Electronic Supplementary Information

Nonadiabatic quantum dynamics calculations of transition state spectroscopy of I + HI and I + DI reactions: the existence of long life vibrational bonding resonances[†]

Toshiyuki Takayanagi[*]
Department of Chemistry
Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama City, Saitama 338-8570, JAPAN

Brief descriptions of *Ab initio* electronic structure calculations

Details of the *ab initio* calculations were described in Ref. 1. We employed the multi-reference configuration interaction plus Davidson correction (MRCI+Q) level to construct the potential energy surfaces of the neutral I + HI reaction system. All the calculations were performed using the MOLPRO program[2] with C_s symmetry. The molecular orbitals used in the MRCI+Q calculation were optimized with the full-valence state-average CASSCF (complete-active-space self-consistent-field) wavefunction, where seven states (4×A' + 3×A" states) were averaged. The augmented cc-pVQZ basis set[3] with additional diffuse functions was used for H while the effective-core SDB-aug-cc-pVTZ basis set[4] was used for I. The lowest seven electronic states (4×A' + 3×A" states) were obtained from the MRCI+Q calculations. These seven states were subsequently used in the Breit-Pauli spin-orbit CI calculations to obtain the final potential energy values for the lowest three electronic states, which are asymptotically correlating to I($^2P_{3/2}$ and $^2P_{1/2}$) + HI($X^1\Sigma$). The above *ab initio* computations yielded the spin-orbit splitting of an isolated I atom to be 0.933 eV which compares well with the experimental value of 0.943 eV.[5] For the IHI$^-$ anion, electronic structure calculations were performed at the CCSD(T) level of theory with the same basis sets used in the neutral system.

The above *ab initio* calculations were done at the geometrical grid points described by the three internal coordinates, R_1(I$_1$–H) and R_2(I$_2$–H) distances, and $\angle$I$_1$–H– I$_2$ angle. 51 points were used for R_1 in the range of 1–8 Å, while 21 points in the range of 1–3 Å were chosen for R_2. As for the $\angle$I$_1$–H– I$_2$ angle, 20 points were chosen in the range of 20–180°. The final potential energy surfaces were symmetrized with the respect to the equivalent exchange of I$_1$ and I$_2$. A total of 21420 points were generated. A cubic spline interpolation technique has been employed to obtain the potential energy values as well as spin-orbit coupling values at a desired set of nuclear coordinates.

References

1. T. Yoshida, K. Sato and T. Takayanagi, First-principles simulations of transition state spectra of the I + HI and I + DI reactions and vibrational bonding in IMuI, *Chem. Phys*. 2015, **457**, 51–56.
2. MOLPRO is a package of *ab initio* programs written by H.-J. Werner, P.J. Knowles, G. Knizia, F.R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K.R. Shamasundar, T.B. Adler, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, S.J. McNicholas, W. Meyer, M.E. Mura, A. Nicklaß, D.P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, see http://www.molpro.net
3. T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys*., 1989, **90**, 1007–1023.
4. J. M. L. Martin and A. Sundermann, Correlation consistent valence basis sets for use with the Stuttgart-Dresden-Bonn relativistic effective core potentials: the atoms Ga–Kr and In-Xe. *J. Chem. Phys*., 2001, **114**, 3408–3420.
5. NIST Chemistry WebBook. http://webbook.nist.gov/chemistry/.

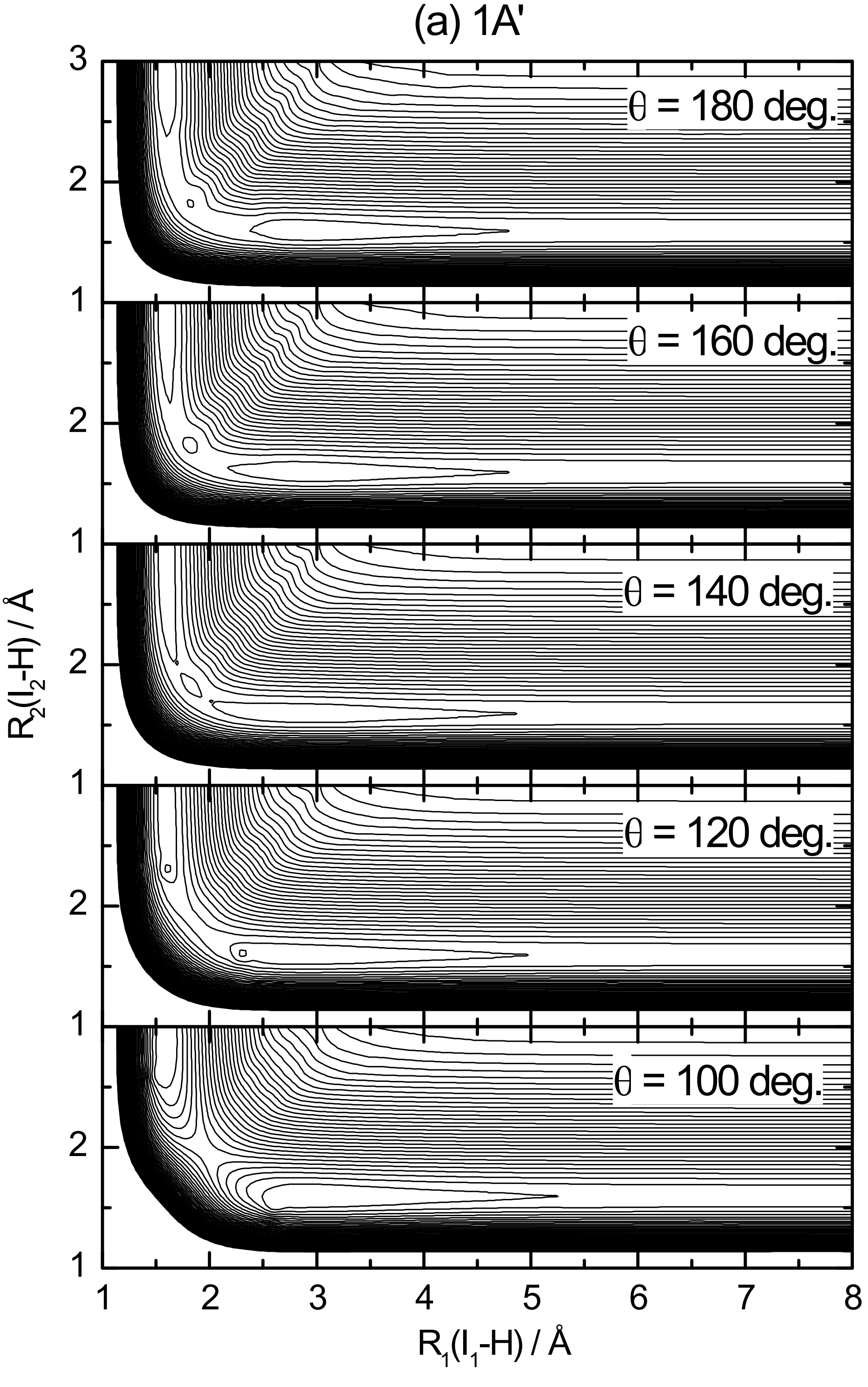
(a) 1A'
θ = 180 deg.
θ = 160 deg.
θ = 140 deg.
θ = 120 deg.
θ = 100 deg.
R$_2$(I$_2$-H) / Å
R$_1$(I$_1$-H) / Å
1
2
3
4
5
6
7
8

