Formation of interstellar anions

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Predictions and discovery

- The presence of anions in astrophysical sources was first considered by Dalgarno and McCray, in 1973
- In 1981, Herbst predicted anion formation in dense clouds from radicals of more than four atoms.
- On the base of large stabilities of charged linear chains, the existence of negative species in the ISM was also predicted theoretically by Rosmus, who determined many spectroscopic properties

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THE FORMATION OF INTERSTELLAR MOLECULES FROM NEGATIVE IONS

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ABSTRACT

The possible contribution of chemical reactions involving negative ions to the formation of interstellar molecules is briefly explored.

Subject headings: interstellar matter — molecules — negative ions

I. INTRODUCTION

Interstellar molecules are produced under various physical conditions, and several different mechanisms may contribute to their formation. Solomon and Klemperer (1972) have examined gas-phase reactions involving neutral and ionized species, and Watson and Salpeter (1972) have examined grain-surface reactions. Here we consider gas-phase reactions involving negative ions.

II. NEGATIVE-ION CHEMISTRY

a) Reactions Involving H^-

McDowell (1961) pointed out that molecular hydrogen is produced in partly ionized interstellar clouds by the reaction sequence, radiative attachment

$$e + H \rightarrow H^- + h\nu \qquad (1)$$

to form H^-, followed by associative detachment

$$H^- + H \rightarrow H_2 + e \qquad (2)$$

to form H_2. The rate coefficient k_1 of reaction (1) has been tabulated by Dalgarno and Kingston (1963) and by de Jong (1972). At low temperatures $T°$ K, its value is about $10^{-18}T$ cm^3 s^{-1}. The rate coefficient k_2 of reaction (2) has been measured at 300° K (Schmeltekopf, Fehsenfeld, and Ferguson 1967) and calculated over a wide range of temperatures (Browne and Dalgarno 1969). It is almost independent of temperature with a rate coefficient of about 1.3×10^{-9} cm^3 s^{-1}. The negative ions can also be removed through photodetachment by starlight at the rate of about $2 \times 10^{-7} \exp(-\tau_v)$, where τ_v is the visual extinction, and through mutual neutralization processes

$$X^+ + H^- \rightarrow X + H\,. \qquad (3)$$

The rate coefficient for mutual neutralization is fairly insensitive to the nature of the ion X^+, and to an accuracy of perhaps a factor of 2 we may take the rate to be proportional to the total ion density with a value of $4 \times 10^{-6}T^{-1/2}n_e$ s^{-1}, where n_e is

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Multireference-CI calculations of radiative transition probabilities in C_2^-

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Electronic transition moment functions for the dipole allowed transitions among the $X\,^2\Sigma_g^+$, $A\,^2\Pi_u$, and $B\,^2\Sigma_u^+$ states of C_2^- have been calculated from highly correlated MCSCF-SCEP wave functions. Vibrational band transition probabilities for all bound–bound transitions have been evaluated, and radiative lifetimes of bound vibrational levels are obtained. For the $B\,^2\Sigma_u^+$, $v' = 0$ state, the calculated lifetime of 76.5 ns is in excellent agreement with recent experimental values. Strong emission from the $A\,^2\Pi_u$ state in the infrared spectral region is predicted.

I. INTRODUCTION

The C_2^- ion is the only experimentally investigated negative ion with bound excited states which can decay to the ground state by dipole allowed radiative transitions. Classical spectroscopic techniques[1–5] as well as data obtained from highly resolved C_2^- autodetachment resonances yielded accurate spectroscopic constants for the $X\,^2\Sigma_g^+$ and $B\,^2\Sigma_u^+$ states,[6] and recently, estimates for the constants of the $A\,^2\Pi_u$ state.[7,8] Very recently, autodetachment linewidths and decay rates have been determined from ultrahigh resolved autodetachment resonances in the A and B states.[9]

So far, relatively little is known about the radiative transition probabilities between the bound states of C_2^-. Cathro and Mackie[10] have estimated the radiative lifetime of the $B\,^2\Sigma_u^+$ state from shock tube measurements to be 270 ± 130 ns. Bondybey and Brus[5] estimated the same quantity for C_2^- trapped in rare gas lattices to be 64, 40, 38, and 34 ns for the hosts Ne, Ar, Kr, and Xe, respectively. Recently, direct measurements by Leutwyler *et al.*[11] of the $B\,^2\Sigma_u^+$ lifetime yielded the values 77 ± 8 ns for $v' = 0$ and 73 ± 7 ns for $v' = 1$. These results are in reasonable agreement with a mean radiative lifetime of 67 ns obtained by Zeitz *et al.*[12] from *ab initio* calculations. In the latter work also a transition moment for the $A\,^2\Pi_u$–$X\,^2\Sigma_g^+$ transition at a single internuclear distance has been reported, but so far no transition rates or radiative lifetimes for the $A\,^2\Pi_u$ state are known.

The aim of the present work was to calculate accurate radiative transition rates, oscillator strengths, and radiative lifetimes for the bound vibrational levels of the X, A, and B states of C_2^- from highly correlated *ab initio* electronic wave functions. For the $B\,^2\Sigma_u^+$, $v' = 0,1$ states radiative lifetimes of 76.5 and 75.8 ns, respectively, are obtained, in excellent agreement with the experimental values of Leutwyler *et al.*[11] For the X–A (0,0) band origin, which lies in the infrared spectral region at about 4160 cm^{-1}, the transition rate A_0^0 is calculated to be 19 112 s^{-1}. This value is about 10^2 times larger than the rate for the vibrational 1–0 transition in hydrogen fluoride, which is known to be an excellent IR emitter.[13] Thus, it should be possible to observe directly the emission from the $A\,^2\Pi_u$ state of C_2^-. The radiative lifetimes of the vibrational levels of the A state lie in the range of microseconds, those of the $X\,^2\Sigma_g^+$ state in the range of milliseconds.

II. COMPUTATIONAL DETAILS

The potential energy and transition moment functions have been calculated from highly correlated multireference configuration-interaction (MR-CI) wave functions. These wave functions were obtained in three steps: first, multiconfiguration-self-consistent field (MCSCF) calculations with about 50 configurations for each state were performed at several internuclear distances. From these MCSCF wave functions the most important configurations (cf. Table I) were selected as reference states for the MR-CI calculations. In a second step, the set of molecular orbitals employed in the CI calculations was optimized by minimizing the energy average of the three reference wave functions using a quadratically convergent MCSCF procedure.[14] In terms of these orbitals appropriate linear combinations of the reference configurations in Table I properly describe dissociation of all three states. The reference wave functions also account for the most important electron correlation effects around the equilibrium distances. In the last step the CI wave functions were calculated using the multireference SCEP procedure.[15] In the CI wave functions all configurations which are singly or doubly substituted relative to any of the reference configurations were taken into account, but the number of variational parameters optimized in the CI procedure were smaller than the number of configuration state functions since the internal contraction scheme[15,16] has been employed. This internal contraction considerably reduces the computational effort but only negligibly influences the results.[15,17,18] Finally, the electronic transition moments were calculated from the CI wave functions using a procedure recently devised.[17] The evaluation of the transition moments was facilitated by the fact that the same set of molecular orbitals has been employed for all states.

The atomic basis set of Gaussian-type functions was derived from Huzinaga's 11*s*,7*p* set[19] by replacing the most diffuse *s* function by two functions with exponents 0.095 and 0.04. Furthermore, one diffuse *p* function with exponent

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 0021-9606/84/105085-04$02.10

Discovery

- The actual interest for anions is recent coming from the discovery of C_6H^- by McCarthy et al., in 2006
- This detection has been crucial and has generated the search of other anions and laboratory studies.
- Actually, 6 anions are discovered: C_4H^-, C_6H^-, C_8H^-, and CN^- , C_3N^- , and C_5N^-.

ANIONS (detected)		
C_6H^-	M.C.McCarthy, et al, *Astrophys.J*, 652, L141 (2006)	IRC +10216
C_4H^-	J. Cernicharo, M. Guélin, M. Agúndez, et al. *A&A*, 467, L37 (2007) M. Agúndez, et al A&A, 478, L19 (2008) N. Sakai, et al, *Astrophys.J.*, 673, L71 (2008)	IRC+10216 L1527 L1527
C_8H^-	A.J.Remijan, et al, *Astrophys.J*, 664, L47 (2007) S. Brünken et al. *Astrophys.J.*, 664, L43 (2007)	IRC +10216 TMC-1
CN^-	M. Agúndez, *A&A*, 517, L10 (2010)	IRC +10216
C_3N^-	P.Thaddeus, ….., M.Agúndez, et al., *Astrophys.J*, 677, 1132 (2008)	IRC +10216
C_5N^-	J. Cernicharo, M. Guélin, M. Agúndez, et al, *Astrophys.J*, 688, L183 (2008).	IRC +10216

C_2H^-?? IRC+10216 (1 single line!)

"A parallel search for the small anion C2H− remains inconclusive, despite the previous tentative identification of the *J* = 1−0 rotational transition. The abundance of C2H− in IRC +10216 is found to be vanishingly small, <0.0014% relative to C2H" (Agúndez et al, 2010)

ANION/NEUTRAL abundances	
C_2H^-	<0.0014
C_4H^-	0.0074
C_6H^-	6.8
C_8H^-	26
CN^-	0.25
C_3N^-	0.42
C_5N^-	58

Carbon chains anions

C_2^-, C_4^-, C_6^-

C_2H^-, C_4H^-, C_6H^-

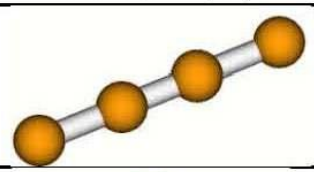
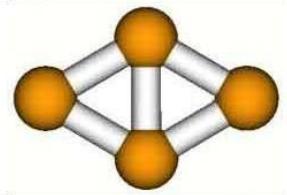
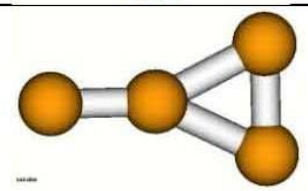
Estimated astrophysical abundances depend on:

a) molecular stabilities and spectroscopic properties
b) radiative and collisional excitation parameters
c) reaction probabilities

a) b) and C) → ab initio studies

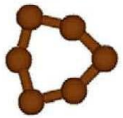
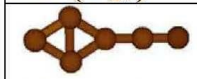
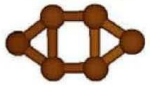
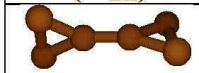
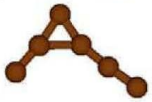
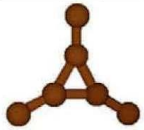
Structure and spectroscopy

neutral		*anion*	
C_2 ($X^1\Sigma_g^+$)	B_e=53828.56 MHz	C_2^- ($X^2\Sigma_g^+$)	B_e= 48621.35 MHz Ea=**3.18 eV**
l-C_4 ($X^3\Sigma_g^-$)	B_e= 4919.90 MHZ	*l*-C_4^- ($X^2\Pi_g$)	B_e= 4944.98 MHz Ea=**3.85 eV**
c-C_4 (X^1A_g)	A_e=36421.79 MHZ B_e=13787.46 MHz C_e=10001.08 MHz		
l-C_6 ($X^3\Sigma_g^-$)	B_e= 1432.11 MHz	*l*-C_6^- ($X^2\Pi_u$)	B_e= 1426.14 MHz Ea=**4.18 eV**
c-C_6 (X^1A_1')	A_e=B_e=8380.82 MHz C_e=4190.20 MHz		
l-C_2H ($X^2\Sigma^+$)	B_e=43706.36 MHz **μ**=0.7178 D	*l*-C_2H^- ($X^1\Sigma^+$)	B_e=41300.25 MHz **μ**=3.9890 D Ea=**2.95 eV**
l-C_2H ($X^2\Pi$)	B_e=39107.10 MHz **μ**=3.1868 D Er=3136 cm^{-1}		
l-C_4H ($X^2\Sigma^+$)	B_e=4727.60 MHz **μ**=0.8924 D	*l*-C_4H^- ($X^1\Sigma^+$)	B_e=4625.65 MHz **μ**=6.8368 D Ea=**3.59 eV**
l-C_4H ($X^2\Pi$)	B_e=4631.48 MHz **μ**=4.3336 D Er=9 cm^{-1}		
l-C_6H ($X^2\Pi$)	B_e= 1367.85 MHz **μ**= 23.2532 D	*l*-C_6H^- ($X^1\Sigma^+$)	B_e=1368.44MHz **μ**= 10.1364 D Ea=**3.83 eV**
l-C_6H ($X^2\Sigma^+$)	B_e= 1375.01 MHz **μ**=14.5871 D Er=1067 cm^{-1}		

