Supplemetary Material to:

Multiquantum vibrational excitation of NO scattered from Au(111): Quantitative comparison of benchmark data to *ab initio* theories of nonadiabatic molecule-surface interactions

BENCHMARK DATA AND COMPARISON TO IESH THEORY

We report the experimental and theoretical values of this work for vibrational excitation for collisions of NO with Au(111) as a function of surface temperature, T_s, and incidence energy of translation,E_i.The numerical values shown in Tables S1 are the data presented in Fig. 3 of the paper.

E_i = 0.1eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.00035		
323	0.000048			
400		0.00091		
500	0.00069	0.0027		
600		0.0053		0.000053
633	0.0019			
700		0.0085		0.000056
753	0.0036			
800		0.013	0.00014	0.00026
848			0.00028	
873	0.0082			
900		0.018		0.00046
918			0.00048	
973	0.011		0.00073	
1000		0.021		0.00063

E_i = 0.28eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.00023		
323	0.00018			
400		0.00089		
500	0.0012	0.0019		
600		0.0039		0.000013
633	0.0026			
700		0.0067		0.00011
733			0.00007	
753	0.0068			
800		0.0098	0.00014	0.00018
848			0.00015	
900		0.014		0.00025
918			0.00027	
973	0.011		0.00039	
1000		0.018		0.00050

E_i = 0.45eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.00031		
373	0.00076			
400		0.00075		
473	0.0017			
500	0.0012	0.0019		0.000012
573	0.00195			
600		0.0038		0.000037
673	0.00689		0.00013	
700		0.0057		0.000042

746			0.00018	
776	0.01102			
800		0.0087	0.00023	0.000059
878	0.01619		0.00050	
900		0.012		0.00025
923			0.00060	
973	0.020		0.00083	
1000		0.016		0.00040
1073	0.02967		0.0019	

E_i = 0.63eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.00050		
353	0.000058			
400		0.00096		
500	0.00091	0.0018		0.000013
600		0.0035		0.000072
613			0.000037	
633	0.0045			
683			0.00011	
700		0.0058		0.000068
753	0.0076			
800		0.0085	0.00023	0.000093
823			0.00043	
873	0.013			
900		0.012	0.00045	0.00021
973	0.019		0.00078	
1000		0.015		0.00044

E_i = 0.93eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.00096		
338	0.00046			
378	0.0017			
400		0.0016		
436	0.0012			
473	0.0046			
500		0.0023		0.000012
568	0.0041			
600	0.0081	0.0039		0.000040
643	0.0082			
660	0.011		0.00016	
700	0.0166	0.0056		0.000098
727			0.00024	
776			0.00028	
800	0.017	0.0080	0.00034	0.00015
850			0.00043	
873	0.013			
900	0.022	0.011	0.00092	0.00039
951	0.035		0.0012	
988	0.032		0.0010	
1000		0.014		0.00049

E_i = 1.05eV

T_s, K	P_{01}, exp.	P_{01}, theor.	P_{02}, exp.	P_{02}, theor.
300		0.0015		
338	0.00046			
378	0.0017			
400		0.0018		

436	0.0012			
473	0.0046			
500	0.0029	0.0028		0.000036
600	0.0081	0.0039	0.00012	0.000074
630	0.0093		0.00018	
700	0.0166	0.0058	0.00029	0.00011
763	0.017		0.00042	
800	0.017	0.0080	0.00083	0.00018
850			0.00090	
873	0.035			
900	0.022	0.011	0.0018	0.00033
973	0.053		0.0029	
1000		0.013		0.00052

THE QUALITY OF AGREEMENT BETWEEN EXPERIMENT AND THEORY

In the main body of the paper we stated that Pearson's χ^2 (Equation 1) was used to evaluate the quality of the agreement between experimental excitation probabilities and those derived from IESH theory. The χ^2 values were derived for each incidence energy of translation and for each vibrational channel. See Figure S1. From Table 1 one can see that there is not a perfect one-to-correspondence between experimental and theoretical surface temperatures. This required interpolation between theoretical points to obtain a theoretical expectation at each experimental value of T_s. The fitted lines shown in Fig. S1 were used for this purpose. This introduces an uncertainty in the evaluation of the errors, however, one that is comparable to the statistical noise of the trajectory calculation. Figure S2 shows a comparison of experiment and theory on a linear scale.