Fig. S1

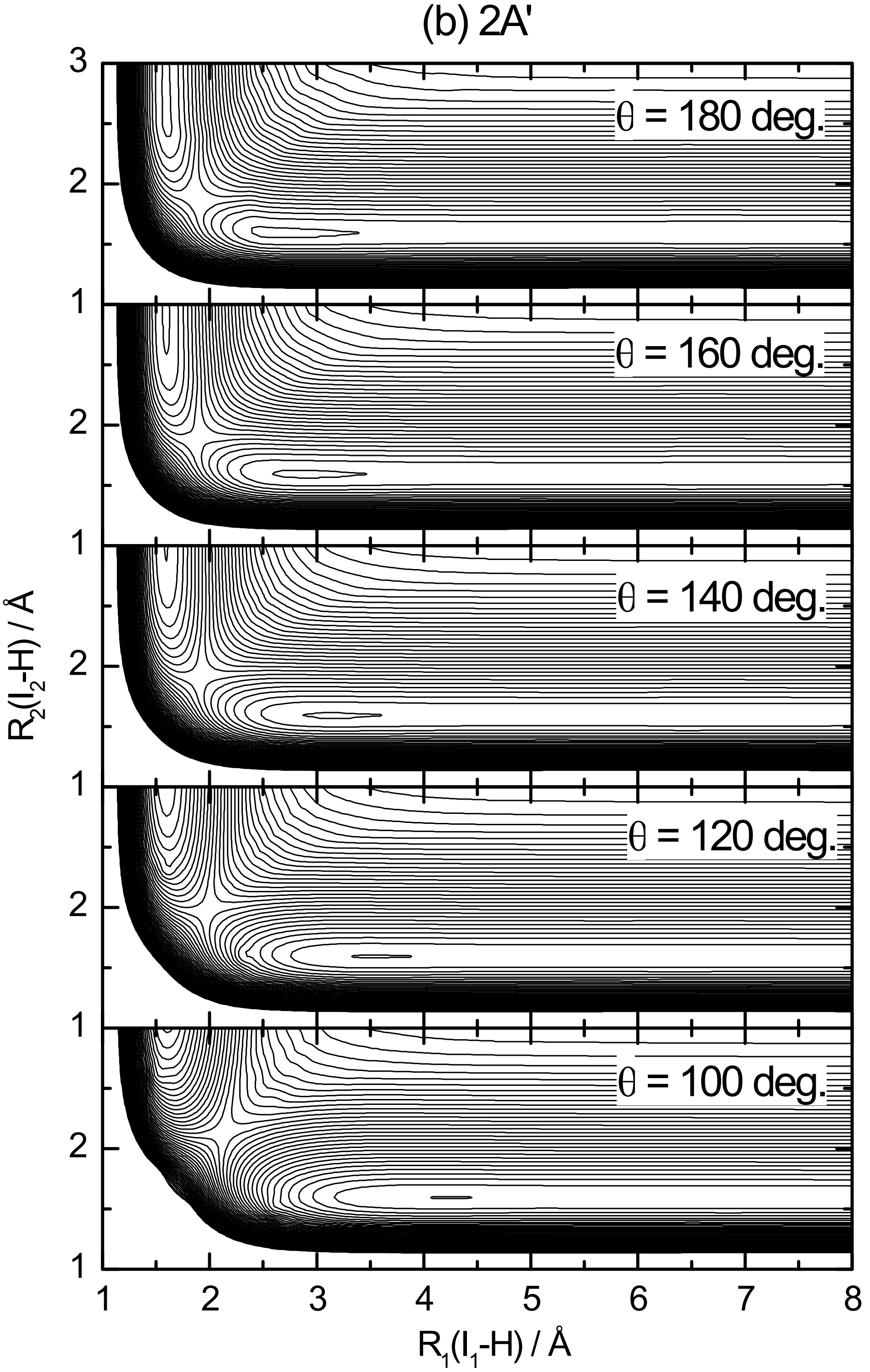

Fig. S1 (continued)

