Understanding the Effect of Vibrational Excitation in Reaction Dynamics: The Ne + H_2^+(v=0-17, j=1) → NeH^+ + H, Ne + H^+ + H Proton Transfer and Dissociation Cross Sections

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Supplementary Information

Table S1. Cross sections (in Å^2) for the Ne + H_2^+(v=0-17,j=1) → NeH^+ + H reaction at E_{col}=0.7 and 1.7 eV.[a,b]

E_{col} /eV	v	QCT (XYTWM)[i]	QCT this work (PHHJ3)[ii]	QCT (PHHJ3)[i]	QCT this work (LZHH)[ii]	QCT (LZHH)[i]	Experiment (Zhang et al)[iii]	QCT (Zhang et al; PHHJ3)[iii]	CC-RWP (LZHH)[iv] / CS-RWP (PHHJ3)[v]
0.7	**0**	0.26	0.116±0.002 [0.0435±0.0009] (0.187±0.002)	0.10	0.227±0.004 [0.0974±0.002] (0.639±0.004)	0.28	0.264 ± 0.005	0.04±0.05	0.26 / 0.11
	1	2.37	0.920±0.004 [0.900±0.004] (2.744±0.007)	1.40	1.73±0.01 [1.59±0.01] (4.19±0.01)	2.56	1.49 ± 0.06 2.24±0.12 2.18±0.49	0.73± 0.15	3.29 / 1.22
	2	5.0	3.23±0.02 [3.14±0.02] (5.80±0.02)	4.75	3.96±0.02 [3.83±0.02] (6.60±0.02)	5.04	5.10±0.27 5.27±0.22 5.34±0.34	3.05±0.26	6.01 / 3.01
	3	7.53	5.76±0.02 [5.66±0.02] (8.07±0.03)	7.18	6.39±0.02 [6.27±0.02] (8.64±0.03)	7.38	7.38±0.22 7.20±0.37	6.05±0.30	8.43 / 5.02
	4	9.42	8.09±0.03 [8.01±0.03] (9.87±0.03)	9.68	8.50±0.03 [8.40±0.03] (10.16±0.03)	9.17	8.88±0.37 9.69±0.72 9.41±0.33	8.55±0.30	10.04 / 6.42
	5	10.77	10.14±0.03 [10.10±0.03] (11.63±0.03)	10.81	9.98±0.03 [9.93±0.03] (11.34±0.03)	10.77	11.2±0.5 11.04±0.63 10.47±0.79	9.25±0.33	
	6	11.94	11.86±0.03 [11.77±0.03] (13.01±0.03)	14.33	11.10±0.03 [11.02±0.03] (12.13±0.03)	12.28	12.0±0.6 12.70±0.71	11.29±0.36	
	7	11.82	13.41±0.04 [13.30±0.04] (14.39±0.04)	15.57	12.07±0.03 [11.99±0.03] (12.96±0.03)	11.91	12.3±0.6 12.39±0.48	12.04±0.42	
	8	12.97	14.81±0.04 [14.61±0.04] (15.58±0.04)	17.84	12.85±0.03 [12.72±0.03] (13.52±0.03)	13.79	12.4±1.0 13.55±0.57	14.17±0.46	
	9	14.70	16.06±0.05 [16.03±0.05] (17.00±0.04)	20.22	13.26±0.04 [13.25±0.04] (13.97±0.04)	15.24	12.3±0.7 13.52±0.56	14.67±0.46	
	10	13.94	16.96±0.05 *16* [16.65±0.05 *16*] (17.33±0.04 *16*)	21.71	13.75±0.04 [13.53±0.04] (14.10±0.04)	14.07	11.4±0.7 11.62±0.76	16.86±0.50	
	11	14.58	16.41±0.05 *20* [16.18±0.05 *20*] (16.72±0.05 *20*)	24.07	12.29±0.05 [12.10±0.05] (12.53±0.04)	15.49	12.3±0.7 12.21±1.03	16.12±0.52	
	12	15.22	12.97±0.03 *20* [12.89±0.03 *20*] (13.41±0.03 *20*)	24.15	9.80±0.04 [9.68±0.04] (10.06±0.04)	15.17	13.2±1.2 13.02±1.05	15.2±0.5	
	13	12.45	8.97±0.04 *25* [8.84±0.04 *25*] (9.20±0.04 *25*)	22.36	5.79±0.03 [5.72±0.03] (5.93±0.04)	12.16	11.1±1.0 12.58±1.09	11.9±0.5	

