On the possible role of triplet electronic states of N_4 on the quenching of $N_2(C\ ^3\Pi_u)$ by $N_2(X\ ^1\Sigma_g^+)$: A preliminary *ab initio* study

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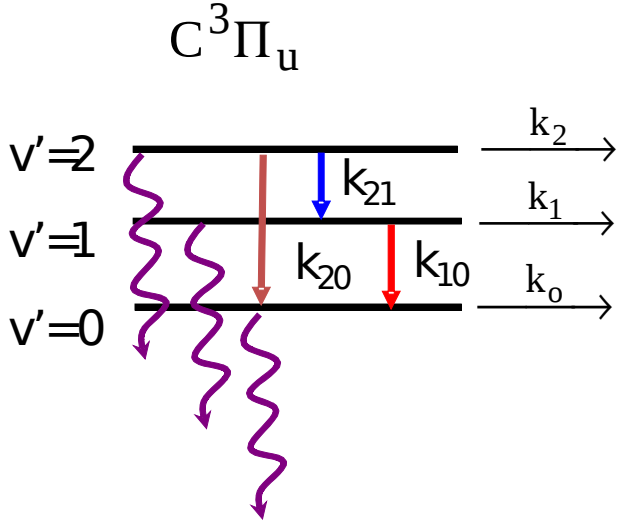
This nitrogen in its ordinary state is an inactive element; no action short of the most intense electric force, and then in the most infinitely small degree, can cause the nitrogen to combine directly with the other element of the atmosphere, or with other things round about it; it is a perfectly indifferent, and therefore to say, a safe substance.

Michael Faraday *The Chemical History of a Candle, cap V*, 1861

Quenching of N_2 UV emission

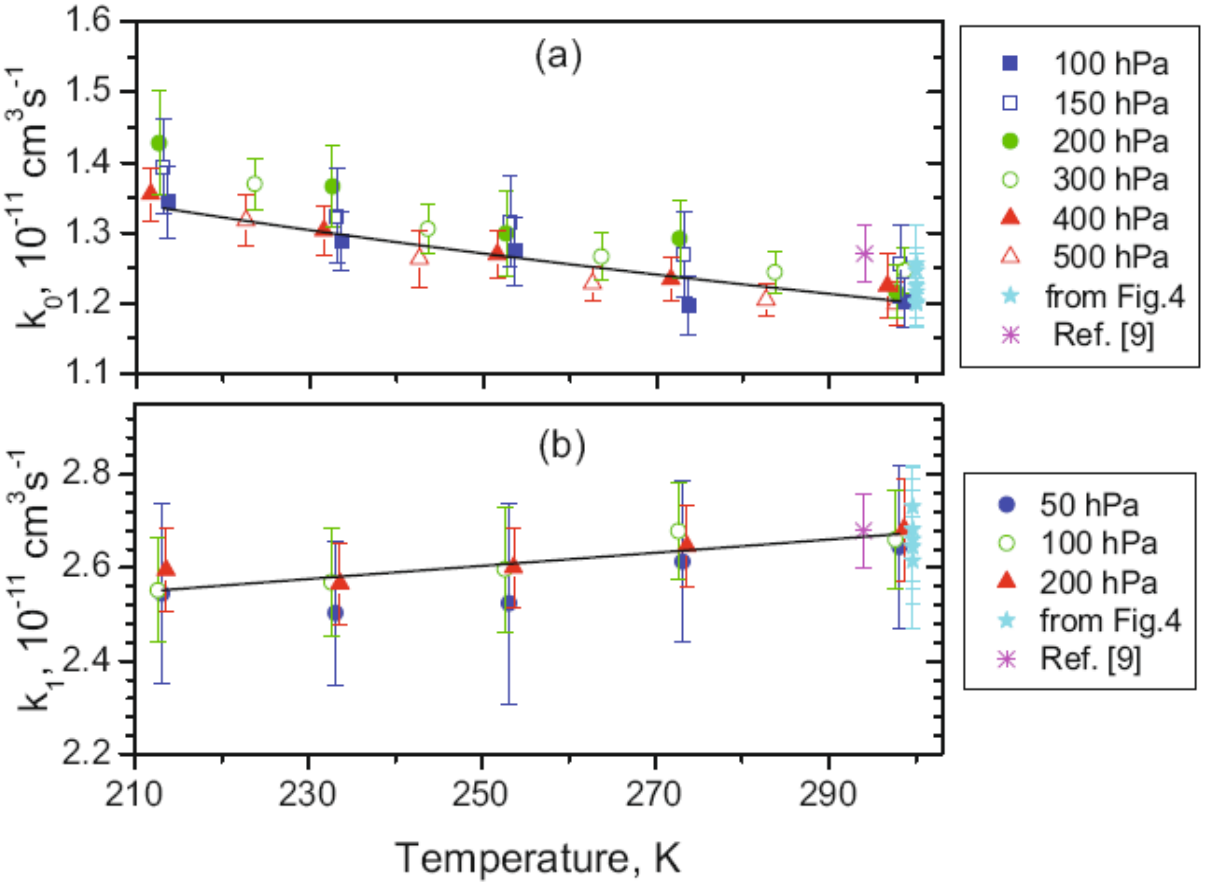


Experimental results:

- v' = 0 is populated by direct excitation and from an upper state (most probably from v' = 1, 2 states by vibrational relaxation)
- G. Dilecce et al., Chem. Phys. Lett. 431 (2006) 241; A. Morozov et al., NIM A 597 (2008) 105-109;
- the temperature dependence of $k_{v'}$ is different for v' = 0 and v' = 1;
- $K_{v'}$ appears to be pressure dependent;

Experimental results

L. Pereira et al. Eur. Phys. J. D 56, 325–334 (2010)



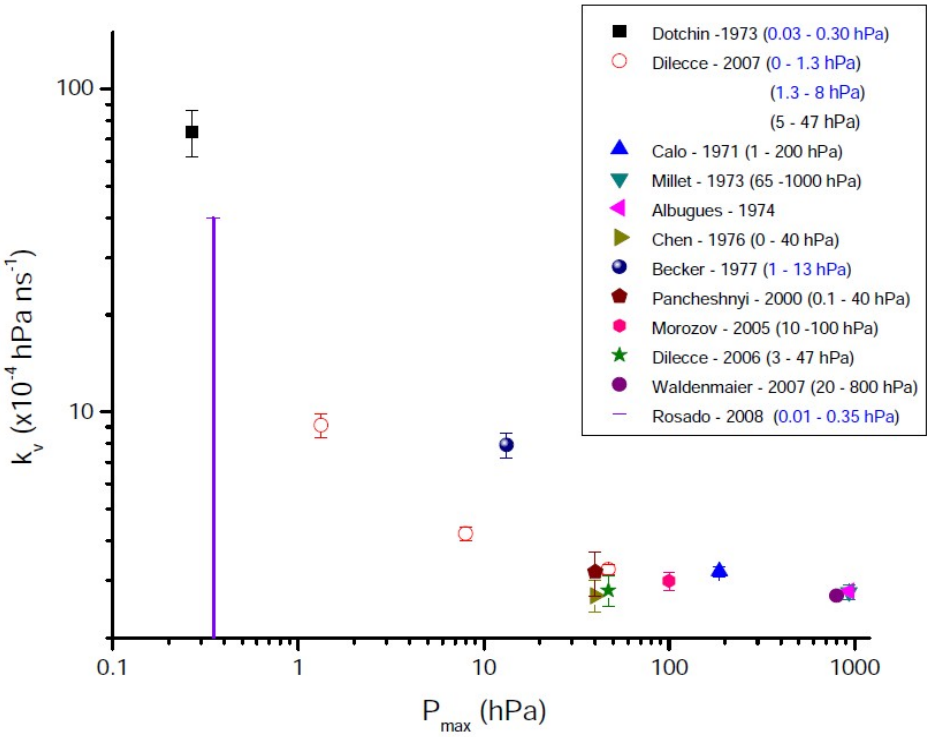
$k_v(T)=C(T/300)^{\beta}$

v'=0, β=-0.33±0.04

v'=1, β=0.14±0.08

Quenching rate constant of (a) the N_2 ($C\ ^3\Pi_u$, v' = 0) state and (b) ($C\ ^3\Pi_u$,the v' =1) state by N_2 as a function of the gas temperature for several pressures. The listed gas pressures correspond to the gas temperature of 298 K. For convenience of presentation, the abscissas are slightly shifted to avoid the overlap.

Variation of the quenching rate constant of the $N_2(C, v'=0)$ state with gas pressure



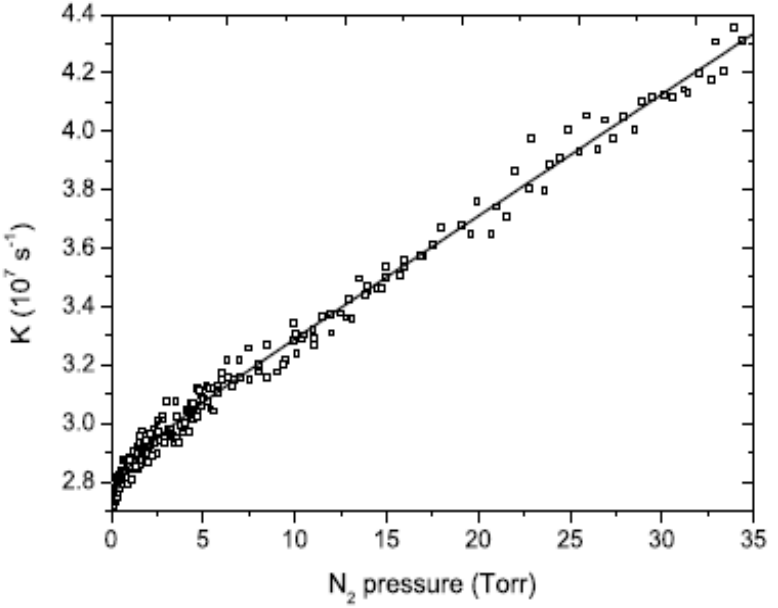


Fig. 1. Quenching rate by N_2 as a function of pressure and fit by formula (4). The error bars of individual points are not shown for clarity (see Figs. 3–5, where error bars are displayed). Fit parameters: $\gamma = (2.7298 \pm 0.0116) \times 10^7\ s^{-1}$; $k_0 = (2.22 \pm 0.56) \times 10^6\ Torr^{-1}\ s^{-1}$; $k_\infty = (4.144 \pm 0.046) \times 10^5\ Torr^{-1}\ s^{-1}$; $P_0 = (0.87 \pm 0.26)\ Torr$.

$$K(P) = \gamma + k_\infty P - (k_0 - k_\infty)P/(1 + P/P_0)$$

Experiments are underway...

Dilecce et al., Chem. Phys. Lett. 444 (2007) 39

Temperature dependence of the quenching rate constant

$$Y_{v'v''}(P,T) = A_{v'v''}\ \tau_{v'}^{eff}(P,T)\ N_{exc}^{v'} \qquad \frac{1}{\tau_{v'}^{eff}} = A_{v'} + k_{v'}N$$

Average of $v\sigma_R(v)$ over the thermal distribution of velocities f(v) , i.e.

$$k_{v'}(T) = \int v\sigma_R(v)\, f(\vec{v})\, d\vec{v}$$

$$k_{v'}(T) = \sqrt{\frac{8k_BT}{\pi\mu}} \int x\, \sigma_R\, \exp(-x)dx = \langle v \rangle \sigma(T), \quad \text{with} \quad x = \frac{\varepsilon}{k_BT}$$

Negative temperature dependence can be related to:

The process being very exothermic

Absence of barriers for the process

The process being governed by very long-range attractive forces ($V(R) \sim -C_nR^{-n}$, $n<4$)

Formation of complexes in a complex formation mechanism

On the potential energy surfaces for the process $N_2(C^3\Pi_u)+N_2(X^3\Sigma_g^+)$

Are processes as $N_2(X^1\Sigma_g^+)+N_2(C^3\Pi_u) \rightarrow N_2(X^1\Sigma_g^+)+N_2(B^3\Pi_g)$ allowed?

$N_2(X^1\Sigma_g^+)+N_2(C^3\Pi_u) \rightarrow ... \rightarrow N_4$ ($^3B_{2u}$ in D_{2h} symmetry) $\rightarrow ... \rightarrow N_4$ ($^3B_1$ in C_{2v} symmetry)
... $\rightarrow N_4$ ($^3A''$ in C_s symmetry) ... $\rightarrow N_4$ (^3A in C_1 symmetry) ... $\rightarrow N_4$ ($^3B_2$ in C_{2v} symmetry)
... $\rightarrow$ ... $N_2(X^1\Sigma_g^+)+N_2(B^3\Pi_g)$ ... $\rightarrow$ ...
... $\rightarrow$ ... $N_2(X^1\Sigma_g^+)+N_2(A^3\Sigma_u^+)$ ... etc.

Can they be adiabatic?

Possible existence of many potential energy surfaces crossings.

Very excited N_4 states are involved.

Extensive exploratory *ab initio* calculations to find minima, barriers and paths.

Deal with non-dynamical correlation effects CASSCF multi-state calculations.

Deal with dynamical correlation effects using CASPT2 methods.

Extra question: What is the importance of long-range resonant energy due to the interaction of different electronic states of the same molecules $N_2(X^1\Sigma_g^+)+N_2(C^3\Pi_u)$?

Potential energy surface

$H = H_e + V_N + T_{vr}$ non-relativistic Hamiltonian

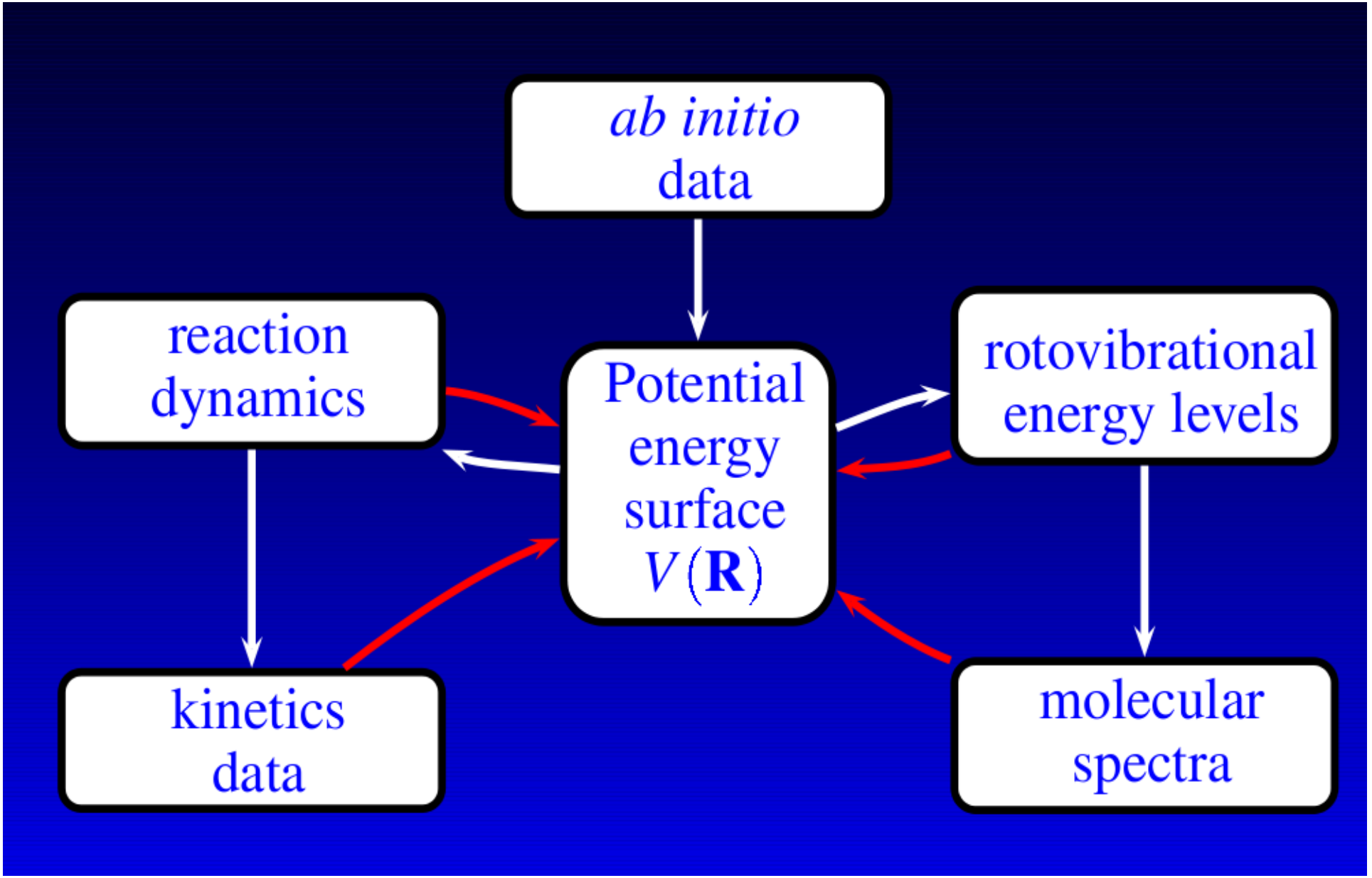
$H\Psi = E\Psi$ Schrödinger equation

$\Psi = \psi_e(\mathbf{r};\mathbf{R})\,\psi_{vr}(\mathbf{R})$ adiabatic approximation

$\left(H_e + V_N\right)\psi_e(\mathbf{r};\mathbf{R}) = V(\mathbf{R})\,\psi_e(\mathbf{r};\mathbf{R})$ electronic equation

$\left[T_{vr} + V(\mathbf{R})\right]\psi_{vr} = E_{vr}\psi_{vr}$ nuclear motion equation

From the potential energy surface to measurable properties



Ab initio calculations in a *nutshell* (is not possible!)

$|\Phi>$ Slater determinants or configuration state functions (CSF)

$\Phi_k=\Sigma_i c_{ik}\phi_i$, ϕ_i Gaussian basis set (6-31G**, 6-311++G(d,2p), cc-pVTZ, ANO, etc)

HF (Hartree-Fock): single Slater determinant $|\Phi_0>$ (single *reference*)

Correlation energy: $E_{exact}=E_{HF}+E_{corr}$

post-Hartree-Fock Methods: multiple CSF or various types of corrections
CI (configuration interaction), MCSCF (multi-configurational SCF),
$|\Phi> = |\Phi_0> + c_1|\Phi_1> + c_2|\Phi_2> + ...$
MP*n* (Moller-Plesset perturbation theory of order *n*), etc

Complete active space self consistent field (CASSCF):
Recover mostly **non-dynamical correlation** (related with correct dissociation, degeneracies and quasi-degeneracies, etc.)

To recover the **dynamical correlation** (related with dispersion energy, etc)**:**
Single-reference methods: MPn, CCSD(T), etc.
Multi-reference methods: MRCI, CASPT2, CASPT3, etc.

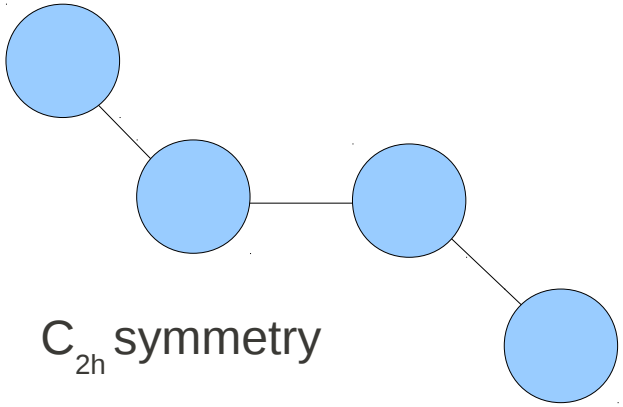
DFT (density functional theory) is not considered *ab initio...*

non-comercial codes: GAMESS, NWChem, Aces2, Dalton, PSI3, etc.
Comercial codes Gaussian, Molpro, MOLCAS, GAMES-US, etc.

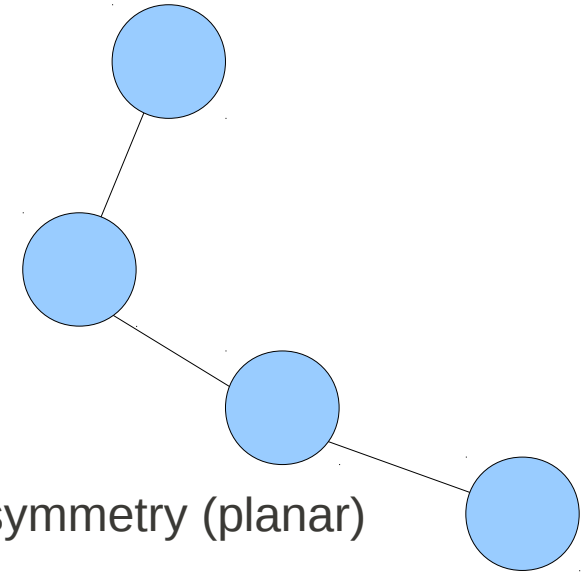
Potential energy surfaces and molecular geometry

4 atoms → 6 internal coordinates

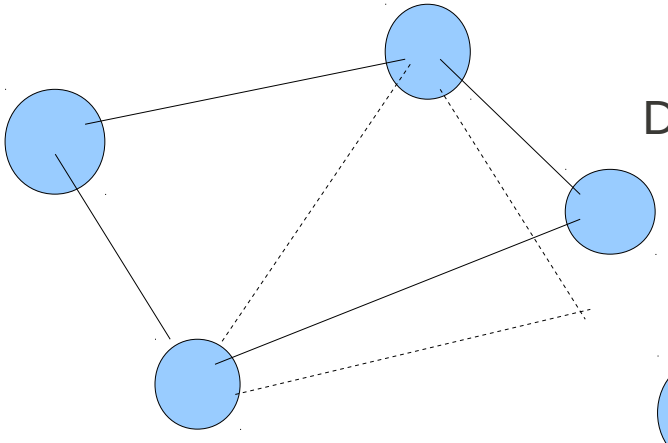
C_1 symmetry
(no symmetry)



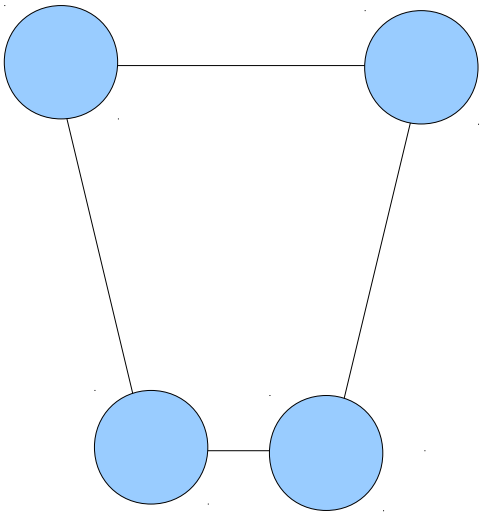
C_{2h} symmetry



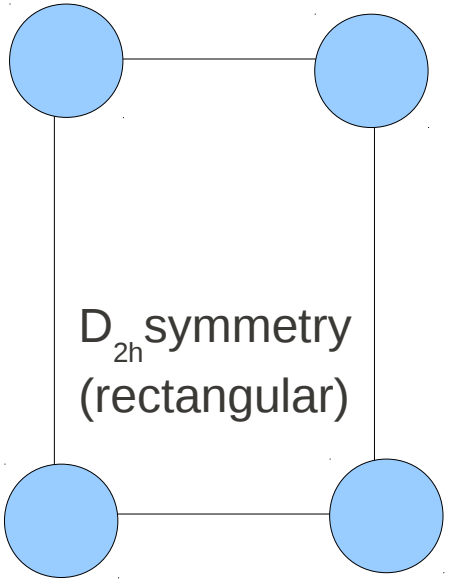
C_s symmetry (planar)



D_{2d} symmetry

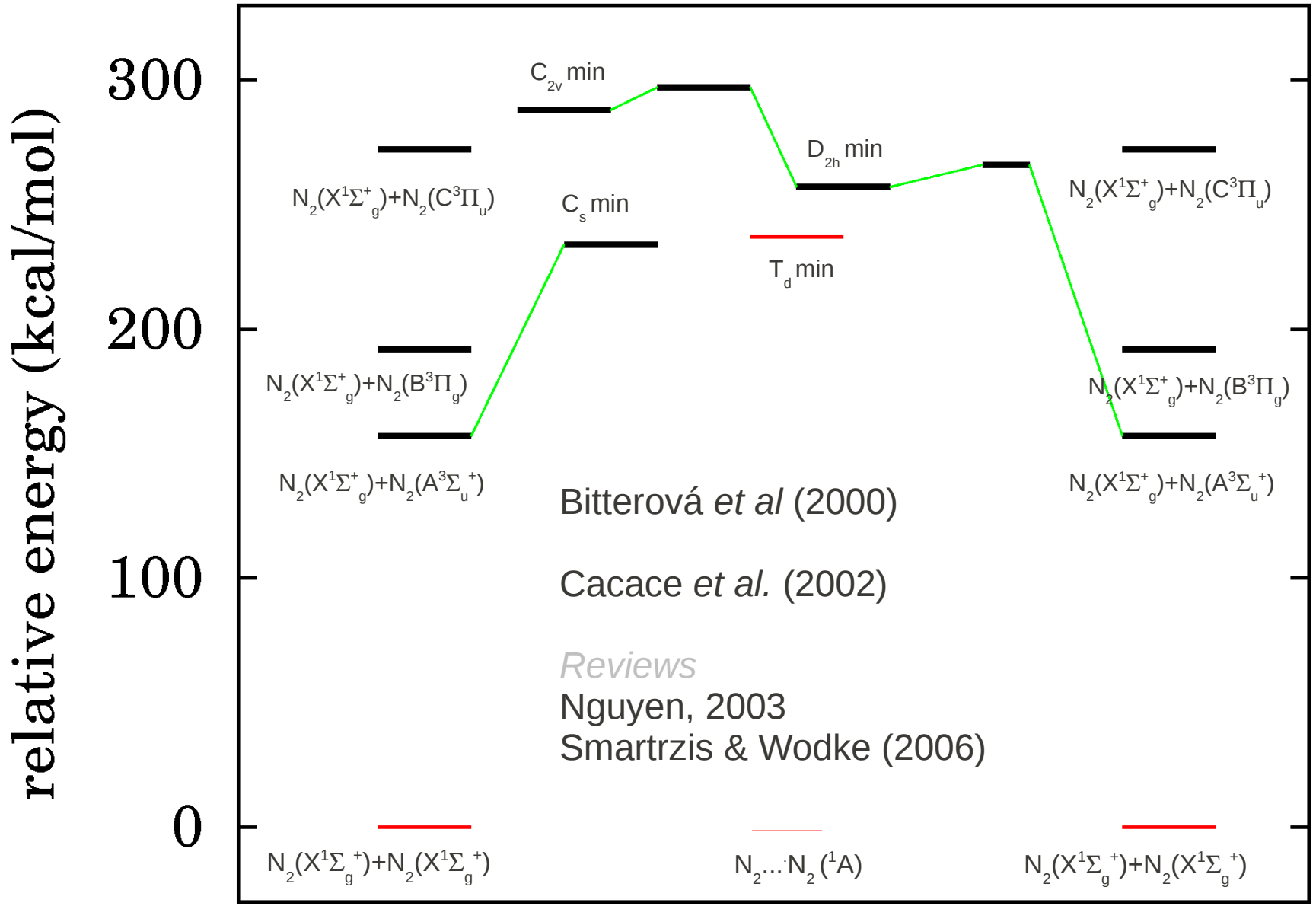


C_{2v} symmetry
(trapezoidal, kite, or others)

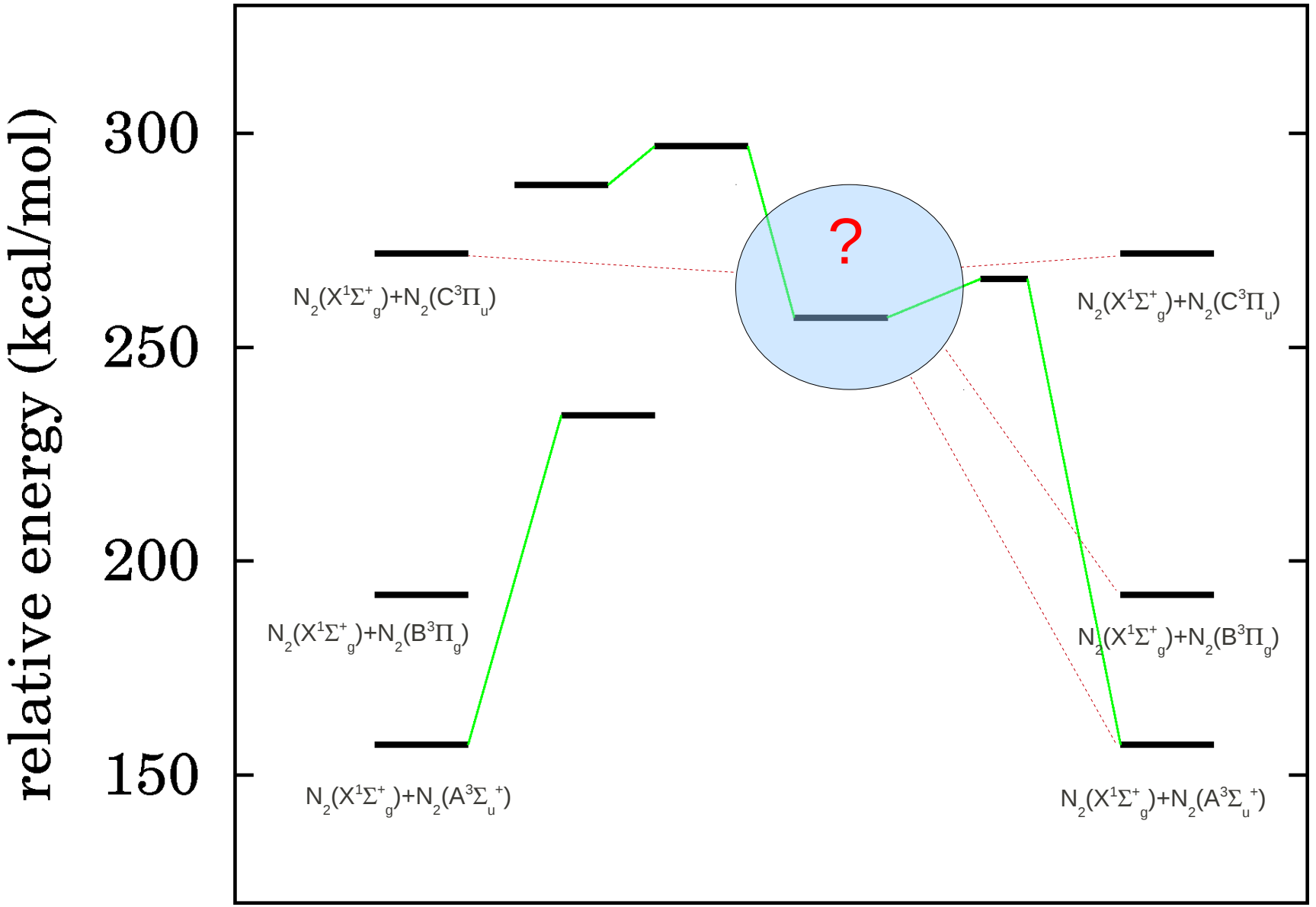


D_{2h} symmetry
(rectangular)

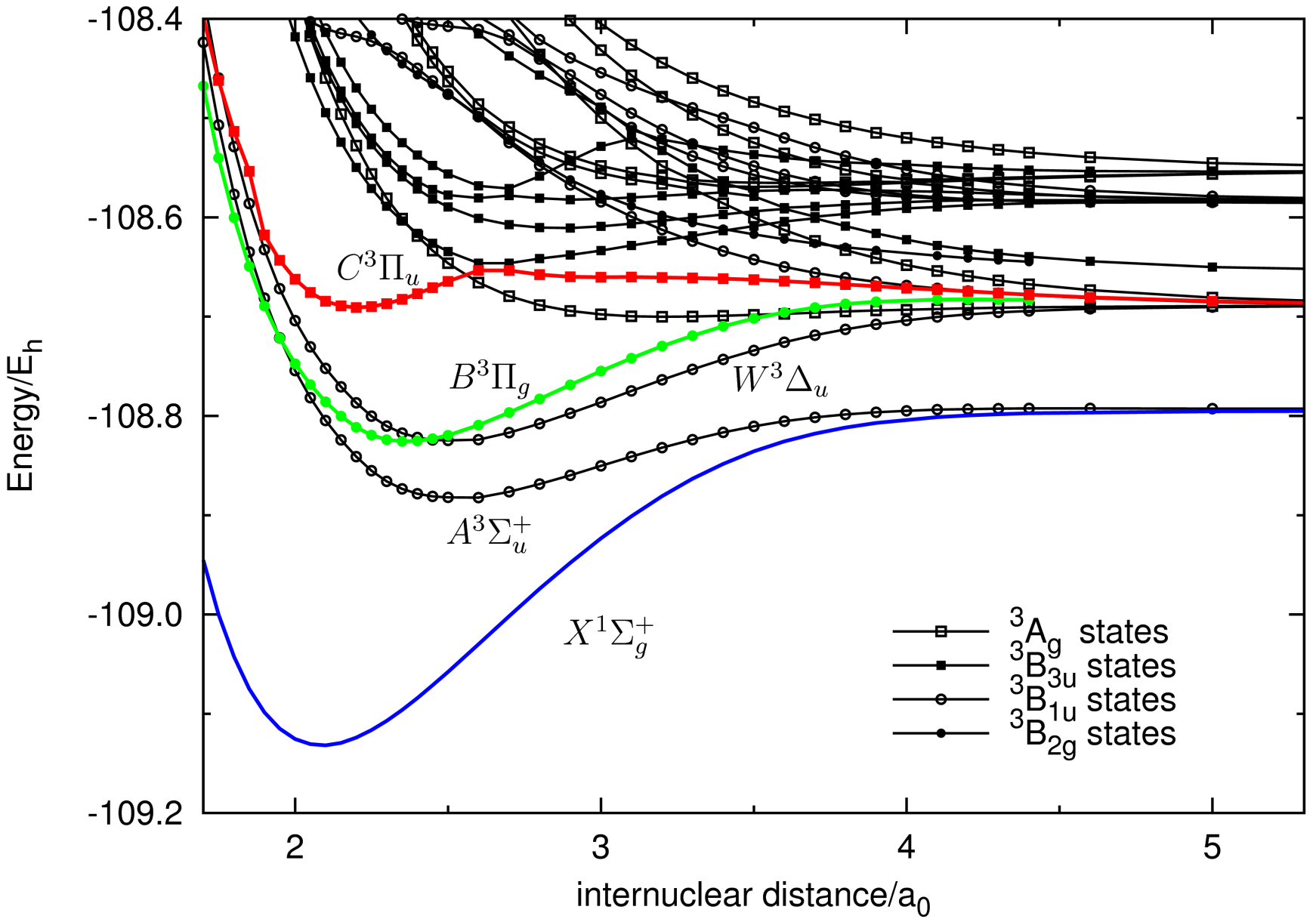
What was already known about N_4?



What are we looking for?



Ab initio CAS(10,8) potential curves for N_2

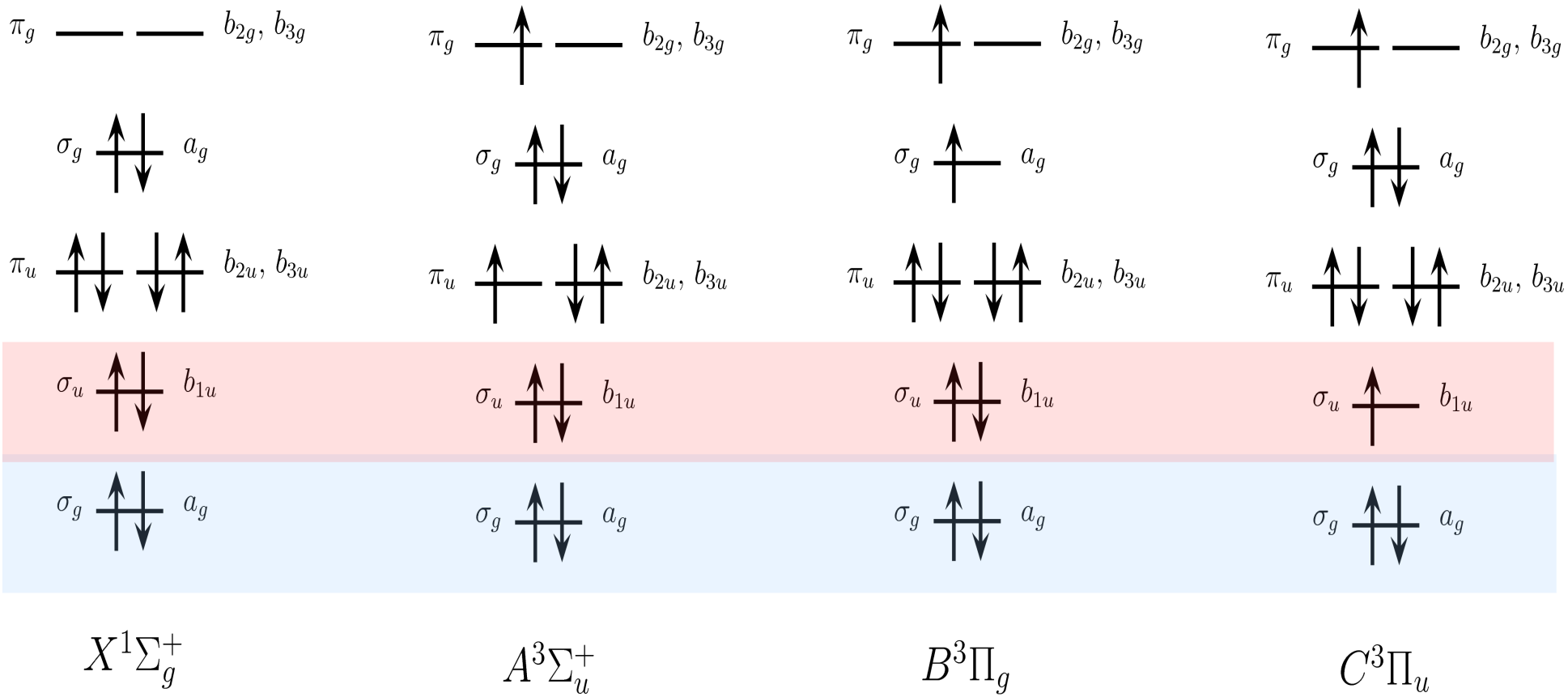


MOLPRO code, D2h symmetry, cc-pVTZ basis

CAS(*n*,*m*): all configurations (of the given symmetry) of *n* electrons in *m* orbitals

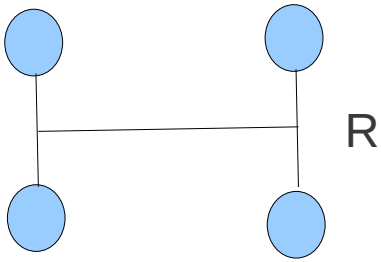
N_2 electronic configurations

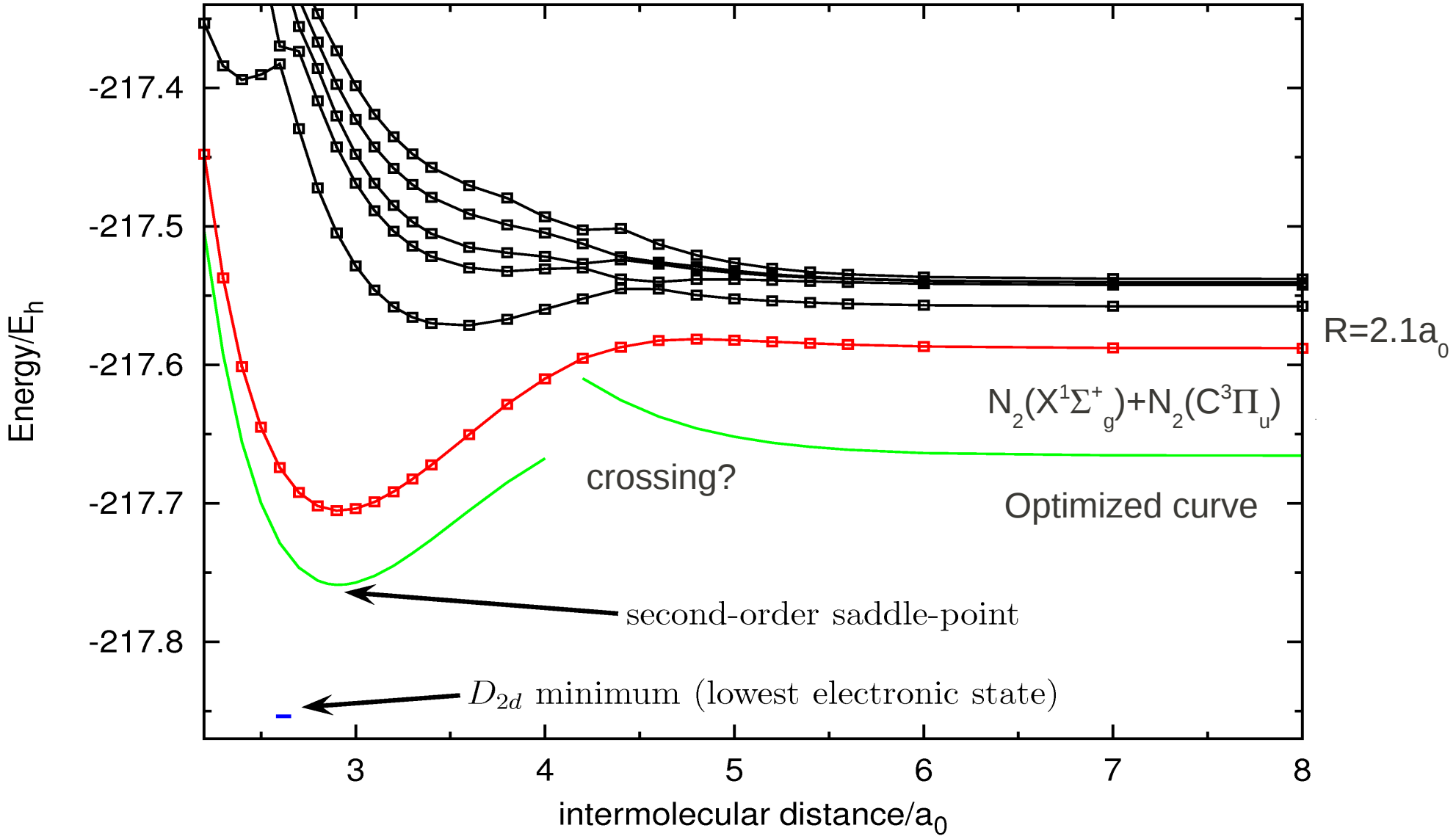
CAS(8,7) is reasonable but not CAS(6,6)