C_4 and C_4^-						
ISOMERS	**C_4**			**C_4^-**		
RCCSD(T)	SM	E_R(eV)	SP(MHz;D)	SM	E_R(eV)	SP(MHz;D)
	T	3.85	B=4919.90 μ=0.0	D	0.0	B=4944.98 μ=0.0
	S	3.88	A=36421.79 B=13787.46 C=10001.08 μ=0.0	D	1.0	A=38715.65 B=13339.40 C=9921.10 μ=0.0
	S	5.25	?	D	0.6	A=46373.56 B=8740.62 C=7354.43 μ=0.9320

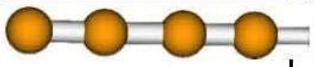
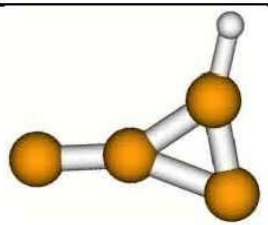
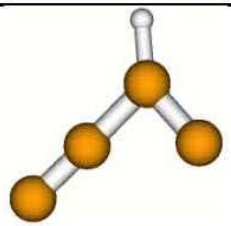
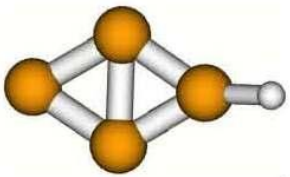
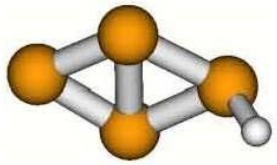
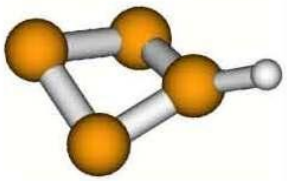
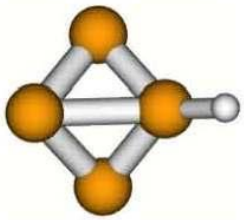
Masso, Hochlaf, Senent, Rosmus , JCP (2006)
Senent Hochlaf ApJ (2010)

Masso
Senent
JPCA(2009)

C_6 and C_6^-						
ISOMERS	C_6			C_6^-		
RCCSD(T)	SM	E_R(eV)	SP(MHz;D)	SM	E_R(eV)	SP(MHz;D)
 *l*-C_6 ($D_{\infty h}$)	T	4.18	B=1459.5 μ=0.0	D	**0.0**	B=1451.15 μ=0.0
 *c*-C_6 (D_{3h})	S	**3.67**	A=B=8389.2 C=4194.6 μ=0.0	D	1.15	A=B=7990.09 C=3995.06 μ=0.0
 *S2* (C_{2v})	S	5.09	A=45174.3 B=1915.6 C=1837.7 μ=0.0668	D	1.34	A=47321.47 B=1882.06 C=1810.07 μ=1.4375
 *S3* (C_{2v})	S	4.80	A=36028.9 B=2476.5 C=2317.2 μ=1.2821			
 *S4* (D_{2h})	S	5.43	A=16071.2 B=5262.7 C=3964.5 μ=0.0			
 *T2* (D_{2d})	T	6.05	A=23293.2 B=C=2560.4 μ=0.0	D	2.34	A=22627.27 B=C=2538.3 μ=3.2336
 *S5* (C_s)	S	6.13	A=11670.1 B=2858.5 C=2296.1 μ=1.6923	D	2.01	A=11657.32 B=2830.19 C=2277.30 μ=2.4319
 *S6* (D_{3h})	S	7.42	A=B=5307.4 C=2653.7 μ=0.0	D	3.74	A=B=5269.02 C=2634.16 μ=0.0
 *T3* (D_{2h})	T	7.66	A=35240.9 B=2684.1 C=2494.2 μ=0.0			

Hammoutene
Senent
Hochlaf
(In prep)

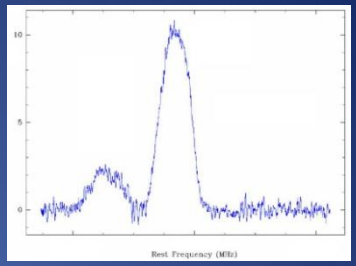
C_4H and C_4H^-: ISOMERS

C_4H				C_4H^-			
RCCSD(T)	SM	E_R(eV)	SP(MHz; D)	RCCSD(T)	SM	E_R(eV)	SP(MHz; D)
	D	3.59	B=4727.60 μ=0.8924		S	0.0	B=4625.65 μ=6.8368
	D	4.89	A=36004.39 B=12658.73 C=9365.83 μ=4.0523		S	2.4	A=36370.35 B=12090.30 C=9357.20 μ=1.9156
	D	4.69	A=21814.91 B=16196.46 C=10427.00 μ=3.1959		S	3.2	A=19643.92 B=170087.13 C=10829.53 μ=3.2335
	D	5.29	A=37277.03 B=8654.94 C=7023.93 μ=3.3652		S	3.2	A=38781.02 B=7807.61 C=6499.16 μ=5.9568

Senent et Hochlaf, Apj (2010)

Non-reactive collisions

Intensities and band shapes



Transition probability

$$\frac{dn_i(\mathbf{r})}{dt} = -n_i(\mathbf{r})\sum_{j\neq i}[R_{ij}(\mathbf{r})+C_{ij}(\mathbf{r})] + n_i(\mathbf{r})\sum_{j\neq i}[R_{ji}(\mathbf{r})+C_{ji}(\mathbf{r})]$$

$$R_{ij}(\mathbf{r}) = A_{ij} + B_{ij}\bar{J}_{ij}(\mathbf{r})$$
$$R_{ji}(\mathbf{r}) = B_{ji}\bar{J}_{ji}(\mathbf{r})$$

Radiative probabilities
Einstein coefficients

$$C_{ij}(\mathbf{r}) \quad f(\text{excitation collisional rates})$$
$$C_{ji}(\mathbf{r}) \quad f(\text{de-excitation collisional rates})$$

Collisional probabilities and rates

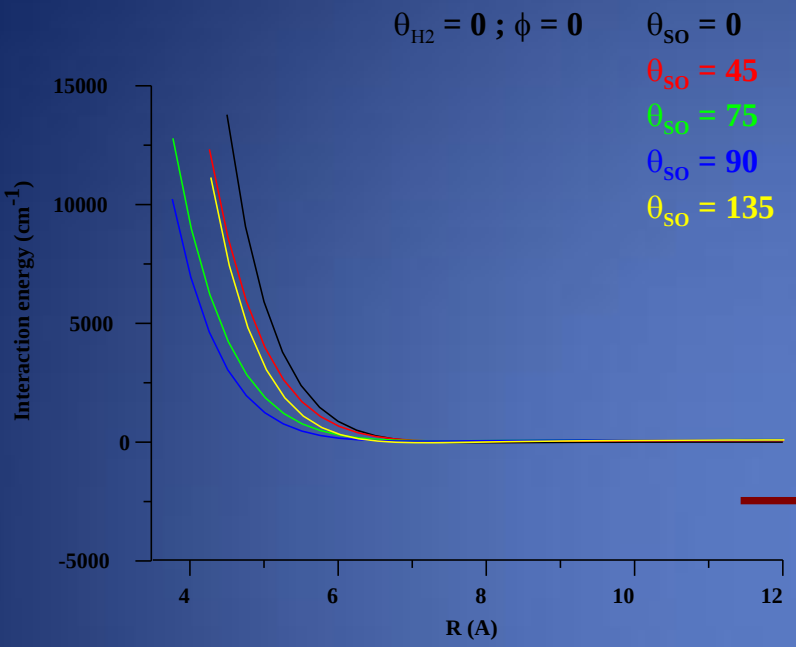
Cross sections and rates

$$k_{j\to i}(E) = \left(\frac{8}{\pi m}\right)^{1/2}\frac{1}{kT^{3/2}}\int_0^\infty \sigma_{j\to i}(E)\, E e^{-E/kT} dE$$

$$k_{j\to i} = \frac{g_j}{g_i}\, k_{i\to j}\, e^{-\frac{E_i - E_j}{kT}}$$

Excitation and de-excitation rate

Ab initio calculations of collisional cross sections σ



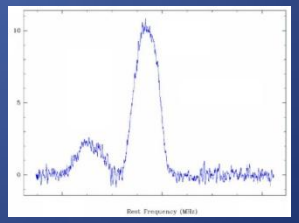
Van-der Walls Surface
Molecule + H2 (or He)

Fit

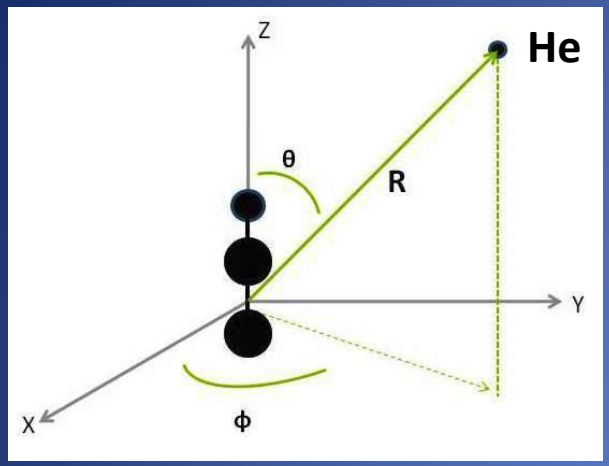
Collision packages
MOLSCAT
HIBRIDON
MOLCOL

Close Coupling Equations CC
(Coupled States CS,
Infinite Order Sudden IOS)

$\sigma \rightarrow K_{j \rightarrow i} \quad K_{i \rightarrow j}$



C_2H (or C_2H^-)+ He (↓T Geom = cte)



$C_2H(X^2\Sigma^+)$ $C_2H^-(X^1\Sigma^+)$

Geometry: rigid body model (in bohr)
C_2H: rCC =2.299, rCH = 1.968
C_2H^-: rCC =2.361, rCH = 2.023

PES (Coordinates: R and θ

MOLPRO 2006
Method: RCCSD(T)/CASSCF/RHF (C_2H) and RCCSD(T)/RHF (C_2H^-)
Basis set: aug-cc-pVQZ) +midbond functions (Cybulski and Toczylowski)
(placed at mid-distance between the C_2H (or C_2H^-) center of mass and He)

Geometries: 684 (C_2H) and 1254 (C_2H^-)
GRID: (C_2H) ΔR(4-25bohr), Δθ=10º ; (C_2H^-) ΔR(4.25-40bohr), Δθ=10º

BSSE (Boys and Bernardi, 1970); FIT: Werner et al. 1989
Minimum: (C_2H) E=-25.5 cm^{-1} ,R=8.0 ,θ=180º ; (C_2H^-) E=-37.8 cm^{-1} , R=7.9, θ=72.3º

C_2H (or C_2H^-)+ He (↓T Geom = cte)

SCATTERING CALCULATIONS

C_2H : HIBRIDON modified for hyperfine structure (Alexander theory 1982)
State-to-state cross sections between the 25 first rotational levels (up to 800 cm^{-1}, T=100K)
C_2H^-: MOLSCAT: Full close coupling approach (CC), State-to-state cross sections between the 13 first rotational levels (up to 100 cm^{-1}, T=100K)