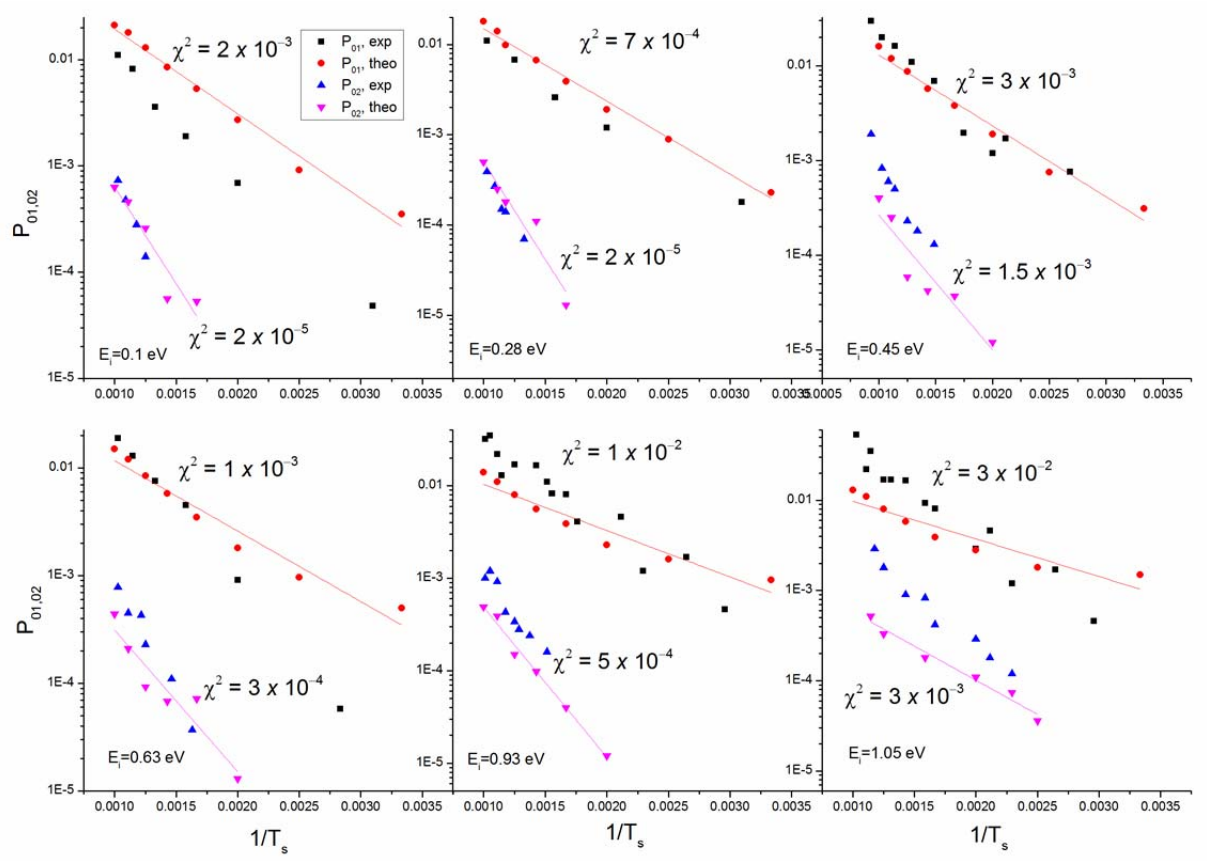

Figure S1: Arrhenius plots of the experimental and theoretical results shown in Table S1. The Arrhenius fits to the theoretical predictions were used in the derivation of the χ^2values. See text.