Ab initio CAS(12,12) for N_2-N_2

Rectangular geometries (D_{2h} symmetry) B_{3u} states

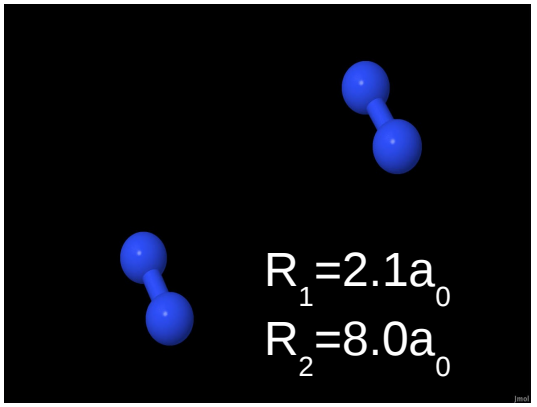


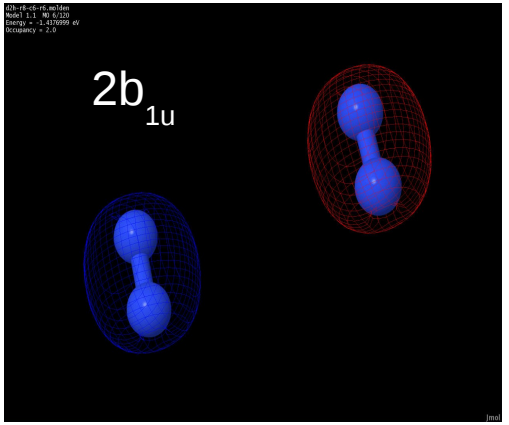


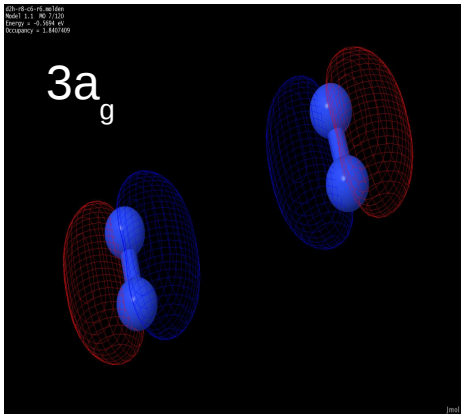
Ab initio CAS(12,12) for N_2-N_2

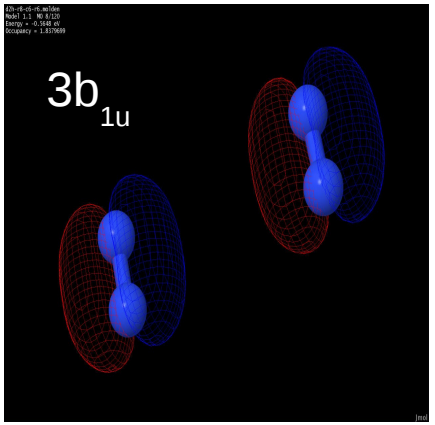
D_{2h} symmetry, B_{3u} state

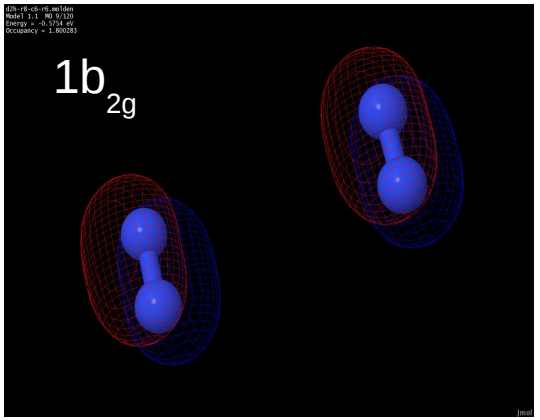
	a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
Dominant CSFs	22	2	100	1	22	2	200	0
	22	2	200	2	22	2	100	1

