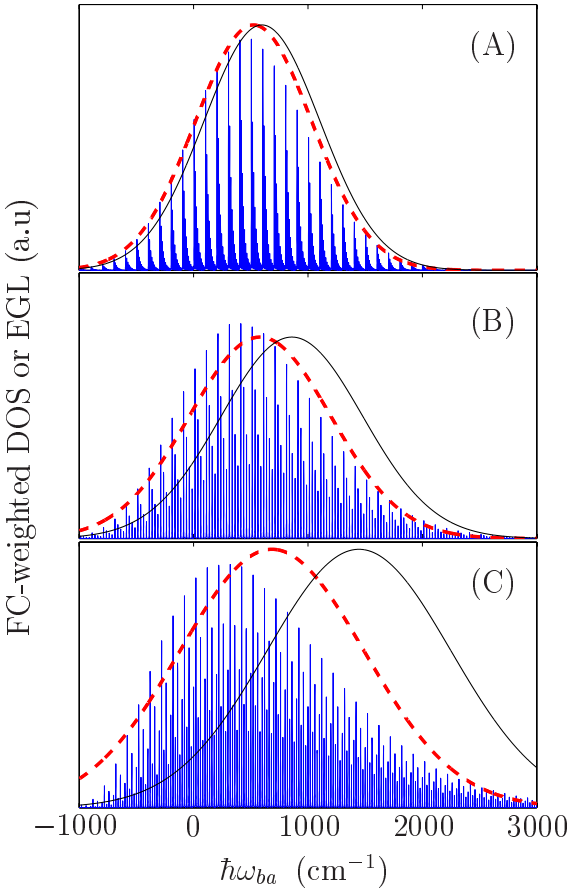
These results clearly shown that in the Marcus theory, assuming the λ in the numerator of the activation energy and the λs in the denominators of the expoenent as well as the pre-exponential part to be the same quanitity may be a very poor approximation in many cases for the intra-molecular contribution to the ET rate. The overall influences of the strength of coupling, the temperature, the degree of distortion and the frequency of the mode involved are too complicated to be summarized in a few simple rules. Hopefully the few results shown here can convince people that the intra-molecular contributions to the ET rate and EGL should be studied with great caution.



ω (cm^{-1})	S	T (K)
100	5	1000

	mean (cm^{-1})			std (cm^{-1})	
λ (cm^{-1})	TCF	CE	Marcus	TCF	CE
626.8	581.7	581.5	553.5	943.6	933.5
994.0	770.6	770.3	793.8	1176.4	1175.5
1938.0	1118.2	1117.8	1582.6	1609.3	1641.3

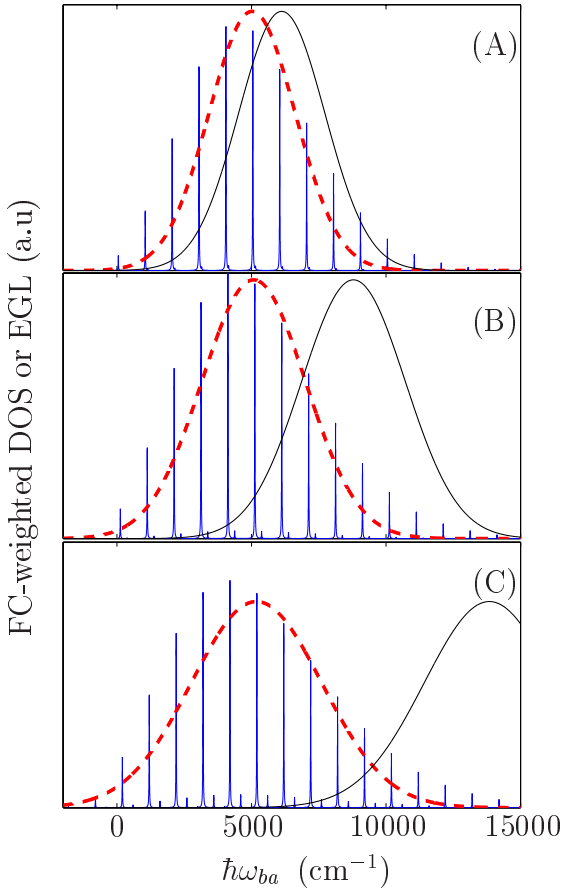
Figure 1:



ω (cm^{-1})	S	T (K)
100	5	300

	mean (cm^{-1})			std (cm^{-1})	
λ (cm^{-1})	TCF	CE	Marcus	TCF	CE
620.2	524.9	524.5	597.8	547.3	508.5
920.4	582.0	581.1	859.6	650.8	619.5
1553.6	686.7	685.3	1445.8	822.8	804.9

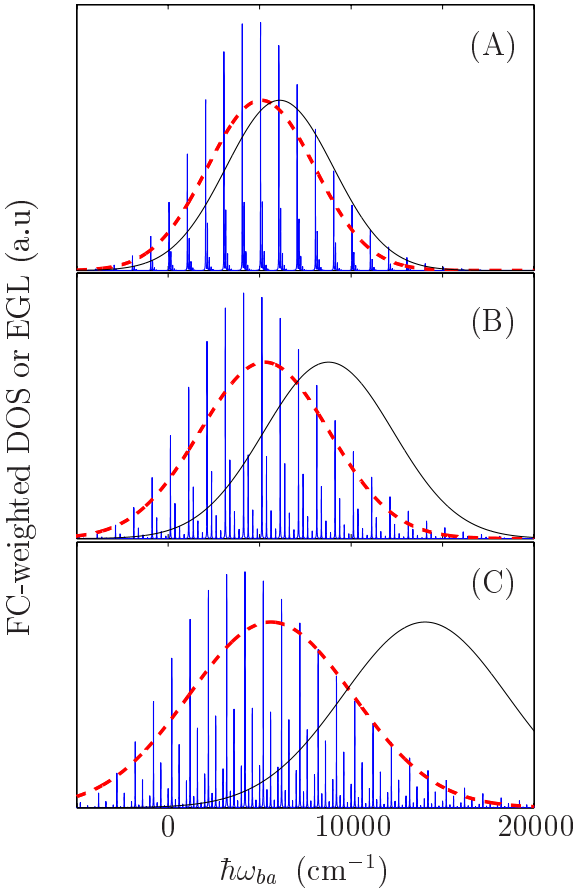
Figure 2:



ω (cm^{-1})	S	T (K)
1000	5	300

	mean (cm^{-1})			std (cm^{-1})	
λ (cm^{-1})	TCF	CE	Marcus	TCF	CE
6175.7	5054.0	5024.5	6124.6	2664.6	1604.8
8920.4	5153.9	5081.1	8791.3	2911.6	1928.7
14054	5298.3	5185.3	13844	3299.5	2420.9

Figure 3:



ω (cm^{-1})	S	T (K)
1000	5	1000

	mean (cm^{-1})			std (cm^{-1})	
λ (cm^{-1})	TCF	CE	Marcus	TCF	CE
6182.4	5092.5	5081.5	6098.1	3269.5	2931.5
8994.0	5295.9	5270.3	8768.5	3823.2	3535.8
14438	5655.6	5617.8	14046	4705.5	4479.9

Figure 4: