On the NIR–Vis–UVA Spectrum of NO_2:

PECs of electronic states and the $\widetilde{A}^2B_2$–$\widetilde{X}^2A_1$ conical intersection

G. J. Vázquez

Instituto de Ciencias Físicas
Universidad Nacional Autónoma de México
Cuernavaca
México

Collaborators

C. Godoy-Alcántar
CIQ IICBA-UAEM
Cuernavaca

J. M. Amero
Cuernavaca

H. P. Liebermann,
FBC–Mathematik und Naturwissenschaften
Bergische Universität
Wuppertal, Germany

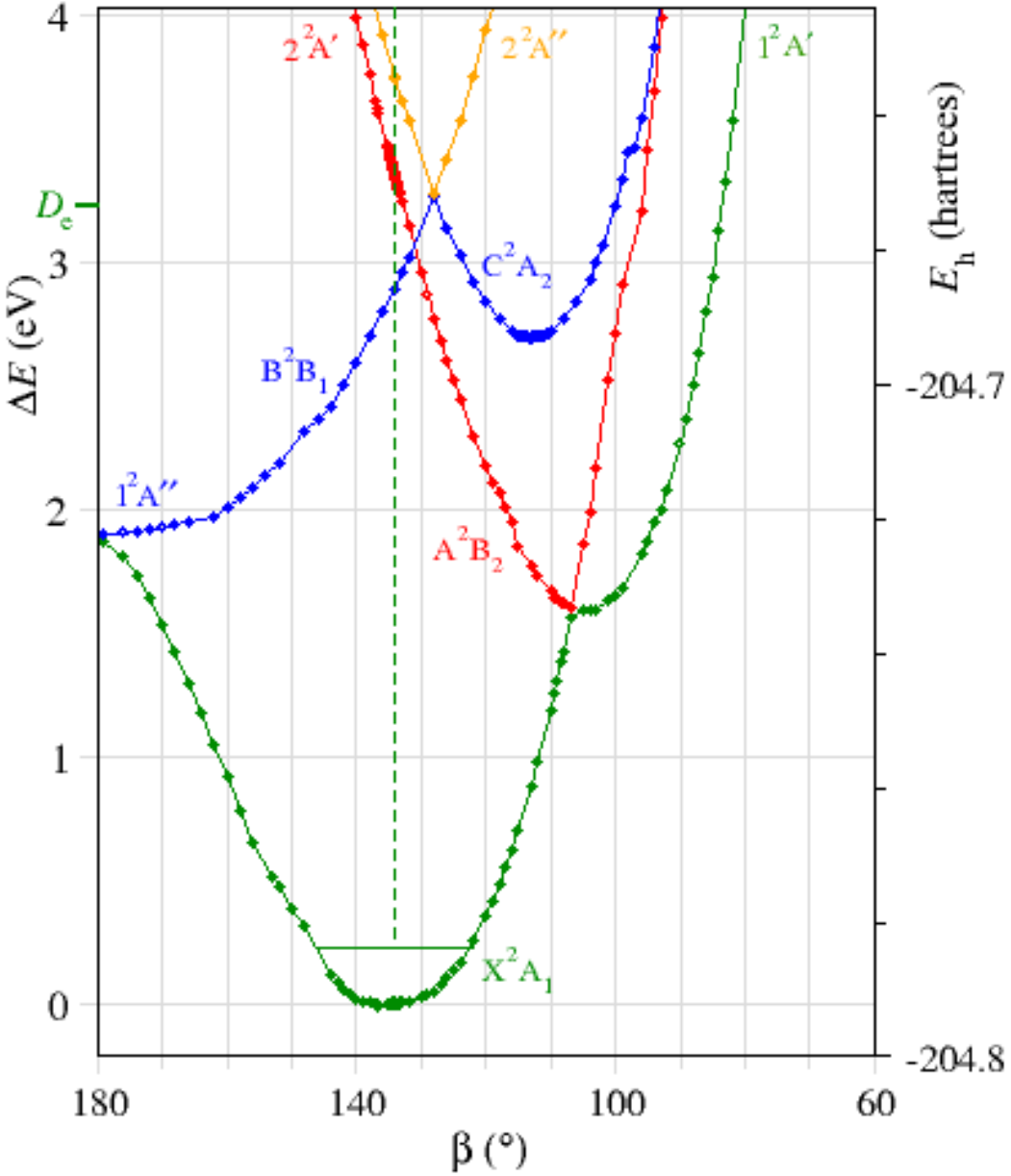
V. N. Serov & O. Atabek
Institut des Sciences Moléculaires d'Orsay ISMO, CNRS
Université Paris-Saclay, France