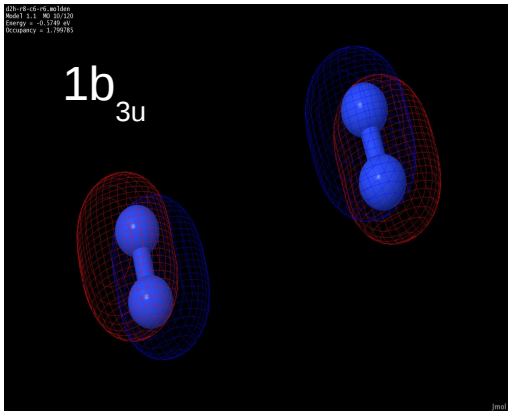


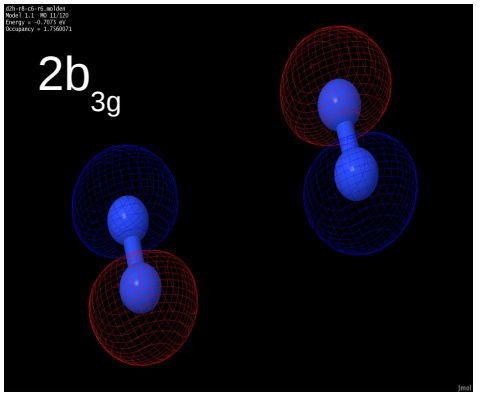


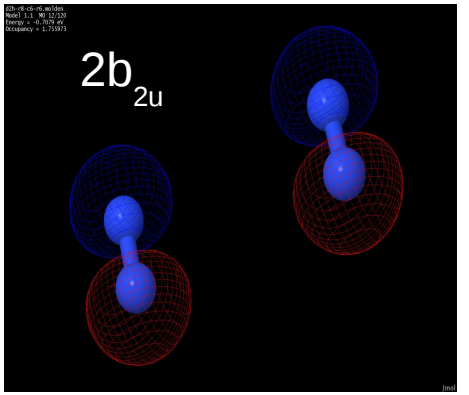


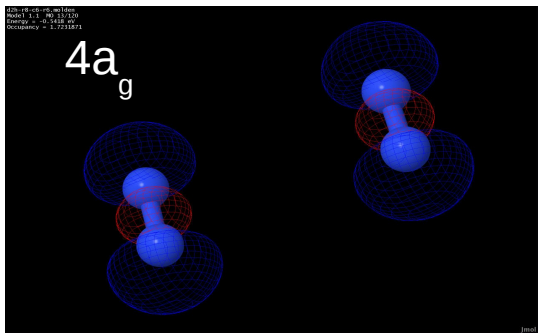


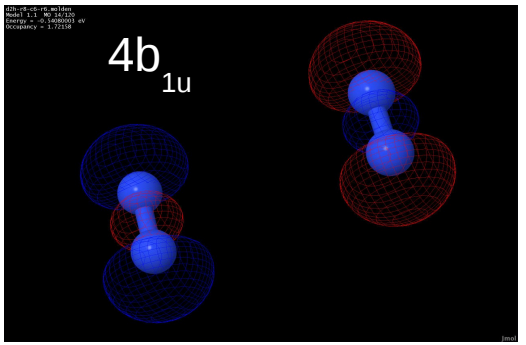


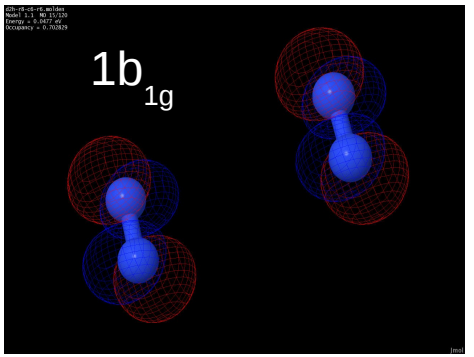


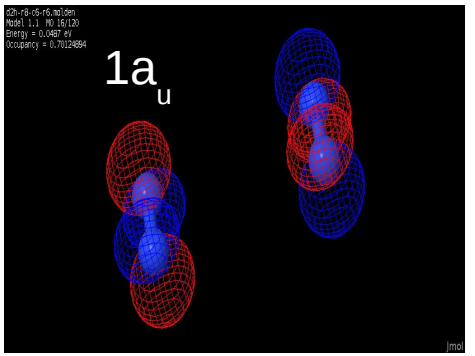












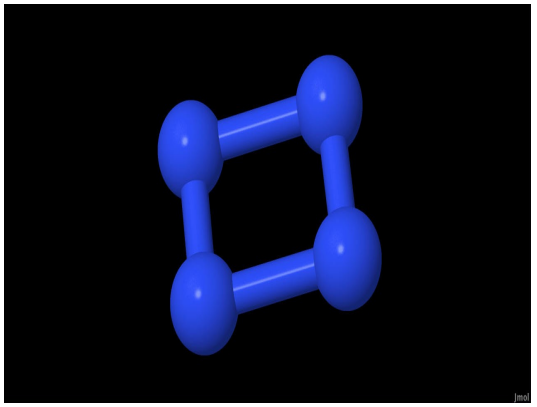
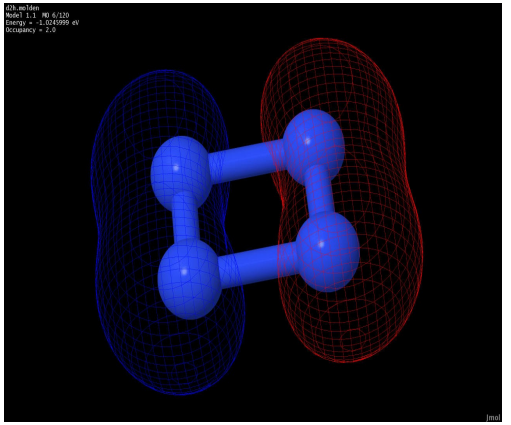
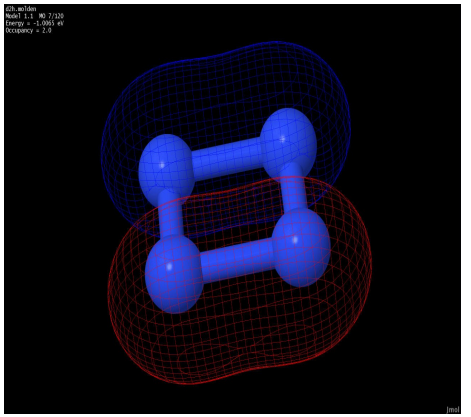
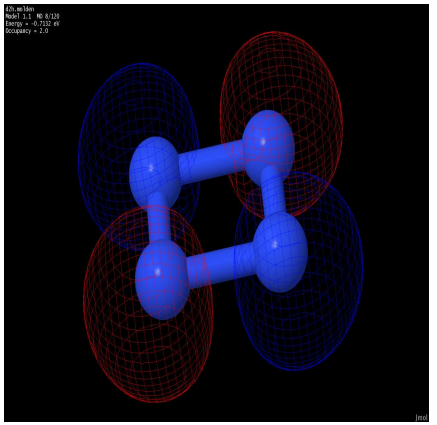
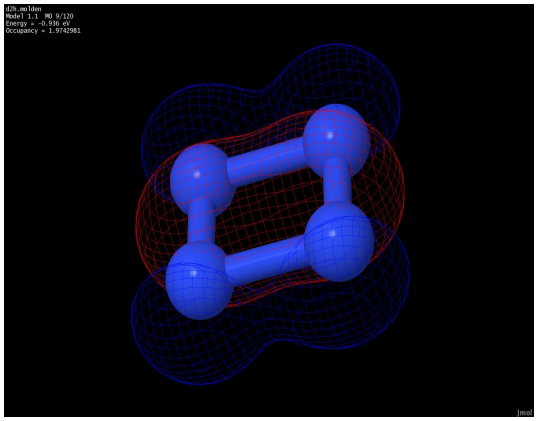
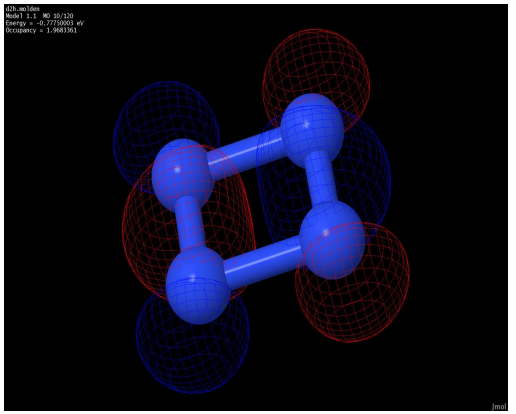
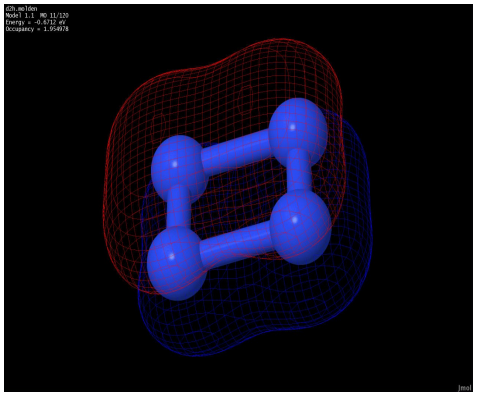
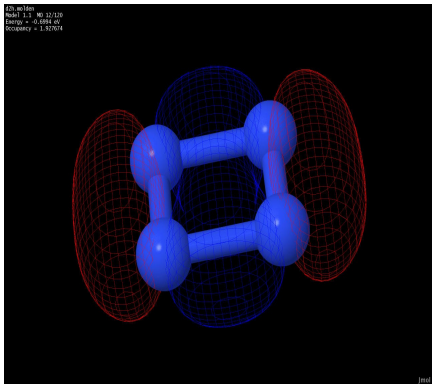
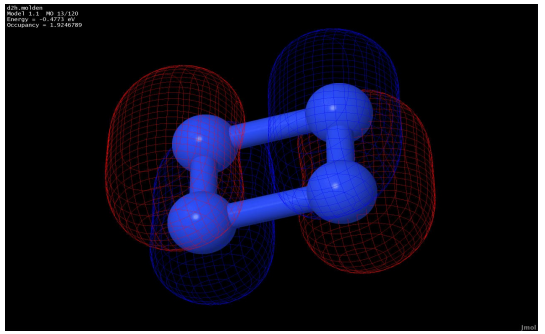
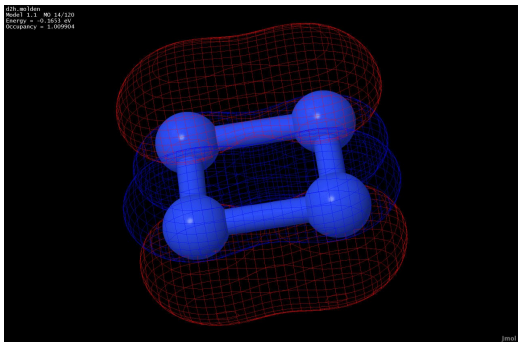
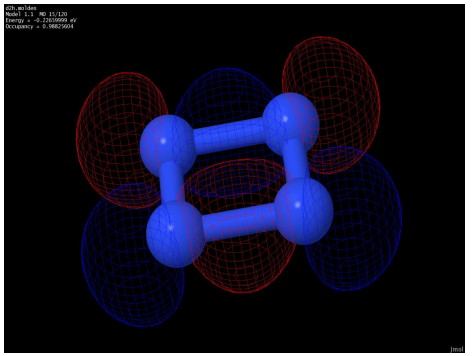
Ab initio CAS(12,12) for N_2-N_2