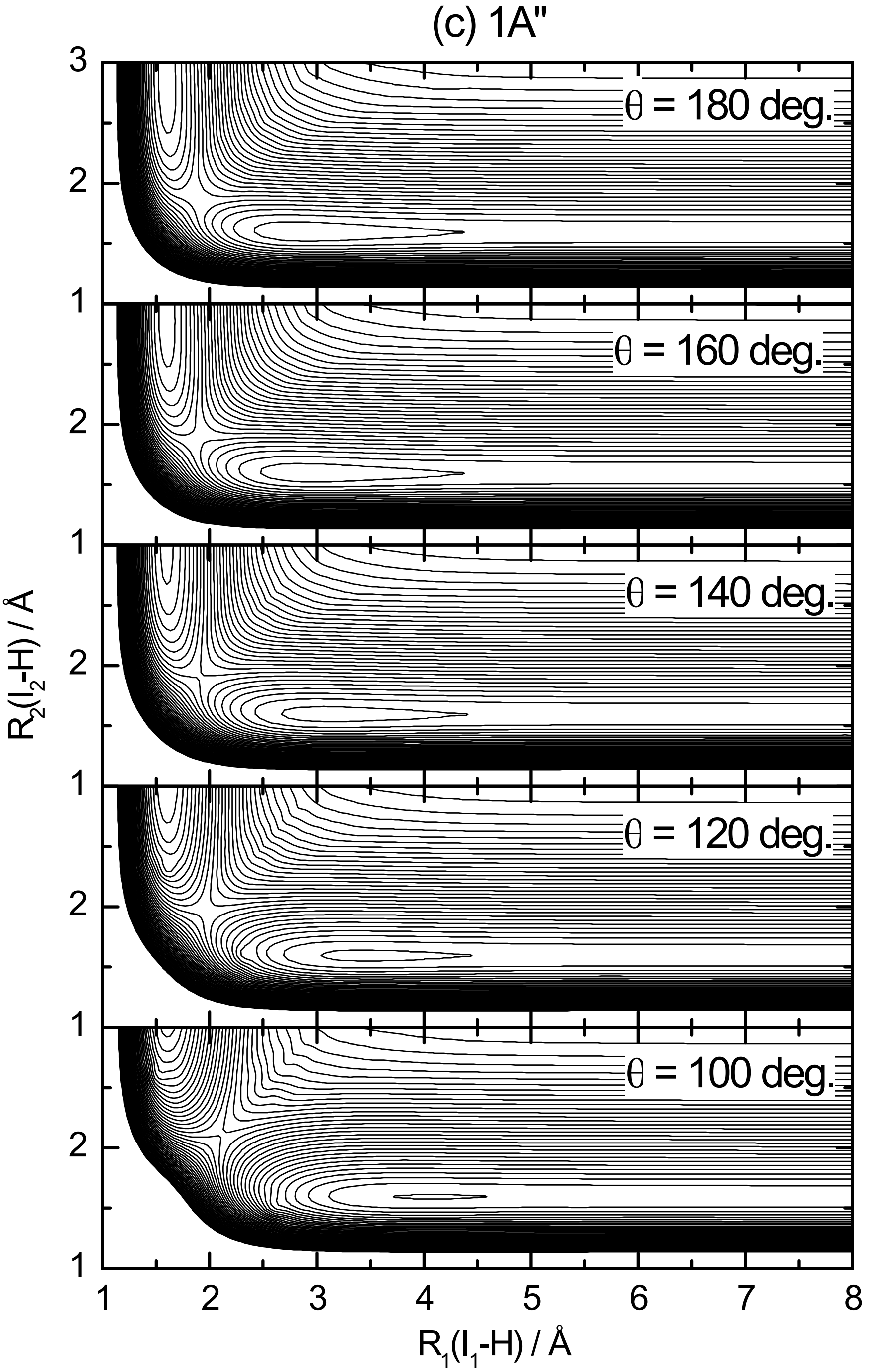

Fig. S1

Contour plots of the lowest three spin-free potential energy surfaces as a function of R_1 and R_2 for some selected $\angle I_1$–H– I_2 angle (θ). The contour increment is set to 0.1 eV. These three ($1^2A'$, $2^2A'$ and $1^2A''$) surfaces were used in the diagonal elements of the (3 × 3) diabatic potential energy surface matrix (see main text).

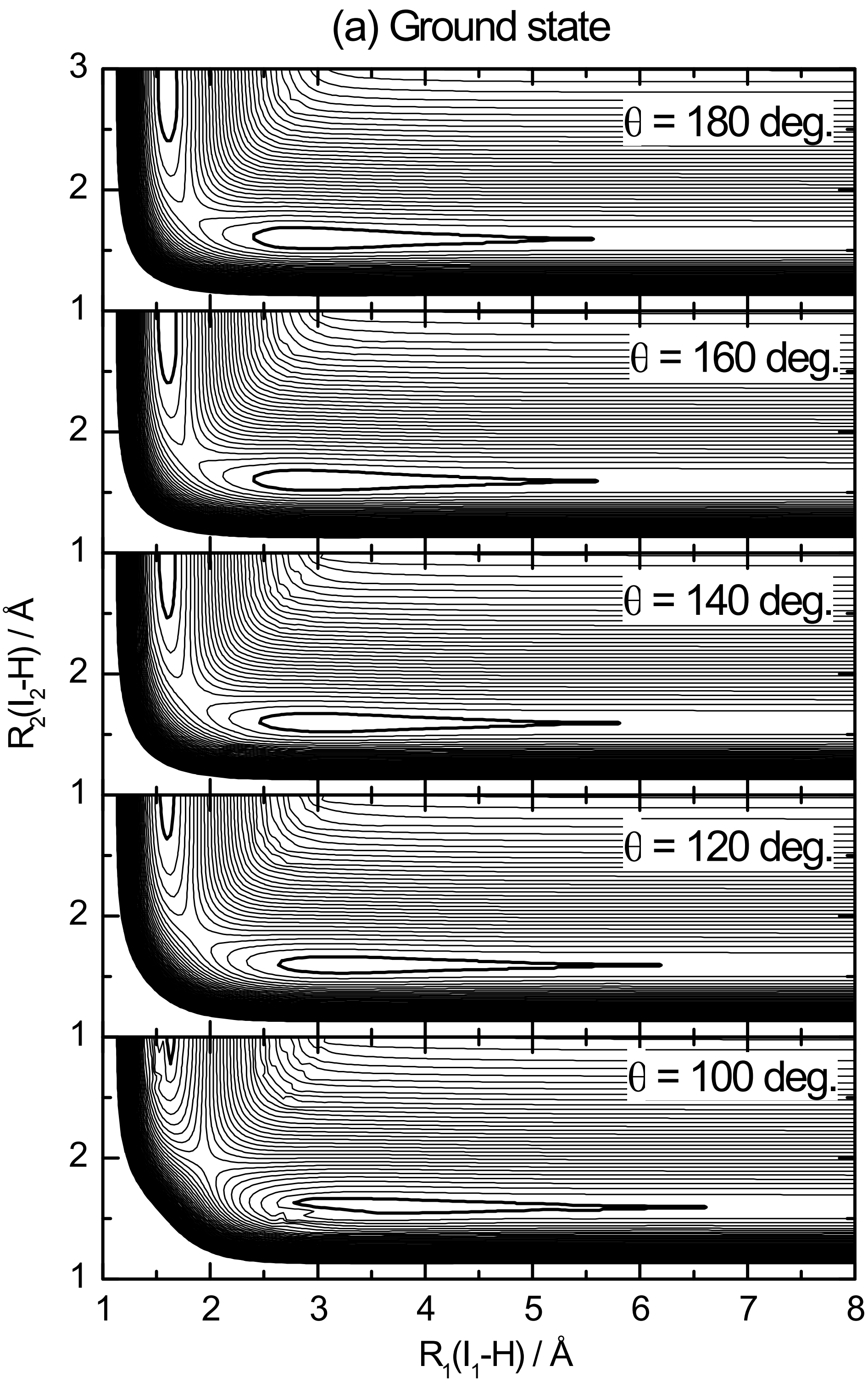
(a) Ground state
θ = 180 deg.
θ = 160 deg.
θ = 140 deg.
θ = 120 deg.
θ = 100 deg.
$R_2(I_2\text{-}H)$ / Å
$R_1(I_1\text{-}H)$ / Å
1
2
3
4
5
6
7
8