Rotational parameters:
C_2H : B0=1.456825 cm^{-1}, D0 = 3.589 10^{-6} cm^{-1} , γ0= -002089678 cm^{-1}
C_2H^-: B0=1.3889354 cm^{-1}, D0 = 3.2345 10−6 cm^{-1}

The energy range was spanned to take into consideration the presence of resonances

Data available in LAMBDA and BASECOL

$C_2H(X^2\Sigma^+)$ +He , $C_2H^-(X^1\Sigma^+)$ +He

RATES (Propensity rules)

Both systems Rates ↑ if ΔN is even (Why? Near homonuclear symmetry)

C2H: Rates ↑ if ΔJ=ΔN and if ΔF=ΔJ; not proportional to the degeneracy 2F+1

Both systems: Rates for ΔN=2 ↑ if N ↑

The depth wells for both species are of the same order of magnitude (-37.8 cm^{-1} for C_2H^--He and –25.5 cm^{-1} for C_2H-He)

$C_2H^-(X^1\Sigma^+)$ +He rates = 10 x $C_2H(X^2\Sigma^+)$ +He rates

C_2H^--He

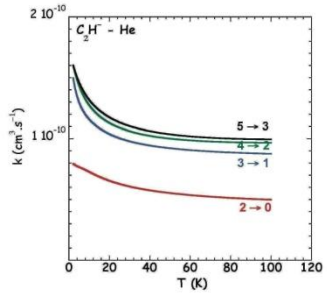


Fig 7: Temperature variation of de-excitation C_2H^--He $N \rightarrow N'$ rate coefficients with $\Delta N = 2$.

= 10 x

C_2H-He

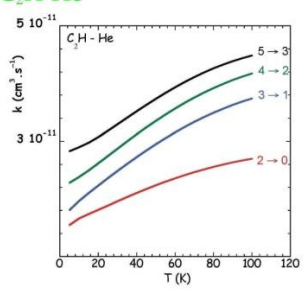


Fig 6: Temperature variation of de-excitation electronic spin averaged C_2H-He $N \rightarrow N'$ rate coefficients with $\Delta N = 2$.

J=N+S

F=|J+I|.....|J-I|)

• For comparison, C_2H-He rate coefficients between fine structure levels are averaged and summed over initial and final electronic spin quantum numbers respectively.

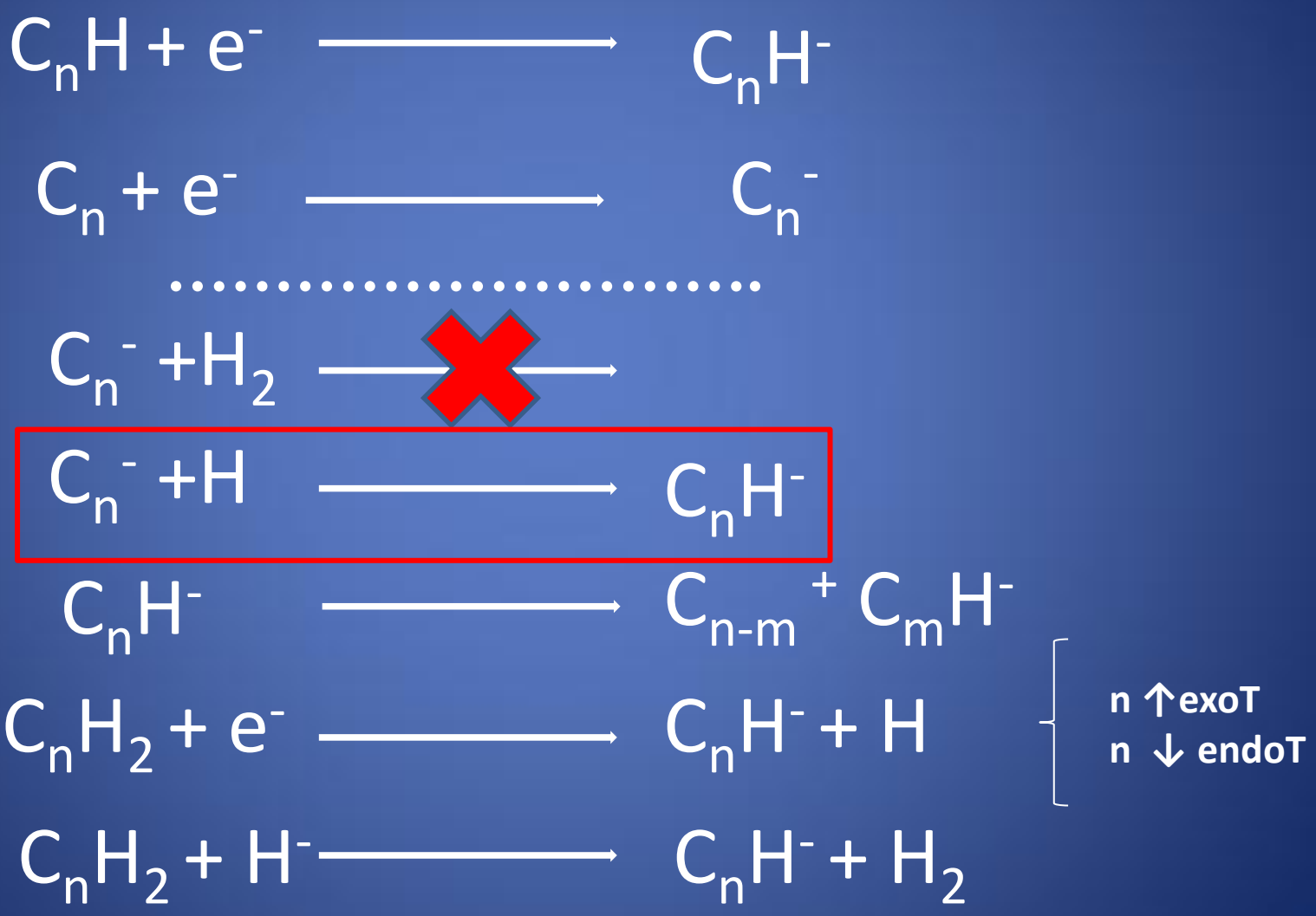
$$k_{N \rightarrow N'}(T) = \frac{\sum_{jj'} k_{N_j \rightarrow N'_{j'}}(T)}{2} \qquad (1)$$