Details of calculations

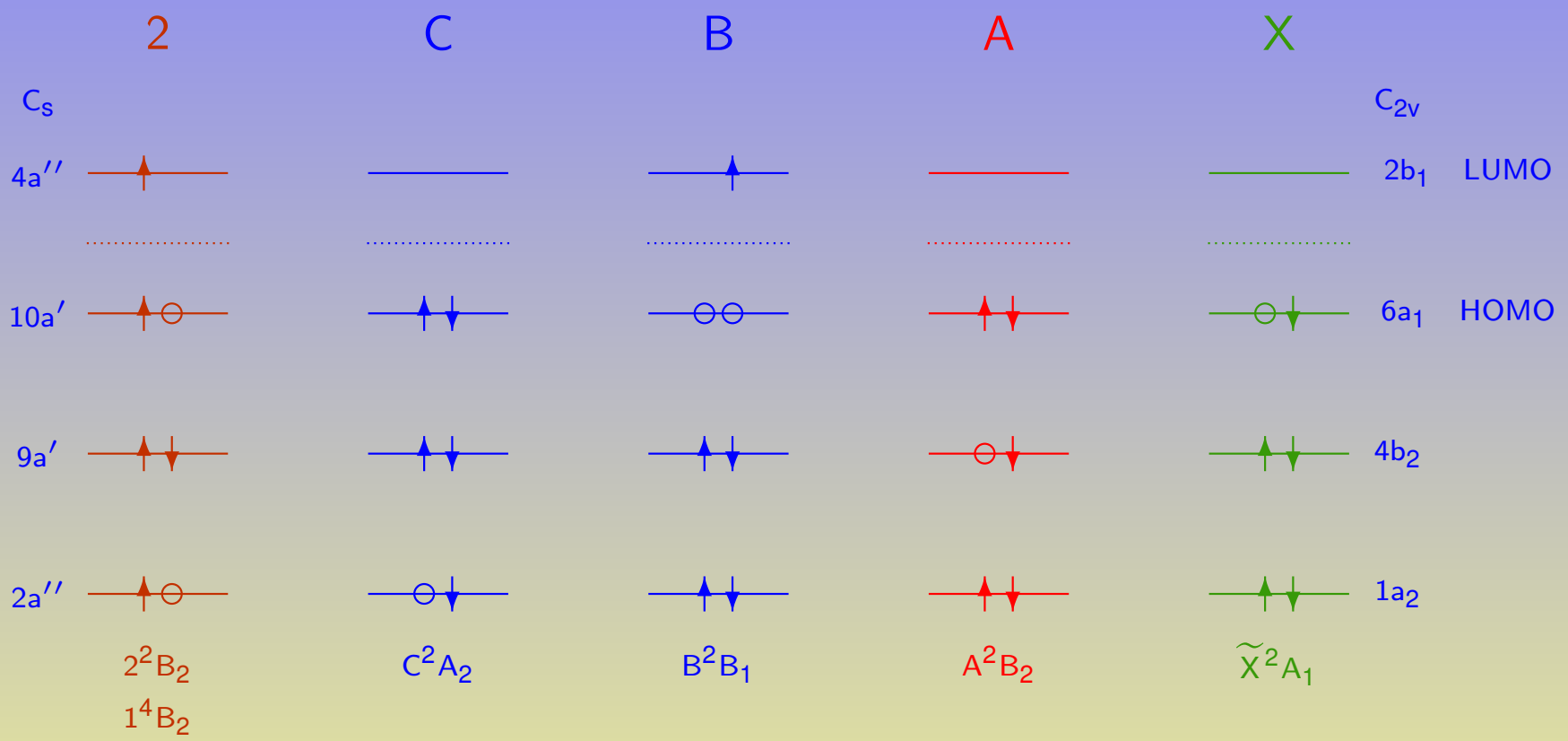
Ab initio Electronic Structure Calculations

