

**SUPPLEMENTARY MATERIAL for electronic deposition:****Dynamics of the Cl+H<sub>2</sub>/D<sub>2</sub> reaction: A comparison of crossed molecular beam experiments with quasiclassical trajectory and quantum mechanical calculations****Michele Alagia, Nadia Balucani, Laura Cartechini, Piergiorgio Casavecchia and Gian Gualberto Volpi***Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy***F. Javier Aoiz and Luis Bañares***Departamento de Química Física. Facultad de Química. Universidad Complutense. 28040 Madrid, Spain***Thomas C. Allison, Steven L. Mielke and Donald G. Truhlar***Department of Chemistry, Chemical Physics Program, and Supercomputer Institute, University of Minnesota, Minneapolis, MN 55455-0431, U. S. A.*

Journal: Physical Chemistry Chemical Physics

Date and location of preparation of final version: Dec. 16, 1999, Minneapolis

**APPENDIX A**

Tables A-I through A-IV give numerical and basis set parameters used in the production runs (sets A, C, E, and G) and the convergence checks (sets B, D, F, and H) for each of the systems as well as some statistics concerning basis set sizes for selected *JPS* blocks for some of the energies studied. Details of the basis set notation are presented in table A-V. For the calculations at the lowest two energies, and at  $J = 0$  in all cases, the basis sets used for the convergence checks differ in a sufficient subset of parameters as compared to the production sets to fully test for convergence. For  $J > 0$  at the two highest energies studied, the convergence checks differ from the production set in a sufficient subset parameters except for  $n_{\text{max}}$  and  $N_{23}^{\text{QA}}$ . Convergence with respect to these two parameters was checked separately (as the computational cost and memory requirements increase markedly with these changes) and the results were excellent – differences in the transition probabilities from changes in these two parameters are much smaller than those seen in the other convergence checks. Convergence checks were run for  $J$  equal to 0 and 20; these checks demonstrated that state-to-state transition probabilities with magnitude greater than  $10^{-4}$  were converged to better than 1%.

**Table A–I: Parameter Sets for Cl+H<sub>2</sub> at  $E= 12.04$  kcal mol<sup>-1</sup>.**

	Set A		Set B	
	Cl + H <sub>2</sub>	HCl + H	Cl + H <sub>2</sub>	HCl + H
$j_{\max}(v = 0)$	13	14	15	15
$j_{\max}(v = 1)$	13	14	15	15
$j_{\max}(v = 2)$	11	14	13	15
$j_{\max}(v = 3)$	11	10	13	11
$j_{\max}(v = 4)$	9	–	11	8
$j_{\max}(v = 5)$	–	–	9	–
$j_{\alpha}^d(\text{all } v)$				
max	3	3	4	4
$R_{\alpha 1}^G(a_0)$	5.0	4.2	4.82	4.02
( $a_0$ )	0.36	0.36	0.36	0.36
$c$	1.152	1.152	1.26	1.26
$m$	8	9	9	10
$N_{\alpha}(\text{HO})$	60	60	90	90
$N_{\alpha\alpha}^{\text{QA}}$	40	40	60	60
$N_{12}^{\text{QA}}, N_{23}^{\text{QA}}$	100	0	150	150
$N_{\alpha}^{\text{QV}}$	25	25	50	50
$N_{\alpha}^{\text{QGLV}}$	1	1	2	2

$r_{\alpha,l}^{QV}$	0.3	0.3	0.0	0.0
$r_{\alpha,u}^{QV}$	3.5	3.5	4.0	4.0
$N_{\alpha}(F)$	226	205	299	271
$N_{\alpha}^{FD}$	13	13	13	13
$N_{\alpha,N_{\alpha}}^{FD}(F)$	8	8	8	8
$R_{\alpha 0}^F(a_0)$	1.0	1.0	0.5	0.5
$R_{\alpha,N_{\alpha}(F)+1}^F(a_0)$	18.0	20.0	20.0	22.0
$R_{\alpha,l}^{QR}$	4.0	3.0	3.0	2.0
$R_{\alpha,u}^{QR}$	10.0	10.0	12.0	12.0
$GSS_{\alpha}$	0	0	0	0
$f_{\alpha}^{SD}$	0.9	0.9	0.9	0.9
$N_{\alpha}^{SD}$	30	30	37	33
$N_{\alpha}^{QS}$	28	25	42	40
$N_{\alpha}^{QGL}$	7	7	7	7
$n_{\alpha}^{FR}$	0	0	0	0
$N_{\alpha}(JPS = 0++)$	31	56	41	69
$N_{\alpha}^{open}(JPS = 0++)$	3	13	3	13
$M_{\alpha}^g(JPS = 0++)$	24	117	27	130
$M_{\alpha}^e(JPS = 0++)$	224	387	342	560