	14	14.77	6.24±0.03 *25* [6.19±0.03 *25*] (6.35±0.03 *25*)	25.38	4.12±0.03 [4.08±0.03] (4.25±0.03)	14.12	10.5±1.2	7.69±0.40	
	15	7.44	5.54±0.03 *25* [5.52±0.03 *25*] (5.75±0.03 *25*)	20.66	4.09±0.03 [4.05±0.03] (4.24±0.03)	7.38	9.34±1.0	6.26±0.4	
	16	7.18	0.979±0.02 *25* [0.98±0.02 *25*] (1.00±0.02 *25*)	20.48	2.05±0.03 [2.03±0.03] (2.13±0.03)	6.45	7.14±0.88	3.25±0.35	
	17		1.66±0.01 *25* [1.66±0.01 *25*] (1.73±0.01 *25*)		2.28±0.04 [2.26±0.04] (2.38±0.05)		7.68±0.7		
1.7	**0**	0.30	0.185±0.002 [0.125±0.001] (0.202±0.002)	0.24	0.289±0.003 [0.184±0.002] (0.259±0.002)	0.28	0.38±0.11	0.18±0.04	0.37 / 0.23
	1	1.25	0.670±0.004 [0.656±0.004] (0.935±0.004)	1.00	1.51±0.01 [1.42±0.01] (2.03±0.01)	1.27	1.60±0.06	1.12±0.10	1.60 / 1.09
	2	3.19	2.49±0.02 [2.45±0.02] (3.22±0.02)	2.28	2.88±0.02 [2.83±0.02] (3.80±0.02)	3.26	3.06±0.13	2.52±0.15	3.83 / 3.17
	3	4.79	3.52±0.02 [3.47±0.02] (4.70±0.02)	4.48	3.95±0.02 [3.89±0.02] (5.23±0.02)	4.63	3.57±0.11 4.70±0.19	3.57±0.20	5.40 / 4.58
	4	5.64	4.46±0.02 [4.38±0.02] (5.88±0.02)	5.11	4.87±0.02 [4.78±0.02] (6.32±0.02)	5.16	5.98±0.13 4.65±0.12	4.39±0.20	6.60 / 5.79
	5	6.45	5.43±0.03 [5.35±0.03] (6.95±0.03)	5.89	5.69±0.03 [5.62±0.03] (7.14±0.02)	6.10	6.04±0.25	5.71±0.30	
	6	7.29	6.30±0.02 [6.15±0.02] (7.59±0.02)	7.34	6.22±0.02 [6.10±0.02] (7.28±0.02)	7.05	5.61±0.25 7.14±0.28 6.07±0.42	6.23±0.35	
	7	7.85	6.64±0.03 [6.52±0.03] (7.67±0.03)	8.33	6.05±0.03 [5.97±0.03] (6.76±0.03)	7.61	7.28±0.26 5.95±0.26	6.121±0.30	
	8	6.97	5.90±0.03 [5.78±0.03] (6.36±0.03)	7.99	4.92±0.02 [4.85±0.02] (5.28±0.03)	6.62	3.82±0.27 4.96±0.30	6.57±0.30	
	9	4.76	4.53±0.03 [4.45±0.03] (4.83±0.03)	6.17	3.89±0.02 [3.84±0.02] (4.16±0.03)	4.29	6.25±0.65 4.37±0.19	6.16±0.30	
	10	2.86	3.46±0.02 [3.41±0.02] (3.69±0.03)	4.34	3.27±0.02 [3.24±0.02] (3.48±0.02)	3.27	4.96±0.47	5.02±0.30	
	11	4.60	2.94±0.02 [2.90±0.02] (3.13±0.03)	5.67	2.78±0.02 [2.75±0.02] (2.95±0.02)	4.95	4.48±0.61 3.45±0.14	3.74±0.30	