Fig. S2

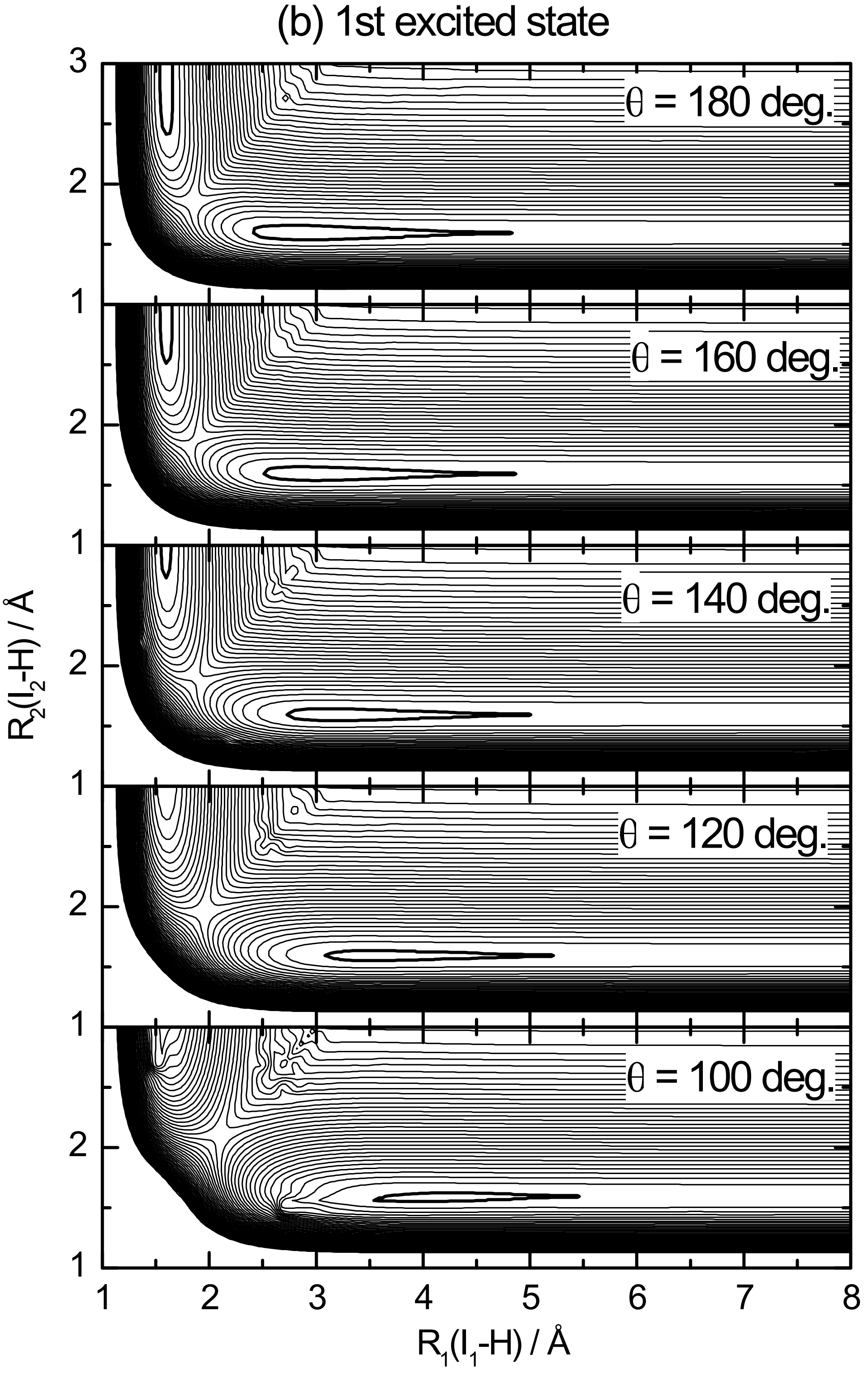

Fig. S2 (continued)