$M_\alpha$ ( $JPS = 0_{++}$ )	248	504	369	690
$N_\alpha$ ( $JPS = 20_{++}$ )	195	426	287	531
$N_\alpha^{\text{open}}$ ( $JPS = 20_{++}$ )	9	91	9	91
$M_\alpha^g$ ( $JPS = 20_{++}$ )	65	459	81	586
$M_\alpha^e$ ( $JPS = 20_{++}$ )	768	1386	1440	2400
$M_\alpha$ ( $JPS = 20_{++}$ )	833	1845	1521	2986
$\epsilon_\chi$		$10^{-6}$		$10^{-8}$
$\epsilon_{\text{rad}}$		$10^{-100}$		$10^{-120}$
$\epsilon_t$		$10^{-8}$		$10^{-10}$
$\epsilon_{\mathcal{R}}$		$10^{-8}$		$10^{-10}$
$\epsilon_{\mathcal{B}}$		$10^{-8}$		$10^{-10}$

---

**Table A–II: Parameter Sets for Cl+D<sub>2</sub> at  $E = 10.60$  kcal mol<sup>-1</sup>.**

	Set C		Set D	
	Cl + D <sub>2</sub>	DCl + D	Cl + D <sub>2</sub>	DCl + D
$j_{\max}(v = 0)$	13	20	15	21
$j_{\max}(v = 1)$	13	19	15	20
$j_{\max}(v = 2)$	11	18	13	19
$j_{\max}(v = 3)$	11	16	13	17
$j_{\max}(v = 4)$	9	12	11	13
$j_{\max}(v = 5)$	–	–	9	8
$j_{\alpha}^d(\text{all } v)$		17		17
max	3	3	4	4
$R_{\alpha 1}^G(a_0)$	5.0	4.2	4.82	4.02
$(a_0)$	0.36	0.36	0.36	0.36
$c$	1.152	1.152	1.26	1.26
$m$	8	9	9	10
$N_{\alpha}(\text{HO})$	60	60	90	90
$N_{\alpha\alpha}^{\text{QA}}$	40	40	60	60
$N_{12}^{\text{QA}}, N_{23}^{\text{QA}}$	100	0	150	150
$N_{\alpha}^{\text{QV}}$	25	25	50	50
$N_{\alpha}^{\text{QGLV}}$	1	1	2	2

$r_{\alpha,l}^{QV}$	0.3	0.3	0.0	0.0
$r_{\alpha,u}^{QV}$	3.5	3.5	4.0	4.0
$N_{\alpha}(F)$	226	205	334	320
$N_{\alpha}^{FD}$	13	13	13	13
$N_{\alpha,N_{\alpha}}^{FD}(F)$	8	8	8	8
$R_{\alpha 0}^F(a_0)$	1.0	1.0	0.5	0.5
$R_{\alpha,N_{\alpha}(F)+1}^F(a_0)$	18.0	20.0	20.0	22.0
$R_{\alpha,l}^{QR}$	4.0	3.0	3.0	2.0
$R_{\alpha,u}^{QR}$	10.0	10.0	12.0	12.0
$GSS_{\alpha}$	0	0	0	0
$f_{\alpha}^{SD}$	0.9	0.9	0.9	0.9
$N_{\alpha}^{SD}$	30	30	40	40
$N_{\alpha}^{QS}$	28	25	42	40
$N_{\alpha}^{QGL}$	7	7	7	7
$n_{\alpha}^{FR}$	0	0	0	0
$N_{\alpha}(JPS = 0++)$	31	90	41	104
$N_{\alpha}^{open}(JPS = 0++)$	5	17	5	17
$M_{\alpha}^g(JPS = 0++)$	40	153	45	170
$M_{\alpha}^e(JPS = 0++)$	208	657	324	180