	12	3.43	2.87±0.02 *16* [2.83±0.02 *16*] (3.05±0.02 *16*)	4.52	1.97±0.02 [1.95±0.02] (2.07±0.02)	3.00	8.22±0.58 6.50±0.78 6.38±0.65	3.05±0.30	
	13	0.85	3.37±0.03 *20* [3.34±0.03 *20*] (3.59±0.03 *20*)	1.31	2.04±0.02 [2.02±0.02] (2.15±0.02)	1.02	5.89±0.86	2.21±0.20	
	14	2.61	2.73±0.03 *20* [2.71±0.02 *20*] (2.90±0.03 *20*)	3.27	1.15±0.02 [1.14±0.02] (1.20±0.02)	2.50	2.39±0.34	2.11±0.20	
	15		0.988±0.02 *20* [0.982±0.02 *20*] (1.04±0.02 *20*)		1.18±0.02 d=16 [1.17±0.02 d=16] (1.24±0.02)d =16				
	16		0.646±0.02 *20* [0.644±0.02 *20*] (0.672±0.02 *20*)		0.826±0.015 [0.822±0.015] (0.871±0.016)				
	17		0.546±0.02 *20* [0.545±0.02 *20*] (0.577±0.02 *20*)		0.488±0.014 [0.487±0.014] (0.519±0.014)				

[a] To make easier the comparison with previous theoretical and experimental results, we have included all these data in the table, where the best QCT results are shown first in all cases. For the QCT calculations of refs. i and iii they correspond to the QCT ZPE corrected in $NeH^+ + H$ products results, while in the present QCT calculations they correspond to the ZPE corrected in all possible non-dissociative products ($NeH^+ + H$ and $Ne + H_2^+$) results. See text.

[b] To show the importance of the ZPE corrections, in the case of the present calculations we have also included the QCT ZPE corrected in $NeH^+ + H$ products results (in brackets) and the standard (non-ZPE conserving) QCT ones (in parentheses). Moreover, the numbers underlined and in italics correspond to the initial distances (ρ_o) considered here for the PHHJ3 PES at high vibrational levels. See text.

Table S2. Cross sections (in Å^2) for the Ne + H_2^+(v=0-17,j=1) → Ne + H^+ + H dissociation process at E_{col}=0.7 and 1.7 eV.[a]

E_{col} /eV	v	QCT this work (PHHJ3)[ii]	QCT (Zhang et al; PHHJ3)[iii]	QCT this work (LZHH)[ii]
0.7	**0**	0	0	0
	1	0	0	0
	2	0	0	0
	3	0	0	0
	4	0	0	0
	5	0	0	0
	6	0	0	0
	7	0	0	0
	8	0	0	0
	9	0	0	0
	10	0.747±0.010	0.2±0.1	0.833±0.011
	11	2.76±0.02	1.59±0.23	4.16±0.03
	12	5.80±0.02	3.32±0.36	8.45±0.04
	13	11.75±0.05	7.46±0.50	13.48±0.04
	14	18.23±0.06	11.8±0.6	15.94±0.05
	15	28.77±0.11	15.2±0.7	20.55±0.06
	16	32.31±0.12	32.6±1.0	22.02±0.06
	17	34.48±0.13		24.62+0.07
1.7	**0**	0	0	0
	1	0	0	0
	2	0	0	0
	3	0	0	0
	4	0.0177±0.0014	0	0.0236±0.0017
	5	0.173±0.005	0.11±0.05	0.323±0.007
	6	0.570±0.008	0.47±0.10	1.22±0.01
	7	1.68±0.02	1.31±0.15	2.82±0.02
	8	4.05±0.02	2.65±0.25	5.38±0.03
	9	6.83±0.03	4.39±0.30	7.67±0.03
	10	9.37±0.04	7.42±0.35	9.76±0.04
	11	12.06±0.04	10.8±0.4	12.13±0.04
	12	14.42±0.05	13.0±0.4	14.23±0.05
	13	18.98±0.06	15.2±0.5	16.01±0.05
	14	20.53±0.07	15.6±0.6	19.47±0.06
	15	30.00±0.08		23.59±0.06
	16	36.09±0.08		27.14±0.09
	17	41.3±0.1		29.6±0.1

[a] ZPE corrections do not affect these QCT cross sections as the dissociative channel is only open at high total energies.