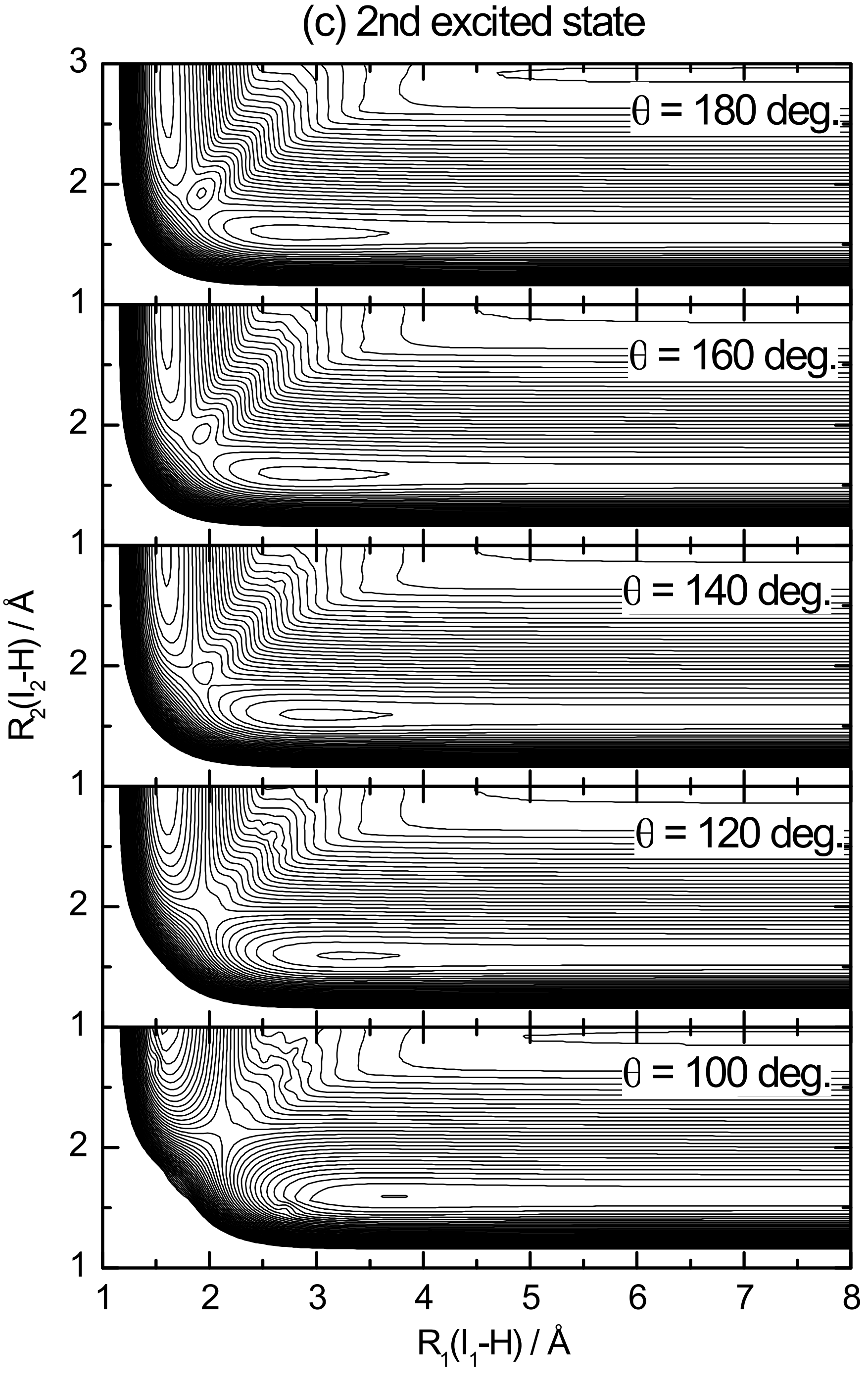

Fig. S2

Contour plots of the lowest three adiabatic potential energy surfaces as a function of R_1 and R_2 for some selected ∠I_1–H– I_2 angle (θ) obtained from the diagonalization of the (3 × 3) diabatic potential energy surface matrix (see main text). The contour increment is set to 0.1 eV.

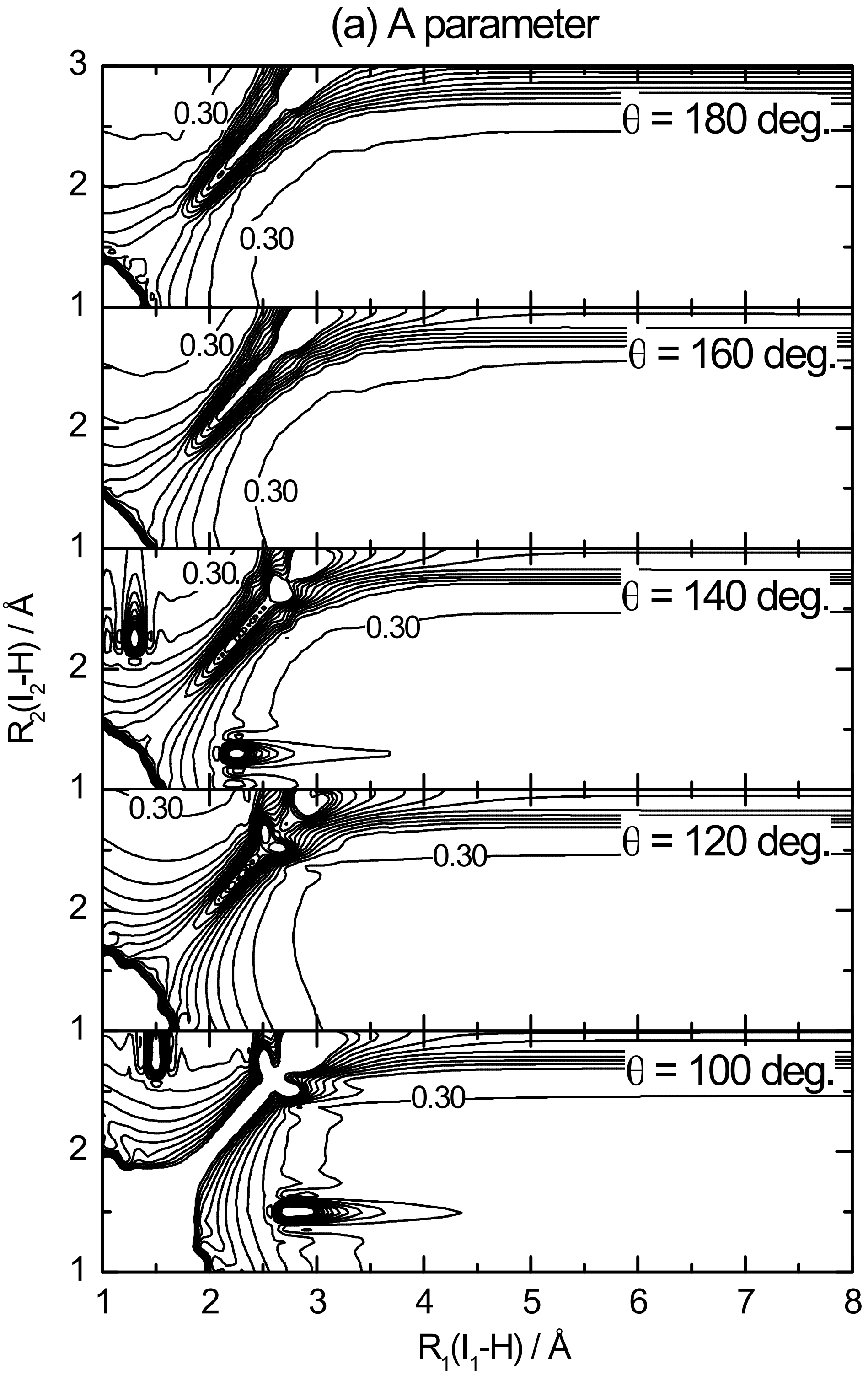
(a) A parameter
θ = 180 deg.
θ = 160 deg.
θ = 140 deg.
θ = 120 deg.
θ = 100 deg.
0.30
R2(I2-H) / Å
R1(I1-H) / Å
1
2
3
4
5
6
7
8