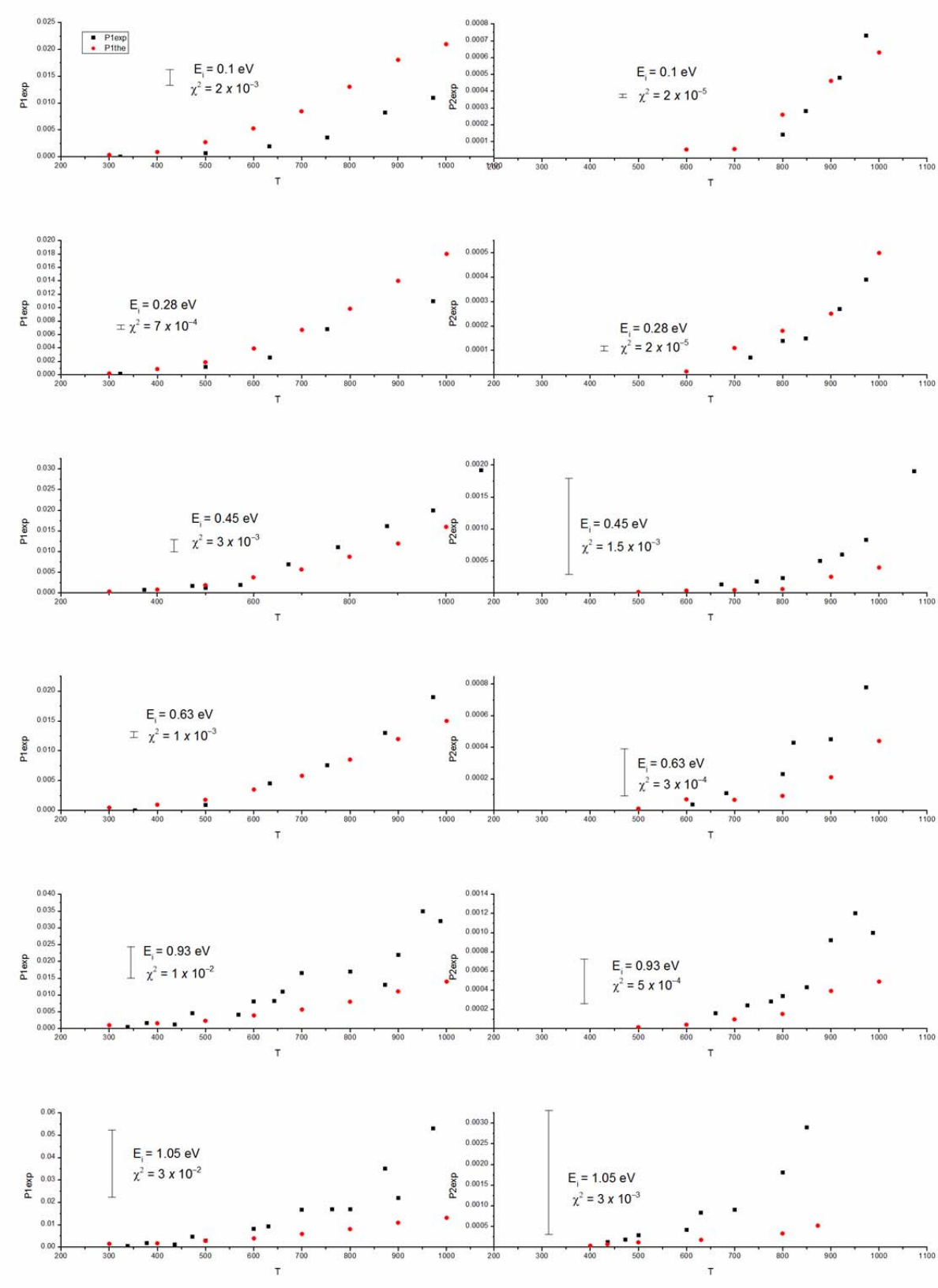

Figure S2: Graphical presentation of the experimental and theoretical results on a linear scale. The data shown here are presents in Table S1. The derived values of Pearson's χ^2 are presented graphically.