Table S3. Maximum impact parameter (b_{max}) in Å for the $Ne + H_2^+(v=0\text{-}17, j=1) \rightarrow NeH^+ + H$, $Ne + H^+ + H$ reactions.

v	$Ne + H_2^+ \rightarrow NeH^+ + H$			
	E_{col}=0.7 eV		E_{col}=1.7 eV	
	PHHJ3	LZHH	PHHJ3	LZHH
0	2.045	2.038	1.863	1.983
1	2.476	2.571	2.189	2.278
2	2.703	2.747	2.314	2.360
3	2.817	2.832	2.420	2.488
4	2.905	2.927	2.553	2.599
5	3.018	2.999	2.680	2.709
6	3.140	3.081	2.826	2.840
7	3.265	3.170	2.974	2.950
8	3.418	3.277	3.128	3.080
9	3.586	3.383	3.308	3.205
10	3.742	3.528	3.444	3.356
11	3.919	3.662	3.505	3.374
12	4.062	3.871	3.602	3.469
13	4.238	4.103	3.681	3.515
14	4.411	4.260	3.808	3.606
15	4.542	4.368	3.764	3.581
16	4.642	4.422	3.561	3.649
17	4.724	4.349	3.600	3.648
$Ne + H_2^+ \rightarrow Ne + H^+ + H$				
3	-	-	-	-
4	-	-	1.665	1.665
5	-	-	2.639	2.233
6	-	-	2.831	2.664
7	-	-	2.948	2.948
8	-	-	3.188	3.080
9	-	-	3.400	3.205
10	3.248	3.031	3.464	3.356
11	3.681	3.662	3.681	3.681
12	4.075	3.871	3.851	3.851
13	4.238	4.103	4.257	4.021
14	4.507	4.260	4.347	4.347
15	5.304	4.779	4.977	4.779
16	5.500	4.905	5.230	4.984
17	5.600	5.102	5.450	5.103

Table S4. Rovibrational energies of H_2^+(v=0-17,j=1) and associated R_-, R_+, and $\tau_{vib}/2$ values.[a]

v	E(v,j=1) / eV	R_-/Å	R_+/Å	$\tau_{vib}/2$ /s
0	0.1496 (0.1482)	0.9076 (0.9083)	1.2544 (1.2532)	0.7453×10^{-14} (0.7450×10^{-14})
1	0.4209 (0.4174)	0.8225 (0.8233)	1.4368 (1.4347)	0.7894×10^{-14} (0.7888×10^{-14})
2	0.6766 (0.6702)	0.7735 (0.7745)	1.5855 (1.5819)	0.8371×10^{-14} (0.8358×10^{-14})
3	0.9169 (0.9007)	0.7386 (0.7399)	1.7230 (1.7171)	0.8892×10^{-14} (0.8868×10^{-14})
4	1.1424 (1.1267)	0.7117 (0.7134)	1.8563 (1.8468)	0.9469×10^{-14} (0.9426×10^{-14})
5	1.3535 (1.3303)	0.6900 (0.6922)	1.9892 (1.9741)	0.1012×10^{-13} (0.1004×10^{-13})
6	1.5504 (1.5175)	0.6720 (0.6749)	2.1243 (2.1008)	0.1086×10^{-13} (0.1073×10^{-13})
7	1.7335 (1.6884)	0.6569 (0.6605)	2.2640 (2.2280)	0.1172×10^{-13} (0.1149×10^{-13})
8	1.9027 (1.8428)	0.6440 (0.6485)	2.4105 (2.3563)	0.1274×10^{-13} (0.1235×10^{-13})
9	2.0581 (1.9809)	0.6330 (0.6384)	2.5663 (2.4858)	0.1395×10^{-13} (0.1330×10^{-13})
10	2.1995 (2.1025)	0.6236 (0.6300)	2.7345 (2.6160)	0.1543×10^{-13} (0.1437×10^{-13})
11	2.3270 (2.2078)	0.6155 (0.6230)	2.9193 (2.7454)	0.1729×10^{-13} (0.1553×10^{-13})
12	2.4402 (2.2967)	0.6086 (0.6174)	3.1263 (2.8717)	0.1970×10^{-13} (0.1679×10^{-13})
13	2.5389 (2.3691)	0.6028 (0.6129)	3.3637 (2.9905)	0.2297×10^{-13} (0.1808×10^{-13})
14	2.6225 (2.4252)	0.5980 (0.6095)	3.6448 (3.0957)	0.2767×10^{-13} (0.1932×10^{-13})
15	2.6902 (2.4649)	0.5943 (0.6071)	3.9925 (3.1793)	0.3507×10^{-13} (0.2038×10^{-13})
16	2.7411 (2.4882)	0.5915 (0.6058)	4.4533 (3.2328)	0.4858×10^{-13} (0.2110×10^{-13})
17	2.7745 (2.4951)	0.5897 (0.6054)	5.1650 (3.2494)	0.8261×10^{-13} (0.2132×10^{-13})