Fig. S3

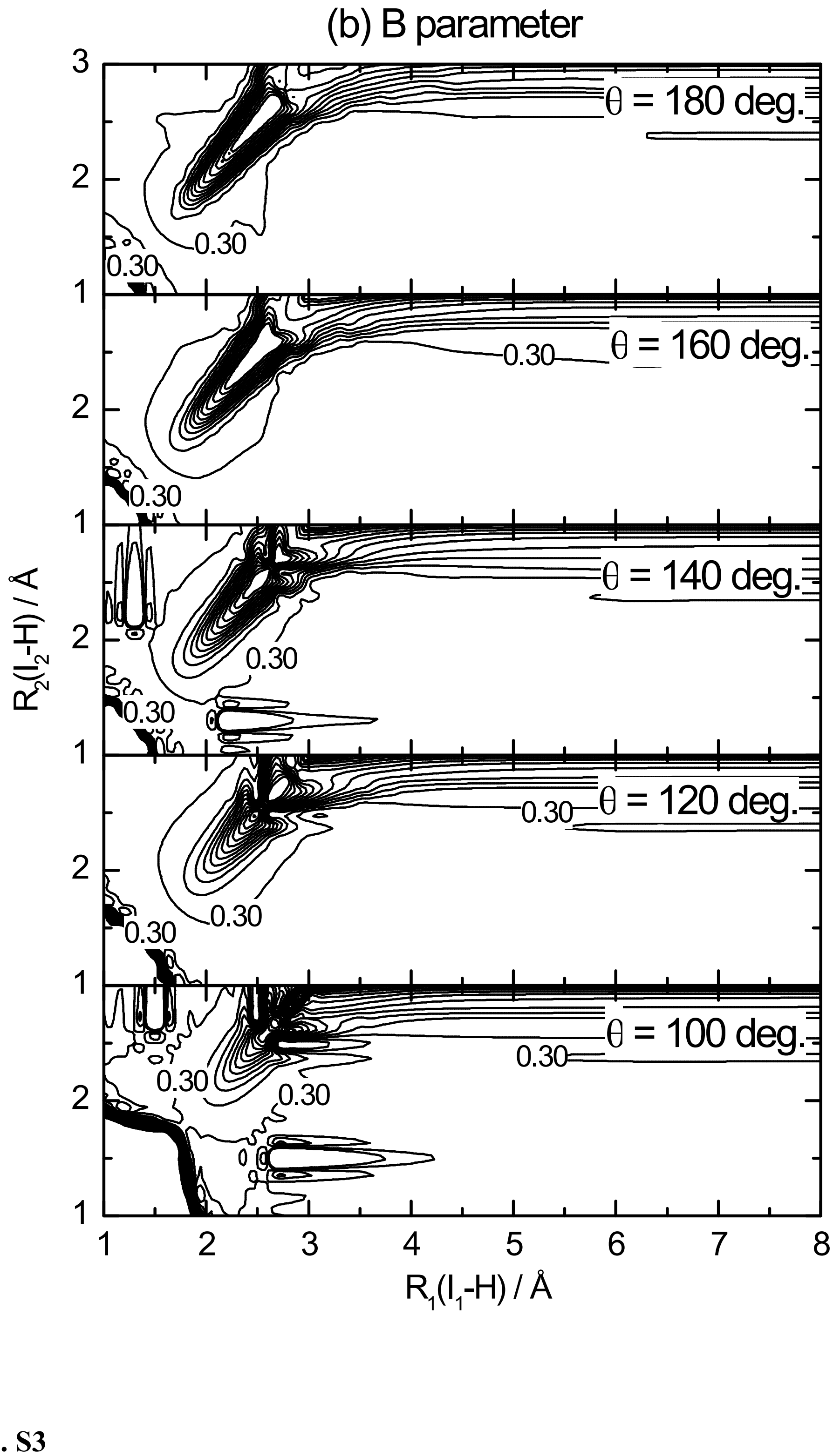

Fig. S3

Contour plots of the spin-orbit coupling terms of (a) A and (b) B as a function of R_1 and R_2 for some selected ∠I$_1$–H– I$_2$ angle (θ) (see main text). The contour increment is set to 0.02 eV.

Table S1

Selected spin-orbit parameters (in units of cm^{-1}) as a function of the I–H–I internal coordinates. Notice that a total of 21420 *ab initio* points were calculated.

R(I$_1$–H) / Å	R(I$_2$–H) / Å	∠I$_1$–H– I$_2$ / deg.	A / cm^{-1}	B / cm^{-1}
5.000	1.000	180.000	2477.554	2477.582
5.000	1.100	180.000	2477.205	2477.255
5.000	1.200	180.000	2468.720	2472.820
5.000	1.300	180.000	2470.327	2475.521
5.000	1.400	180.000	2480.887	2483.353
5.000	1.500	180.000	2503.339	2495.146
5.000	1.600	180.000	2506.788	2493.980
5.000	1.700	180.000	2508.080	2491.397
5.000	1.800	180.000	2504.678	2490.047
5.000	1.900	180.000	2502.164	2487.308
5.000	2.000	180.000	2497.445	2484.245
5.000	2.100	180.000	2500.407	2475.171
5.000	2.200	180.000	2489.296	2469.746
5.000	2.300	180.000	2473.001	2461.391
5.000	2.400	180.000	2449.691	2447.273
5.000	2.500	180.000	2461.651	2399.246
5.000	2.600	180.000	2361.654	2378.751
5.000	2.700	180.000	2297.628	2225.150
5.000	2.800	180.000	1904.989	1827.803
5.000	2.900	180.000	1718.413	1488.853
5.000	3.000	180.000	1320.606	1030.946
6.000	1.000	180.000	2478.879	2478.400
6.000	1.100	180.000	2478.023	2477.624
6.000	1.200	180.000	2470.425	2471.611
6.000	1.300	180.000	2471.245	2473.132
6.000	1.400	180.000	2500.192	2500.521
6.000	1.500	180.000	2498.635	2500.944
6.000	1.600	180.000	2496.038	2500.523
6.000	1.700	180.000	2492.750	2499.797
6.000	1.800	180.000	2485.638	2500.196
6.000	1.900	180.000	2480.352	2498.816
6.000	2.000	180.000	2473.835	2496.656
6.000	2.100	180.000	2469.975	2491.030
6.000	2.200	180.000	2459.478	2485.303
6.000	2.300	180.000	2444.913	2476.058
6.000	2.400	180.000	2423.800	2460.769
6.000	2.500	180.000	2468.394	2396.304
6.000	2.600	180.000	2340.990	2389.182
6.000	2.700	180.000	2281.151	2238.978
6.000	2.800	180.000	1891.388	1844.456
6.000	2.900	180.000	1744.028	1491.202