Second-order saddle point

(D_{2h} symmetry) B_{3u} state

a_g b_{3u} b_{2u} b_{1g} b_{1u} b_{2g} b_{3g} a_u

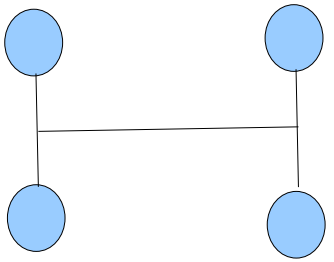
Dominant CSF |2 2 210 1 0 2 200 0|

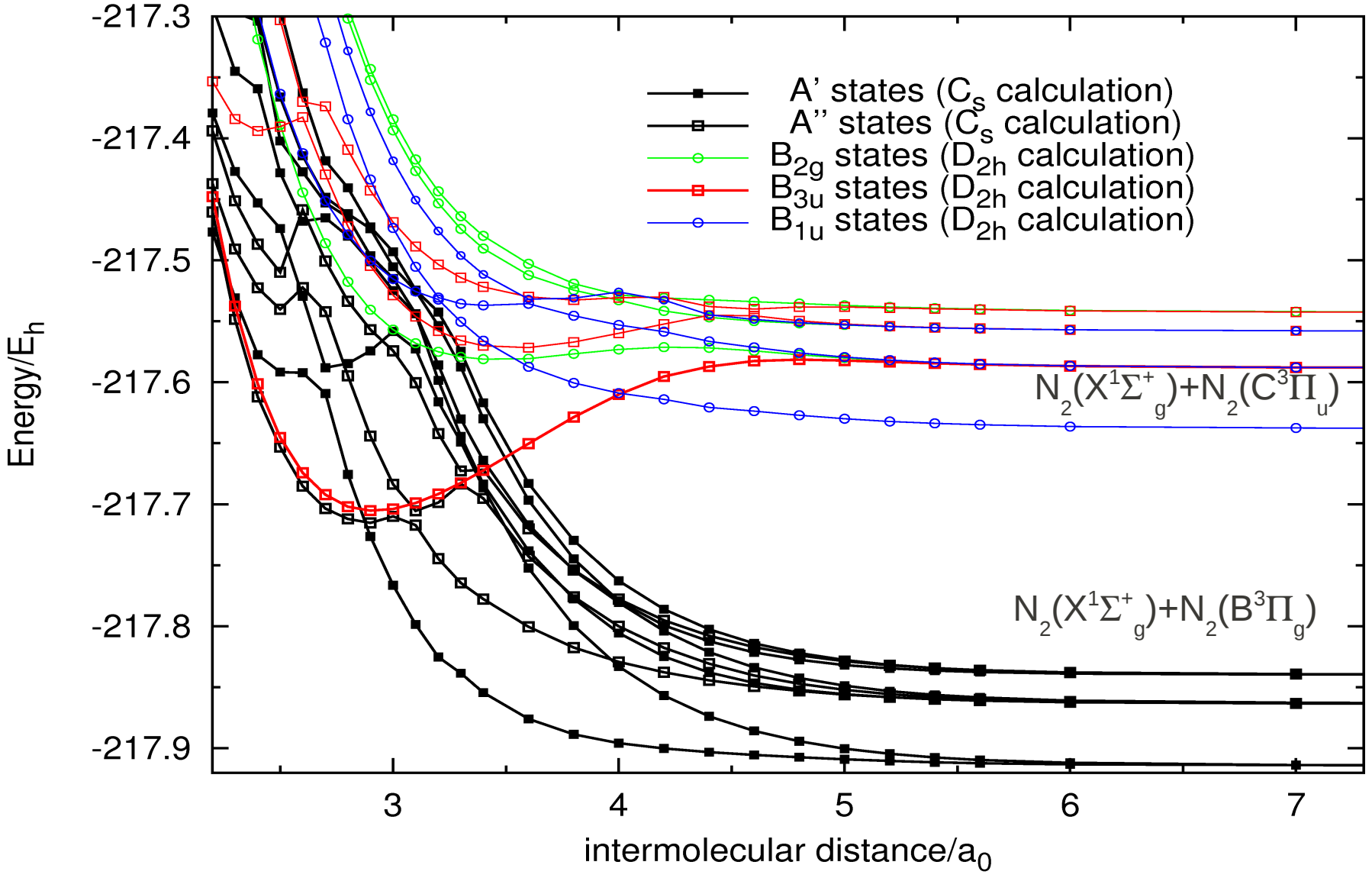
$R_1=2.39a_0$

$R_2=2.95a_0$

Ab initio CAS(12,12) for N_2-N_2

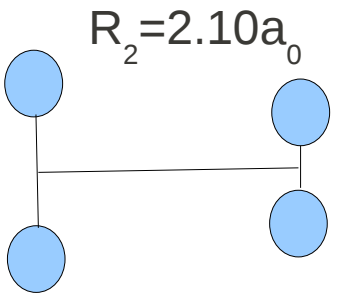


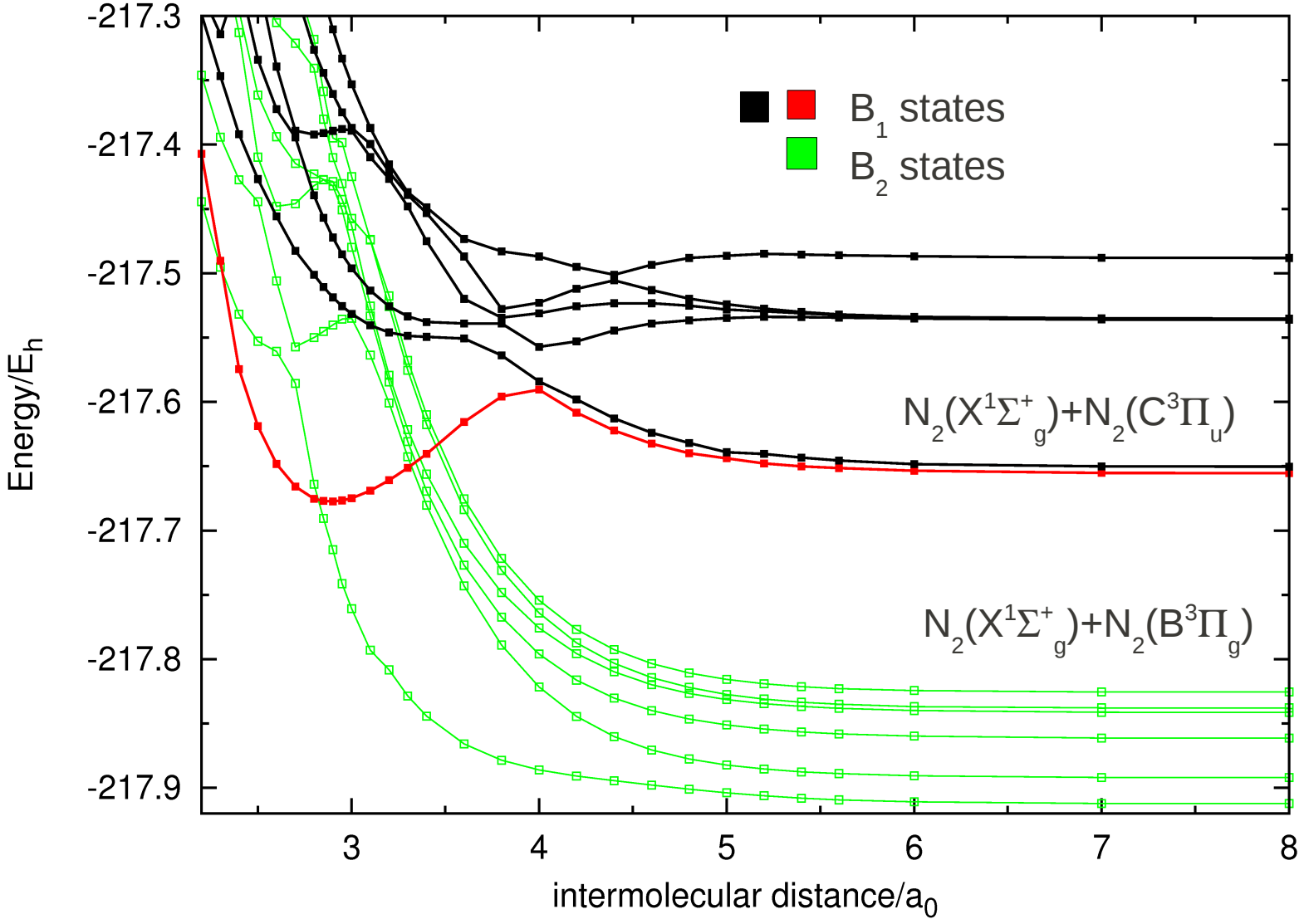
Rectangular geometries (D_{2h} and C_s symmetry calculations)



Ab initio CAS(12,12) for N_2-N_2

Trapezoidal geometries (C_{2v} symmetry) B_1 states and B_2 states





Calculations that are being done or planned

Calculations on other symmetrical (and less symmetrical) geometries

Multi-states CAS(16,14) calculations with CASPT2 corrections

Find better ways of dealing with reference configurations in the CAS(12,12) calculations!

Search for minima and saddle-points at excited states
and perform IRC calculations

Estimate the spectra and lifetimes of the related metastable species

Investigate potential energy surfaces crossings

Investigate the role of the long-range resonant energy

Obtain analytical potential energy surfaces for dynamics studies

Conclusions and prospects

Ab initio calculations appear to indicate that triplet electronic states of N_4 have a role in the quenching of $N_2(C^3\Pi_u)$

A complex species N_4 can be involved in the process but there are some doubts about the path from $N_2(C^3\Pi_u)+N_2(X^1\Sigma_g^+)$

A barrier seems to exist for the process $N_2(C^3\Pi_u)+N_2(X^1\Sigma_g^+)$ but its not clear if its energy is below or above dissociation because dynamical correlation energy have not been taken into account.

Thus, more work has to be done!

Aknowledgments

This work has the support of Fundação para a Ciência e Tecnologia (FCT), Portugal, under projects:

PTDC/QUI-QUI/099744/2008
PTDC/AAC-AMB/099737/2008
CERN/FP/83527/2008.