[a] Exact (quantum calculation) data were derived from the description of the diatomic molecule provided by the LZHH PES, and approximate results (eqs. (2)-(3)) are given between parentheses. See also Figure S1.

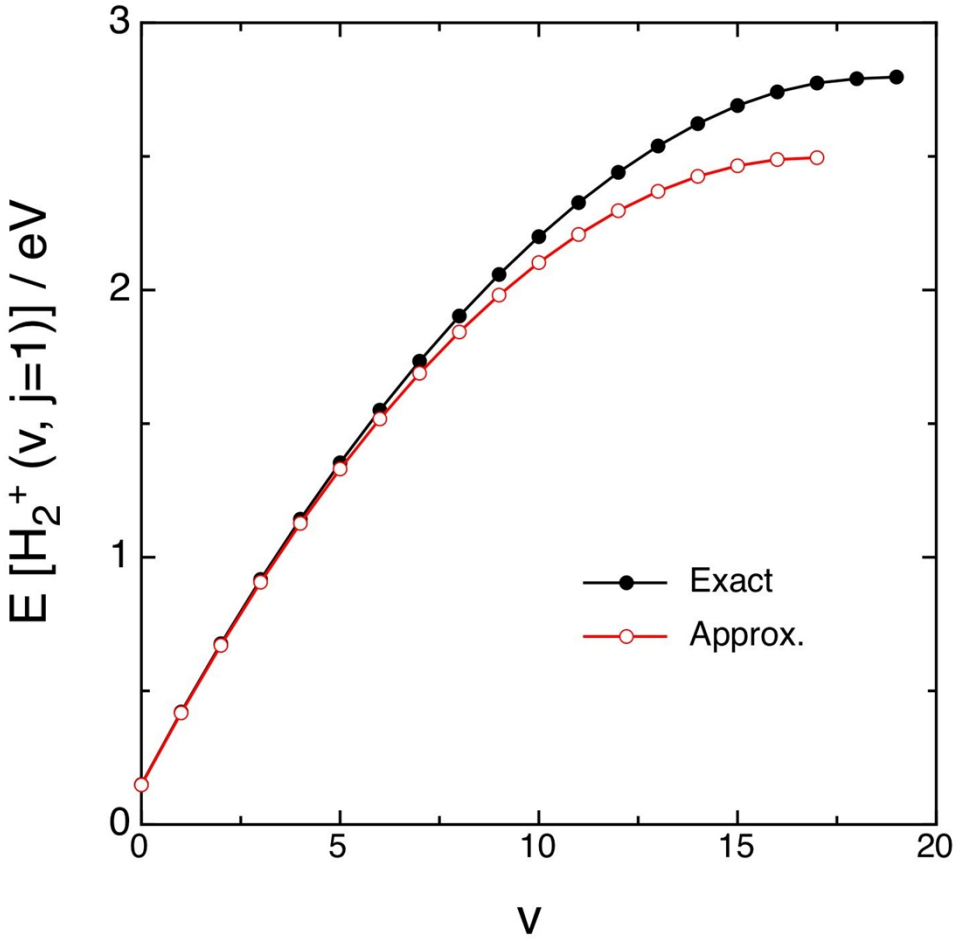

Figure S1. Comparison between the exact (quantum calculation) and approximate (eqs. (2)-(3)) rovibrational energies of H_2^+(v=0-17,j=1). Data derived from the description of the diatomic molecule provided by the LZHH PES.