Formation processes

CARBON CHAINS ANIONS: FORMATION AND DESTRUCTION

Anions can be produced via a variety of mechanisms

(dependence on n)



	ΔH (eV)
$l\text{-}C_2 + H \rightarrow l\text{-}C_2H$	5.05
$l\text{-}C_4 + H \rightarrow l\text{-}C_4H$	5.05
$l\text{-}C_6 + H \rightarrow l\text{-}C_6H$	5.14
$l\text{-}C_2^- + H \rightarrow l\text{-}C_2H^-$	4.83
$l\text{-}C_4^- + H \rightarrow l\text{-}C_4H^-$	4.80
$l\text{-}C_6^- + H \rightarrow l\text{-}C_6H^-$	4.80

Senent Hochlaf ApJ (2010)

C_2 and C_2H vertical electronic energies (eV) (MRCI/aug-cc-pVTZ)					
C_2			C_2H		
$C_2\,(X^1\Sigma_g^+)$	0.0	$(2\sigma_u)^2(1\pi_u)^4$	$C_2H\,(X^2\Sigma^+)$	0.0	$(3\sigma)^1(1\pi)^4$
$C_2\,(^3\Pi_u)$	0.21	$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^1$	$C_2H\,(^2\Pi)$	0.64	$(3\sigma)^2(1\pi)^3$
$C_2\,(^1\Pi_u)$	1.19	$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^1$			
$C_2\,(^3\Sigma_g^-)$	1.20	$(2\sigma_u)^2(1\pi_u)^2(3\sigma_g)^2$			
$C_2\,(^3\Sigma_u^+)$	1.23	$(2\sigma_u)^1(1\pi_u)^4(3\sigma_g)^1$			
$C_2^-\,(X^2\Sigma_g^+)$	-3.16	$(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^1$	$C_2H^-\,(X^1\Sigma^+)$	-3.02	$(3\sigma)^2(1\pi)^4$
$C_2^-\,(^2\Pi_u)$	-2.64	$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2$	$C_2H^-\,(^1\Sigma^+)$, [illegible]	0.81	
$C_2^-\,(^2\Sigma_u^+)$	-0.75	$(2\sigma_u)^1(1\pi_u)^4(3\sigma_g)^1$	$C_2H^-\,(^3\Pi)$, [illegible]	1.01	

C_4 and C_4H vertical electronic energies (eV) (MRCI/aug-cc-pVTZ)

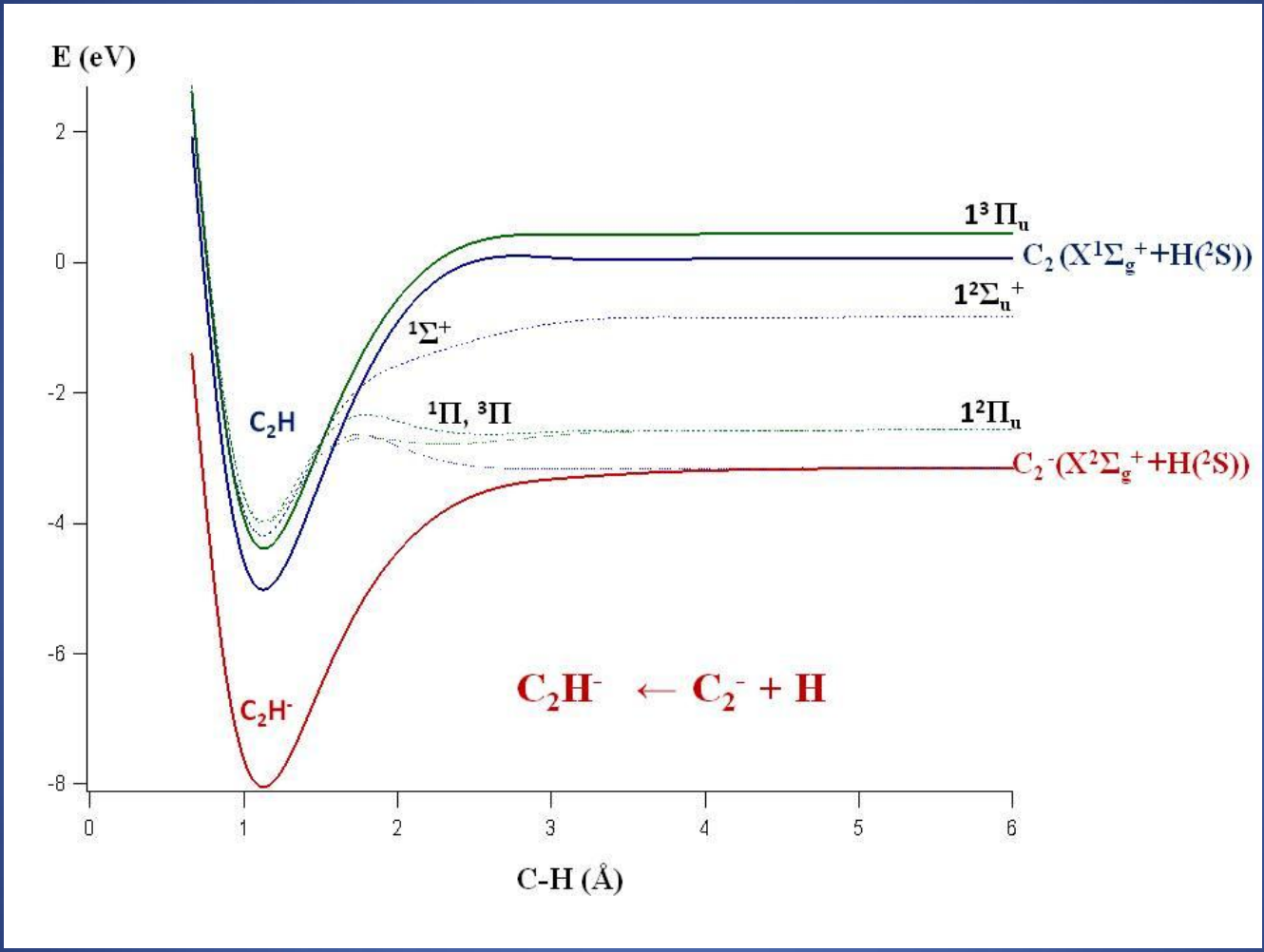
C_4			C_4H		
C_4 ($X^3\Sigma_g^-$)	0.0	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^2$	C_4H ($X^2\Pi$)	0.0	$(9\sigma)^2(1\pi)^4(2\pi)^3$
C_4 ($^1\Delta_g$)	0.34	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^2$	C_4H ($^2\Sigma^+$)	0.26	$(9\sigma)^1(1\pi)^4(2\pi)^4$
C_4 ($^1\Sigma_g^+$)	0.51	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^2$			
C_4 ($^3\Pi_g$)	0.95	$(4\sigma_g)^1(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^3$			
C_4 ($^3\Pi_u$)	1.24	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^1(1\pi_g)^3$			
C_4^- ($X^2\Pi_g$)	-3.70	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^3$	C_4H^- ($X^1\Sigma^+$)	-3.42	$(9\sigma)^2(1\pi)^4(2\pi)^4$
C_4^- ($^2\Sigma_g^+$)	-2.57	$(4\sigma_g)^1(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^4$	C_4H^- ($^3\Sigma^+$), C_4H^- ($^3\Delta$)	0, 0.80	
C_4^- ($^2\Sigma_u^+$)	-2.24	$(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^1(1\pi_g)^4$	C_4H^- ($^3\Pi$), C_4H^- ($^1\Sigma^-$)	0.46, 0.48	
C_4^- ($^2\Pi_u$)	-0.80	$(4\sigma_g)^2(1\pi_u)^3(3\sigma_u)^2(1\pi_g)^4$			