$M_\alpha$ ( $JPS = 0++$ )	248	810	369	1040
$N_\alpha$ ( $JPS = 20++$ )	195	875	287	1014
$N_\alpha^{\text{open}}$ ( $JPS = 20++$ )	25	153	25	153
$M_\alpha^g$ ( $JPS = 20++$ )	137	649	177	828
$M_\alpha^e$ ( $JPS = 20++$ )	704	2412	1350	3850
$M_\alpha$ ( $JPS = 20++$ )	841	3061	1527	4678
$\epsilon_\chi$		$10^{-6}$		$10^{-8}$
$\epsilon_{\text{rad}}$		$10^{-100}$		$10^{-120}$
$\epsilon_t, \epsilon_{\mathbb{B}}$		$10^{-8}$		$10^{-10}$
$\epsilon_{\mathbb{B}}$		$10^{-8}$		$10^{-10}$

---

**Table A-III: Parameter Sets for Cl + D<sub>2</sub> at  $E = 13.498$  kcal mol<sup>-1</sup>.**

	Set E		Set F	
	Cl + D <sub>2</sub>	DCl + D	Cl + D <sub>2</sub>	DCl + D
$j_{\max}(v = 0)$	13	25	15	26
$j_{\max}(v = 1)$	13	25	15	26
$j_{\max}(v = 2)$	13	24	15	25
$j_{\max}(v = 3)$	12	23	14	24
$j_{\max}(v = 4)$	11	22	13	23
$j_{\max}(v = 5)$	10	-	12	10
$j_{\max}(v = 6)$	-	-	10	-
$j^d(\text{all } v)$		13	15	13
$\max(v = 0, 1)$	4	7	4	7
$\max(v > 1)$	4	4	4	4
$R_1^G$ (a <sub>0</sub> )	4.7	3.9	4.55	3.75
(a <sub>0</sub> )	0.30	0.30	0.30	0.30
$c$	0.96	0.96	1.05	1.05
$m$	11	10	12	11
$N$ (HO)	60	60	90	90
$N^{QA}$	40	40	60	60
$N_{12}^{QA}, N_{23}^{QA}$	100	0	150	0
$N^{QV}$	25	25	100	100
$N^{QGLV}$	1	1	4	4
$r_1^{QV}$	0.5	0.5	0.3	0.3
$r_u^{QV}$	3.5	4.0	5.0	4.5
$N$ (F) ( $J < 35$ )	492	247	670	327

$N(F)(J < 35)$	646	247	880	327
$N^{FD}$	13	13	13	13
$N_{,N}^{FD}(F)$	8	8	8	8
$R_0^F(a_0)$	2.0	1.0	1.0	0.5
$R_{,N(F)+1}^F(a_0)(J < 35)$	34.0	20.0	39.0	22.0
$R_{,N(F)+1}^F(a_0)(J < 35)$	44.67	20.0	51.67	22.0
$R_{,l}^{QR}$	4.0	3.2	2.8	2.0
$R_{,u}^{QR}$	12.0	12.0	14.0	14.0
$GSS$	0	0	0	0
$f^{SD}$	0.9	0.9	0.9	0.9
$N^{SD}$	30	30	40	40
$N^{QS}(J < 35)$	66	31	90	41
$N^{QS}(J < 35)$	88	31	120	41
$N^{QGL}$	7	7	7	7
$n^{FR}$	0	0	0	0
$N(JPS = 0++)$	40	124	52	140
$N^{open}(JPS = 0++)$	8	32	8	32
$M^g(JPS = 0++)$	88	320	96	352
$M^e(JPS = 0++)$	352	920	528	1188
$M(JPS = 0++)$	440	1240	624	1540
$N(JPS = 40++)$	268	1603	390	1798
$N^{open}(JPS = 40++)$	40	308	40	308
$M^g(JPS = 40++)$	320	2108	348	2308
$M^e(JPS = 40++)$	1496	4900	2280	6226
$M(JPS = 40++)$	1816	7008	2628	8534