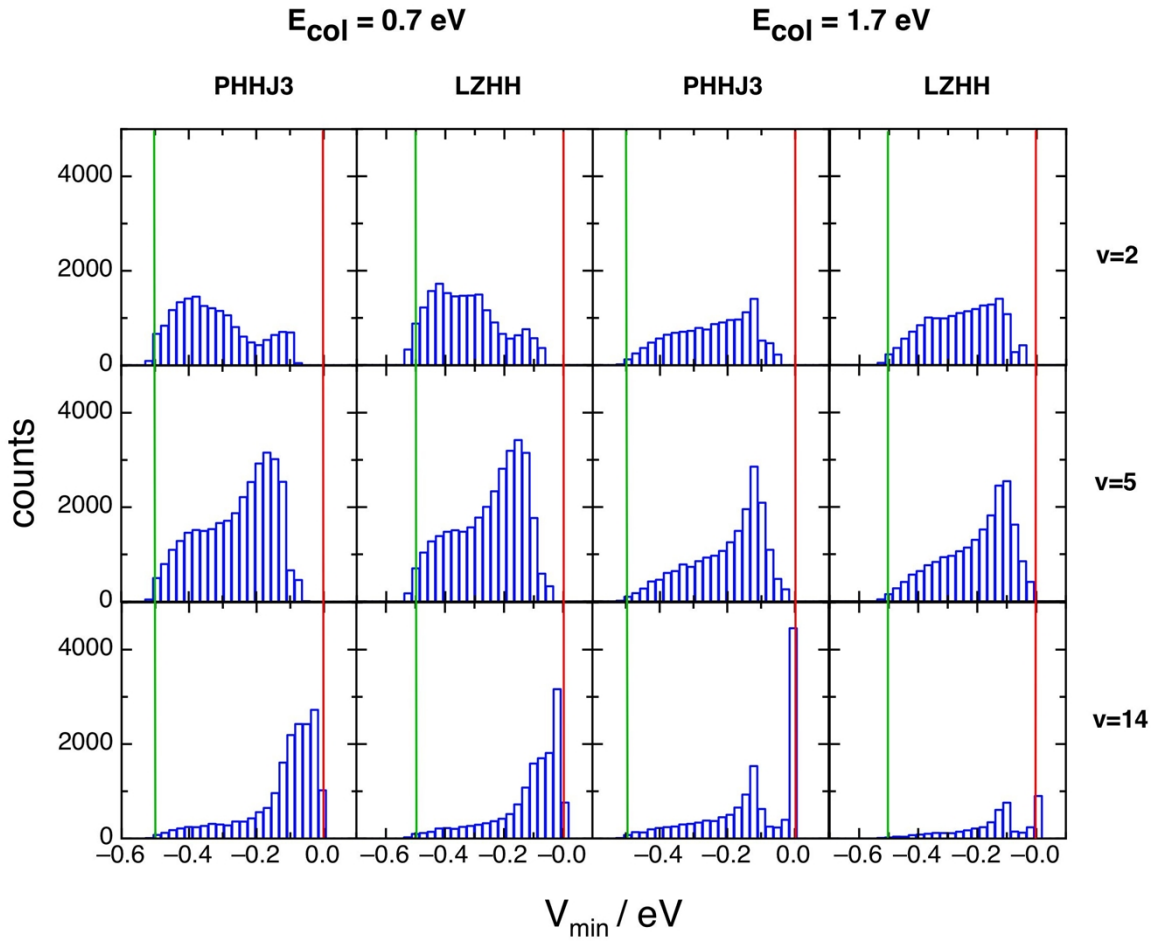

Figure S2. Minimum value of the potential energy of the system (V_{min}) observed in the reactive trajectories for Ne + H_2^+(v=2,5,14,j=1) → NeH^+ + H at E_{col}=0.7 and 1.7 eV on the PHHJ3 and LZHH PESs. The zero of potential energy is taken in Ne + H_2^+ and the lowest potential energy corresponds to the $[NeHH]^+$ collinear minimum, which are indicated by the red and green lines, respectively.