6.000	3.000	180.000	1342.177	1028.595
7.000	1.000	180.000	2484.775	2485.108
7.000	1.100	180.000	2481.133	2481.509
7.000	1.200	180.000	2471.763	2470.834
7.000	1.300	180.000	2472.703	2472.221
7.000	1.400	180.000	2497.970	2502.869
7.000	1.500	180.000	2494.214	2503.352
7.000	1.600	180.000	2490.139	2503.525
7.000	1.700	180.000	2485.662	2503.365
7.000	1.800	180.000	2477.305	2504.355
7.000	1.900	180.000	2471.313	2503.315
7.000	2.000	180.000	2464.296	2501.389
7.000	2.100	180.000	2460.613	2495.683
7.000	2.200	180.000	2450.401	2489.785
7.000	2.300	180.000	2436.565	2480.160
7.000	2.400	180.000	2416.690	2464.224
7.000	2.500	180.000	2454.174	2403.515
7.000	2.600	180.000	2337.396	2390.801
7.000	2.700	180.000	2291.686	2234.172
7.000	2.800	180.000	1900.355	1840.442
7.000	2.900	180.000	1751.781	1487.737
7.000	3.000	180.000	1350.639	1025.219
8.000	1.000	180.000	2503.368	2502.976
8.000	1.100	180.000	2502.911	2502.819
8.000	1.200	180.000	2472.508	2470.396
8.000	1.300	180.000	2499.449	2503.254
8.000	1.400	180.000	2496.740	2503.536
8.000	1.500	180.000	2493.393	2503.753
8.000	1.600	180.000	2489.512	2503.831
8.000	1.700	180.000	2485.154	2503.624
8.000	1.800	180.000	2477.465	2504.285
8.000	1.900	180.000	2471.508	2503.236
8.000	2.000	180.000	2464.524	2501.303
8.000	2.100	180.000	2460.262	2495.897
8.000	2.200	180.000	2450.079	2490.003
8.000	2.300	180.000	2436.266	2480.368
8.000	2.400	180.000	2416.424	2464.423
8.000	2.500	180.000	2460.467	2400.361
8.000	2.600	180.000	2337.248	2390.916
8.000	2.700	180.000	2296.941	2231.652
8.000	2.800	180.000	1904.828	1838.228
8.000	2.900	180.000	1755.546	1485.721
8.000	3.000	180.000	1354.917	1023.365

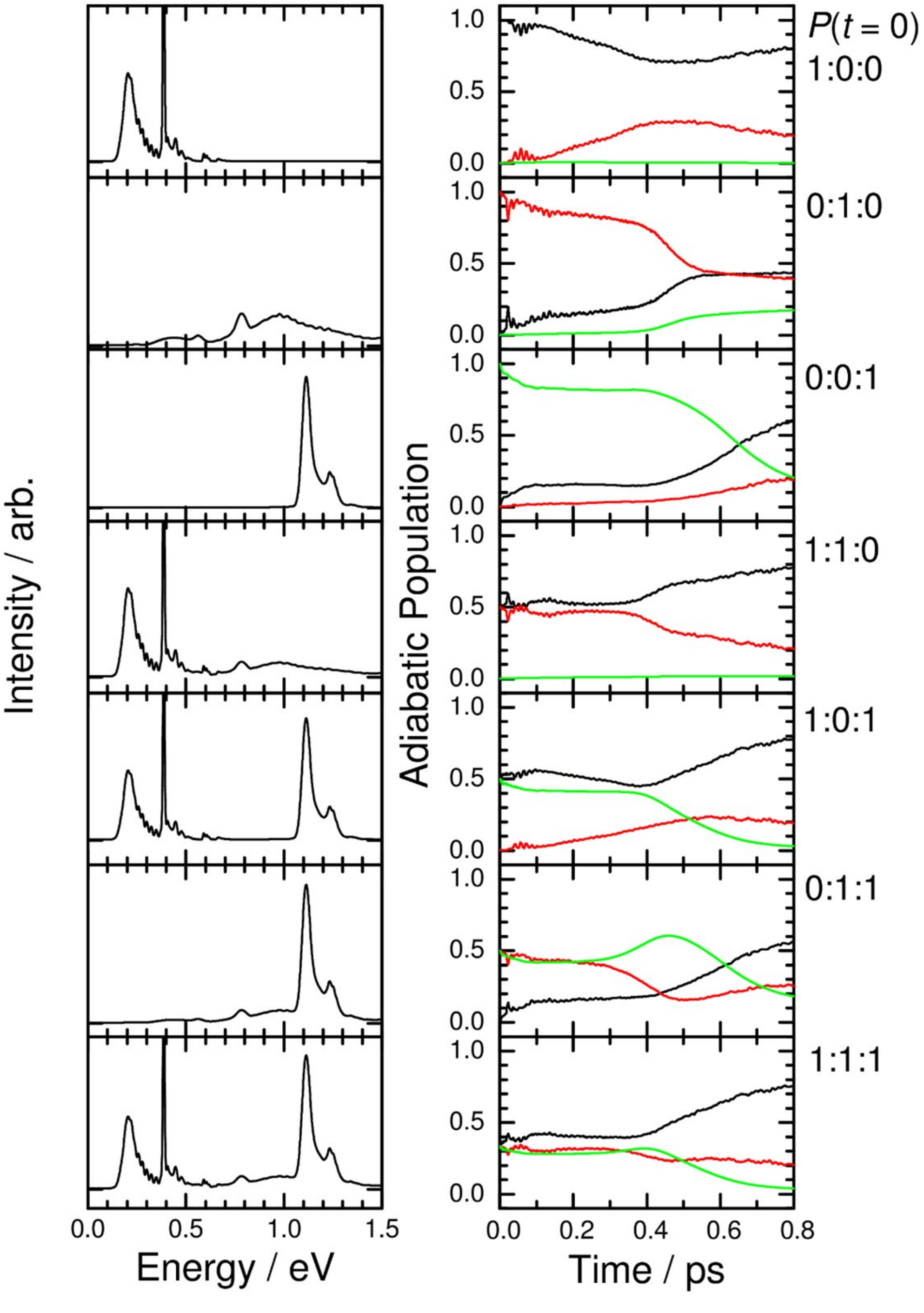

Fig. S4

The effect of the initial adiabatic population values on the photodetachment spectrum (left panels) and on the nonadiabatic population changes (right panels) for the IHI⁻(00^00) anion case. Black, red and green lines correspond to the adiabatic populations on the ground, first and second excited states, respectively.