C_6 and C_6H vertical electronic energies (eV) (MRCI/aug-cc-pVTZ)

C_6			C_6H		
C_6 ($X^3\Sigma_g^-$)	0.0	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2$	C_6H ($X^2\Pi$)	0.0	$(13\sigma)^2(3\pi)^3$
C_6 ($^1\Delta_g$)	0.20	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2$	C_6H ($^2\Sigma^+$)	0.46	$(13\sigma)^1(3\pi)^4$
C_6 ($^1\Sigma_g^+$)	0.31	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2$			
C_6 ($^3\Pi_u$)	1.19	$(6\sigma_u)^2(7\sigma_g)^1(1\pi_g)^4(2\pi_u)^3$			
C_6 ($^3\Pi_g$)	1.20	$(6\sigma_u)^1(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^3$			
C_6^- ($X^2\Pi_u$)	-3.93	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^3$	C_6H^- ($X^1\Sigma^+$)	-3.61	$(13\sigma)^2(3\pi)^4$
C_6^- ($^2\Sigma_g^+$)	-2.53	$(6\sigma_u)^2(7\sigma_g)^1(1\pi_g)^4(2\pi_u)^4$	C_6H^- ($^3\Sigma^+$)	-0.52	$(13\sigma)^2(3\pi)^3(3\pi)^1$
C_6^- ($^2\Sigma_u^+$)	-2.49	$(6\sigma_u)^1(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^4$	C_6H^- ($^3\Delta$) , C_6H^- ($^3\Sigma^-$)	~0.0	
C_6^- ($^2\Pi_g$)	-1.71	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^3(2\pi_u)^4$	, C_6H^- ($^1\Sigma^-$) , C_6	0.17. 0.28	
C_6^- ($^4\Pi_g$)	-1.14	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2(2\pi_g)^1$	C_6H^- ($^1\Pi$), C_6H ($^3\Pi$)	40, 0.39	
C_6^- ($^2\Pi_g$)	-0.81	$(6\sigma_u)^2(7\sigma_g)^2(1\pi_g)^4(2\pi_u)^2(2\pi_g)^1$			