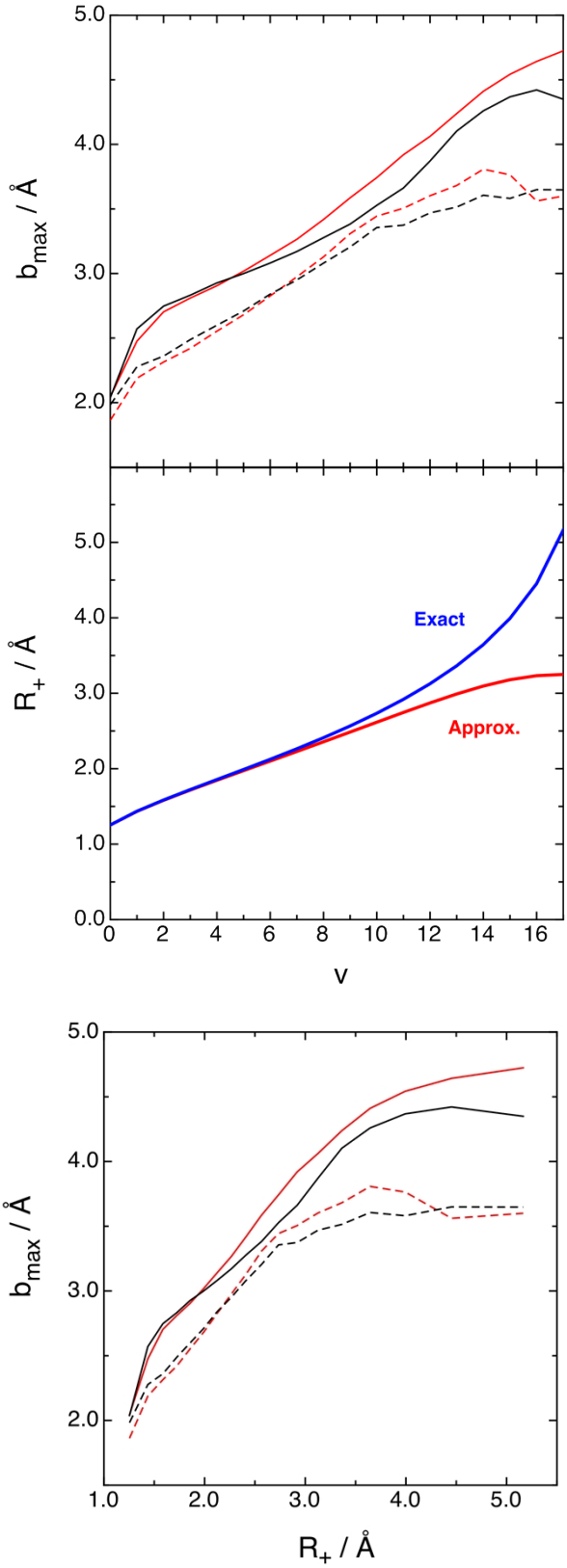

Figure S3. b_{max} *vs.* v (up), R_+ *vs.* v (middle), and b_{max} *vs.* R_+ (down) dependences for the Ne + H_2^+(v=0-17,j=1) → NeH^+ + H reaction: PHHJ3 PES 0.7 eV (———) and 1.7 eV (- - - - -); LZHH PES 0.7 eV (———) and 1.7 eV (- - - - -).