 $10^{-6}$  $10^{-8}$

rad	$10^{-100}$	$10^{-120}$
t	$10^{-6}$	$10^{-8}$
W	$10^{-6}$	$10^{-8}$
B	$10^{-6}$	$10^{-8}$

---

**Table A-IV: Parameter Sets for Cl + D<sub>2</sub> at  $E = 14.670$  kcal mol<sup>-1</sup>.**

	Set G		Set H	
	Cl + D <sub>2</sub>	DCl + D	Cl + D <sub>2</sub>	DCl + D
$j_{\max}(v = 0)$	13	25	15	26
$j_{\max}(v = 1)$	13	25	15	26
$j_{\max}(v = 2)$	13	24	15	25
$j_{\max}(v = 3)$	12	23	14	24
$j_{\max}(v = 4)$	11	22	13	23
$j_{\max}(v = 5)$	10	-	12	10
$j_{\max}(v = 6)$	-	-	10	-
$j^d(\text{all } v)$		13		13
$\max(v = 0, 1)$	4	7	4	7
$\max(v > 1)$	4	4	4	4
$R_1^G$ (a <sub>0</sub> )	4.7	3.9	4.55	3.75
(a <sub>0</sub> )	0.30	0.30	0.30	0.30
$c$	0.96	0.96	1.05	1.05
$m$	11	10	12	11
$N$ (HO)	60	60	90	90
$N^{\text{QA}}$	40	40	60	60
$N_{12}^{\text{QA}}, N_{23}^{\text{QA}}$	100	0	150	0
$N^{\text{QV}}$	25	25	100	100
$N^{\text{QGLV}}$	1	1	4	4
$r_1^{\text{QV}}$	0.5	0.5	0.3	0.3
$r_u^{\text{QV}}$	3.5	4.0	5.0	4.5
$N$ (F)	261	247	355	327
$N^{\text{FD}}$	13	13	13	13

$N_{,N}^{FD} (F)$	8	8	8	8
$R_0^F (a_0)$	2.0	1.0	1.0	0.5
$R_{,N}^F (F)+1 (a_0)$	18.0	20.0	20.0	22.0
$R_{,l}^{QR}$	4.0	3.2	2.8	2.0
$R_{,u}^{QR}$	12.0	12.0	14.0	14.0
$GSS$	0	0	0	0
$f^{SD}$	0.9	0.9	0.9	0.9
$N^{SD}$	30	30	40	40
$N^{QS}$	33	31	45	41
$N^{QGL}$	7	7	7	7
$n^{FR}$	0	0	0	0
$N (JPS = 0++)$	40	124	52	140
$N^{open} (JPS = 0++)$	9	37	9	37
$M^g (JPS = 0++)$	99	370	108	407
$M^e (JPS = 0++)$	341	870	516	1133
$M (JPS = 0++)$	440	1240	1212	1540
$N (JPS = 40++)$	268	1603	390	1798
$N^{open} (JPS = 40++)$	45	391	45	391
$M^g (JPS = 40++)$	375	2551	408	2791
$M^e (JPS = 40++)$	1441	4500	2220	5786
$M (JPS = 40++)$	1816	7051	2628	8577
		$10^{-5}$		$10^{-7}$
rad		$10^{-100}$		$10^{-120}$
t		$10^{-6}$		$10^{-8}$
W		$10^{-6}$		$10^{-8}$
B		$10^{-6}$		$10^{-8}$