C_2^- +H

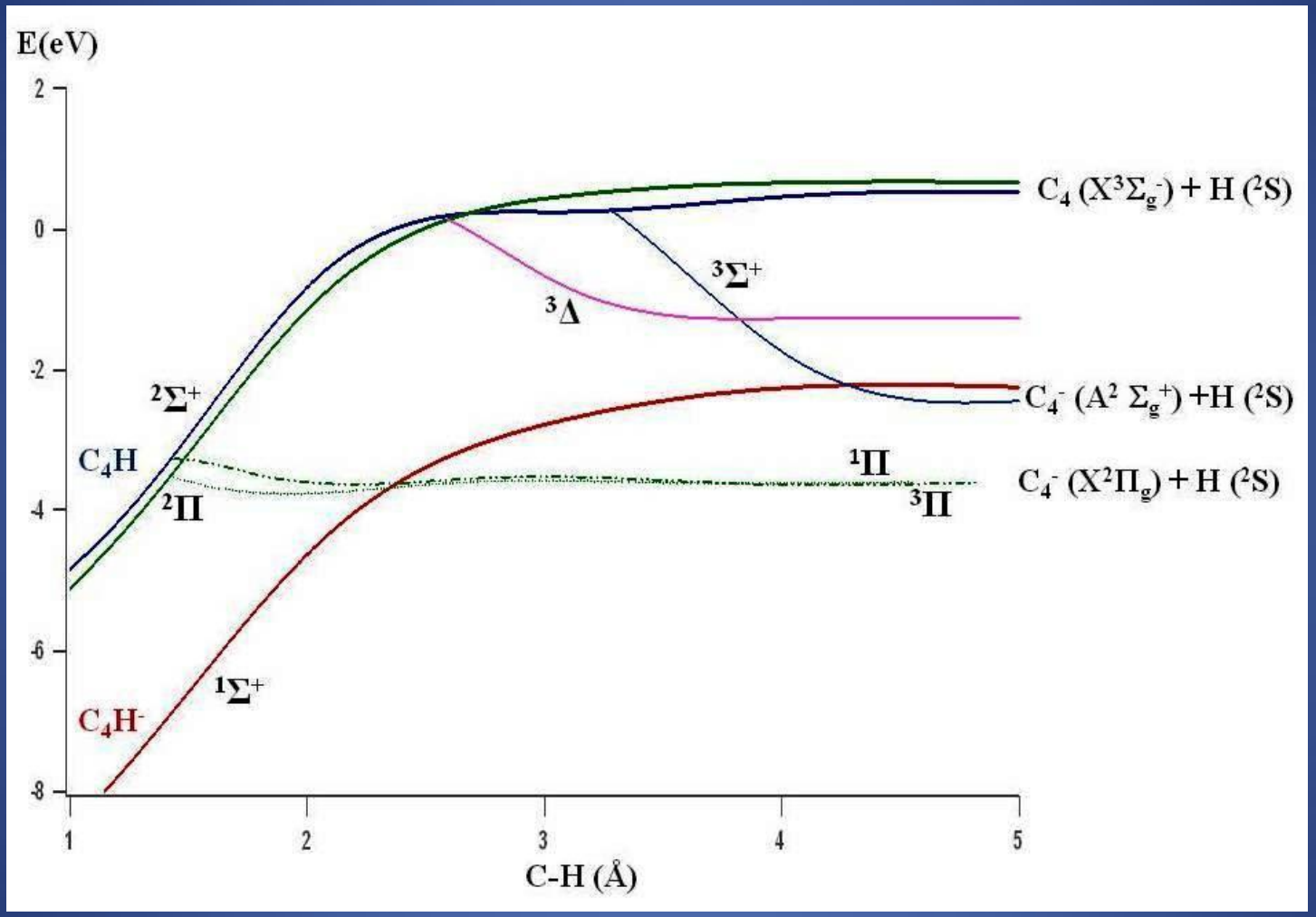
MRCI+Q



C_2H^- ⟵ C_2^- +H

C_4^- +H

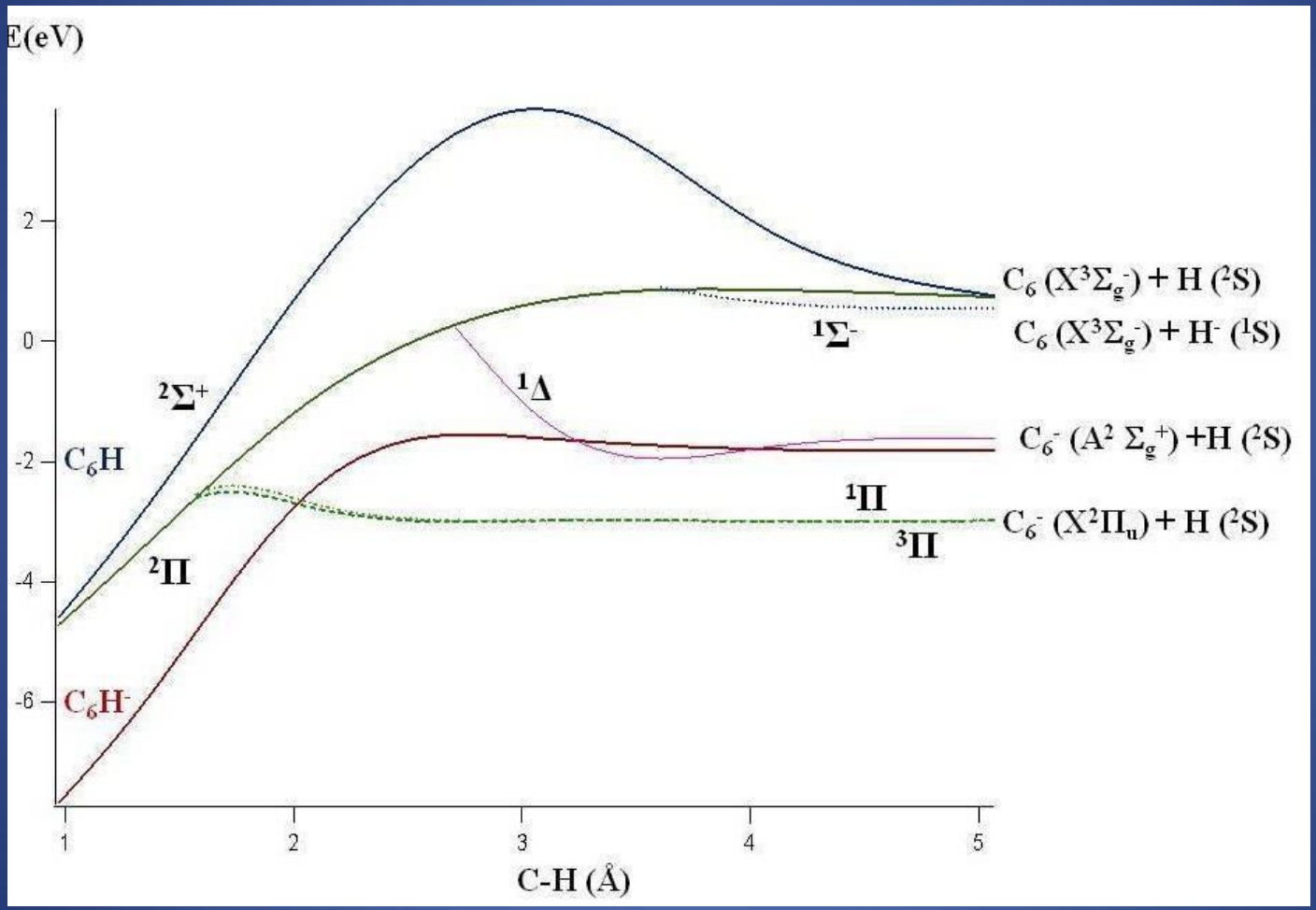
MRCI+Q



C_4H ⟵ C_4^- +H

$C_6^- + H$

CASSCF



C_6H ⟵ $C_6^- + H$

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