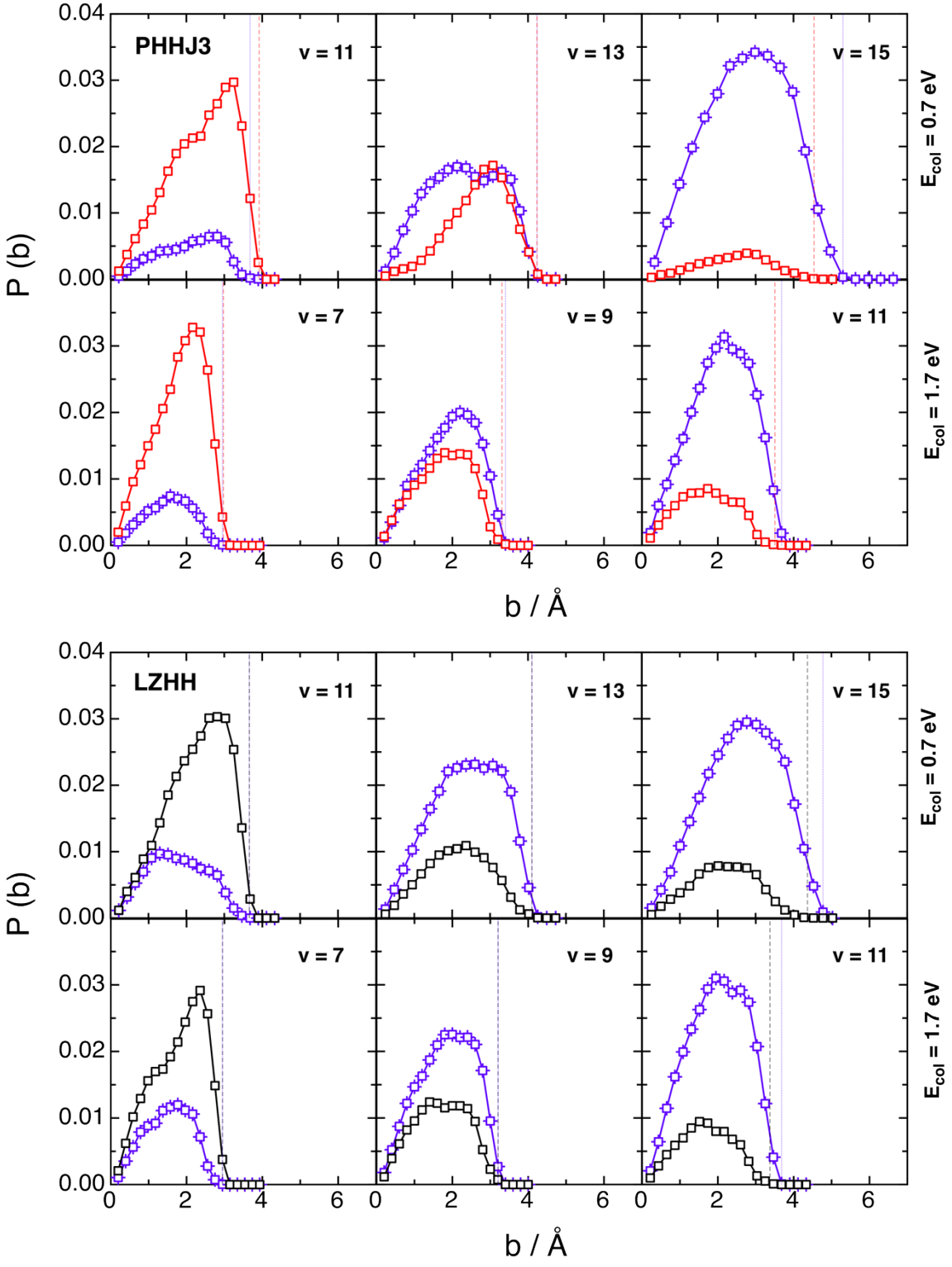

Figure S4. Opacity functions ($P(b)$ vs b) for Ne + $H_2^+(v,j=1)$ → NeH^+ + H (square), Ne + H^+ + H (square with cross) at selected vibrational levels and E_{col}=0.7 and 1.7 eV, on the PHHJ3 (up) and LZHH (down) PESs.

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