---

**Table A–V: Description of Scattering Basis Set Parameters Used in Tables A–I through A–IV.**

$\alpha$	quantum number associated with a particular asymptotic arrangement. For the present work, $\alpha=1$ corresponds to Cl + HH', $\alpha=2$ corresponds to HCl + H', and $\alpha=3$ corresponds to H'Cl + H. Thus, $\alpha=2$ and $\alpha=3$ represent indistinguishable arrangements.
$j_{\max}(v)$	maximum value of the rotational quantum number for vibrational level $v$ included in the vibrational-rotational-orbital basis.
$j_{\alpha}^d(v)$	number of rotational states that are fully coupled in the distorted waves. Channels with $j > j_{\alpha}^d(v)$ are treated as uncoupled in the distorted waves, as explained in Ref 33. This quantity needs to be specified only for open $v$ since we use Green's function as basis functions only in open channels.
max	maximum allowed value of the body-frame projection of the total angular momentum.
$R_{\alpha}^G$	value of $R_{\alpha}$ , the mass-scaled atom-to-diatom distance as defined in Ref 33, at the center of the innermost radial Gaussian function. Radial Gaussians are used both directly as outgoing wave basis functions and to generate half-integrated Green's functions.
	spacing in $R_{\alpha}$ between successive radial Gaussians.
$c$	radial Gaussian overlap parameter which determines the widths of the Gaussian functions as explained in Ref 35.
$m$	number of basis functions per channel.
$N_{\alpha}(\text{HO})$	number of harmonic oscillator basis functions used to expand the diatomic adiabatic vibrational eigenfunctions. These are used, in turn, as vibrational basis functions for the scattering calculations.
$N_{\alpha\alpha}^{\text{QA}}$	number of points in the Gauss-Legendre quadrature used in the single arrangement angular quadrature.
$N_{12}^{\text{QA}}, N_{23}^{\text{QA}}$	number of points in the Gauss-Legendre quadrature used in the multi-arrangement angular quadrature.
$N_{\alpha}^{\text{QV}}$	total number of points in the quadratures of the interaction potential over the vibrational coordinate.
$N_{\alpha}^{\text{QGLV}}$	number of points in each segment of the Gauss-Legendre quadrature of the interaction potential.
$r_{\alpha,1}^{\text{QV}}$	lower bound of the mass-scaled vibrational coordinate $r_{\alpha}$ which is used in the integration of the interaction potential.
$r_{\alpha,u}^{\text{QV}}$	upper bound of the mass-scaled vibrational coordinate $r_{\alpha}$ which is used in the integration of the interaction potential.

$N_\alpha(F)$	total number of points in the finite difference grid used for the calculation of the regular solution of the distortion problems and the half-integrated Green's functions.
$N_\alpha^{FD}$	number of points used in the representation of the second derivative operator in the main body of the finite difference grid.
$N_{\alpha, N_\alpha}^{FD}(F)$	number of points used in the representation of the second derivative operator at the last grid point.
$R_{\alpha 0}^F$	location of the lower finite difference boundary condition point.
$R_{\alpha, N_\alpha(F)+1}^F$	location of the upper finite difference boundary condition point.
$R_{\alpha, l}^{QR}$	lower bound of the region of $R_\alpha$ over which quadratures of the variational function are carried out.
$R_{\alpha, u}^{QR}$	upper bound of the region of $R_\alpha$ over which quadratures of the variational function are carried out.
$GSS_\alpha$	grid spacing scheme for the radial quadrature grids. The grid spacing schemes are discussed in Ref 33.
$f_\alpha^{SD}$	stepsize decrease factor for the spacing of the final finite difference grid points.
$N_\alpha^{SD}$	number of points appended to the main part of the finite difference grid with geometrically decreasing spacing.
$N_\alpha^{QS}$	number of repetitions of Gaussian quadrature used in the generation of the finite difference grid and the integrations over $R_\alpha$ .
$N_\alpha^{QGL}$	number of points in the Gaussian quadrature used in the generation of the finite difference grid and the integrations over $R_\alpha$ .
$n_\alpha^{FR}$	number of extra points inserted between neighboring points in the third step of the finite difference grid generation scheme as explained in Ref 33.
$N_\alpha$	number of channels included in arrangement $\alpha$ .
$N_\alpha^{open}$	number of open channels in arrangement $\alpha$ .
$M_\alpha^g$	total number of radial half-integrated Green's functions.
$M_\alpha^e$	total number of radial Gaussians used as $+2$ basis functions for the outgoing wave.
$M_\alpha$	total number of radial functions per channel.
$\epsilon_\chi$	vibrational screening parameter. (All screening parameters are described in Refs 30 and 33.)
$\epsilon_{rad}$	radial screening parameter.
$\epsilon_t$	translational basis screening parameter.

☞ screening parameter involving the **W** matrix.

☞ screening parameter involving the **B** matrix.

---

---