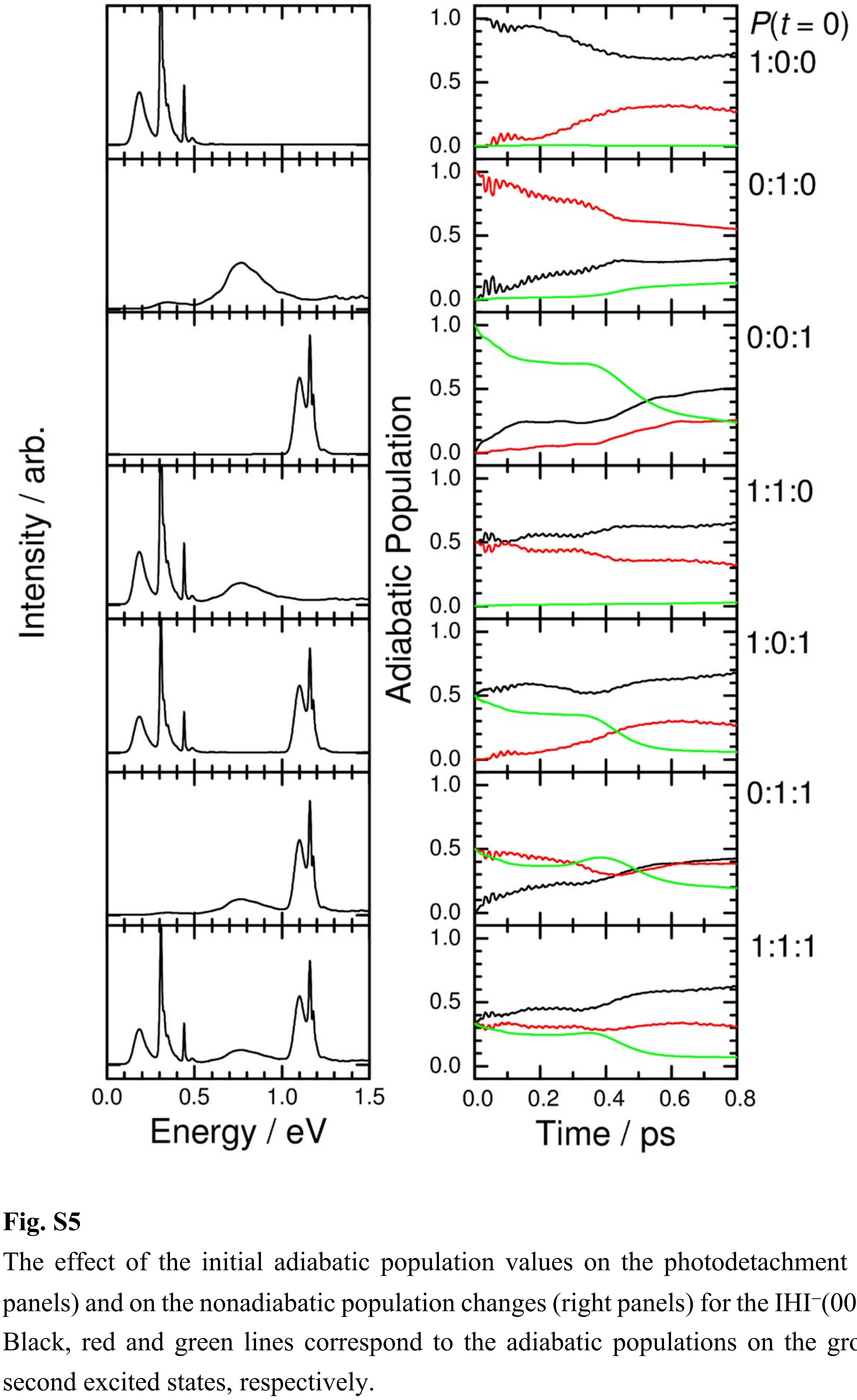

Fig. S5

The effect of the initial adiabatic population values on the photodetachment spectrum (left panels) and on the nonadiabatic population changes (right panels) for the IHI⁻(00^00) anion case. Black, red and green lines correspond to the adiabatic populations on the ground, first and second excited states, respectively.

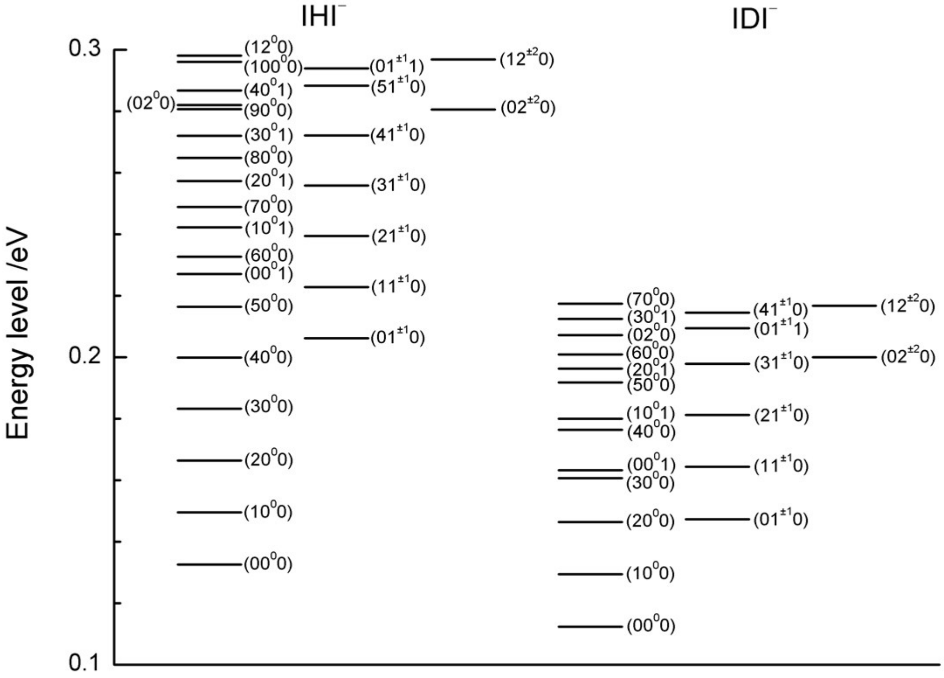

Fig. S6

Vibrational levels of the IHI^- and IDI^- anions obtained from the DVR calculations on the CCSD(T) level potential energy surface. The vibrational quantum numbers ($v_1v_2^lv_3$) for the linear triatomic molecule convention are also used. The energy is measured from the potential energy bottom corresponding to the linear I–H–I minimum.