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NO2^-/NO2体系电子转移的外电场效应和温度效应

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摘要 用半经典模型研究NO2^-/NO2体系自交换电子转移的反应机理和速率常数,
探讨了外电场对反应过程势能面, 反应能垒及电子转移速率常数的影响, 确定了能垒崩溃的阈值;
讨论了低能垒条件下电子转移反应的速率常数随温度变化的特征。研究表明,
一定方向的外电场能显著降低电子转移反应的活化能垒并提高反应速率常数k, 而对非绝热电子转移反应,
当温度T和活能能垒Ec满足T=2Ec/R时, k取得极大值。

关键词 活化能 反应速度常数 亚硝酸 场效应 温度效应 电子转移 二氧化氮

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Influences of external electric field and temperature on the electron transfer in NO2^-/NO2 system

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Abstract In this article, the self-exchange electron transfer (ET) reaction NO2^-...NO2→NO2...NO2^- has been investigated by using the semiclassical model. The authors have focused on the influence of external electric field upon the diabatic potential energy surfaces and the temperature effect of the rate constant. It has been found that when the applied electric field reached a strength of 5.760× 10^9V.m^-^1, the energy barrier collapsed and therefore the ET reaction became a barrier-free one. It is interesting to note a new feature of the temperature effect on a nonadiabatic ET. Unlike those conclusions in simple collision theory and activated complex theory, there exists a maximum rate constant for a nonadiabatic ET as the value of temperature being 2Ec/R. Discussions have been made for this new feature.

Key words ACTIVATION ENERGY REACTION RATE CONSTANT NITROUS ACID FIELD EFFECT TEMPERATURE EFFECT

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