Package	MRD–CI (Buenker & Peyerimhoff)
Basis	aug–cc–pVQZ
	+ Ryd (3s, 3p, 3d)
SCF	C_s symmetry
	Three MOs in core ($1s_{O_1}$, $1s_N$, $1s_{O_2}$)
CI	17 active electrons
	S & D + selected T, Q

$^2A'$ and $^2A''$ states of NO_2 in the NIR–Vis–UVA



States of NO_2 in the NIR–Vis–UVA



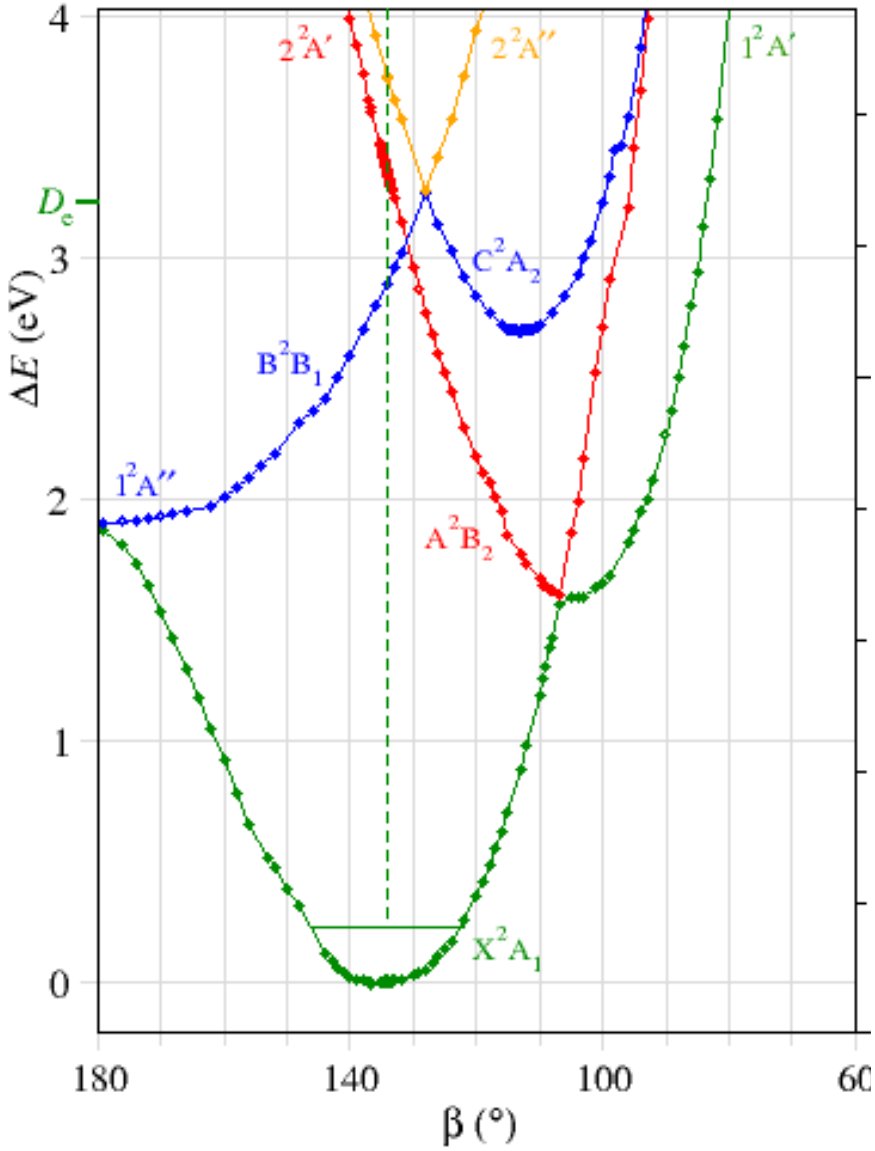
$\widetilde{X}^2A_1$ C_{2v} $(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2(3b_2)^2(5a_1)^2(1b_1)^2(1a_2)^2(4b_2)^2(6a_1)^1$ 23 electrons

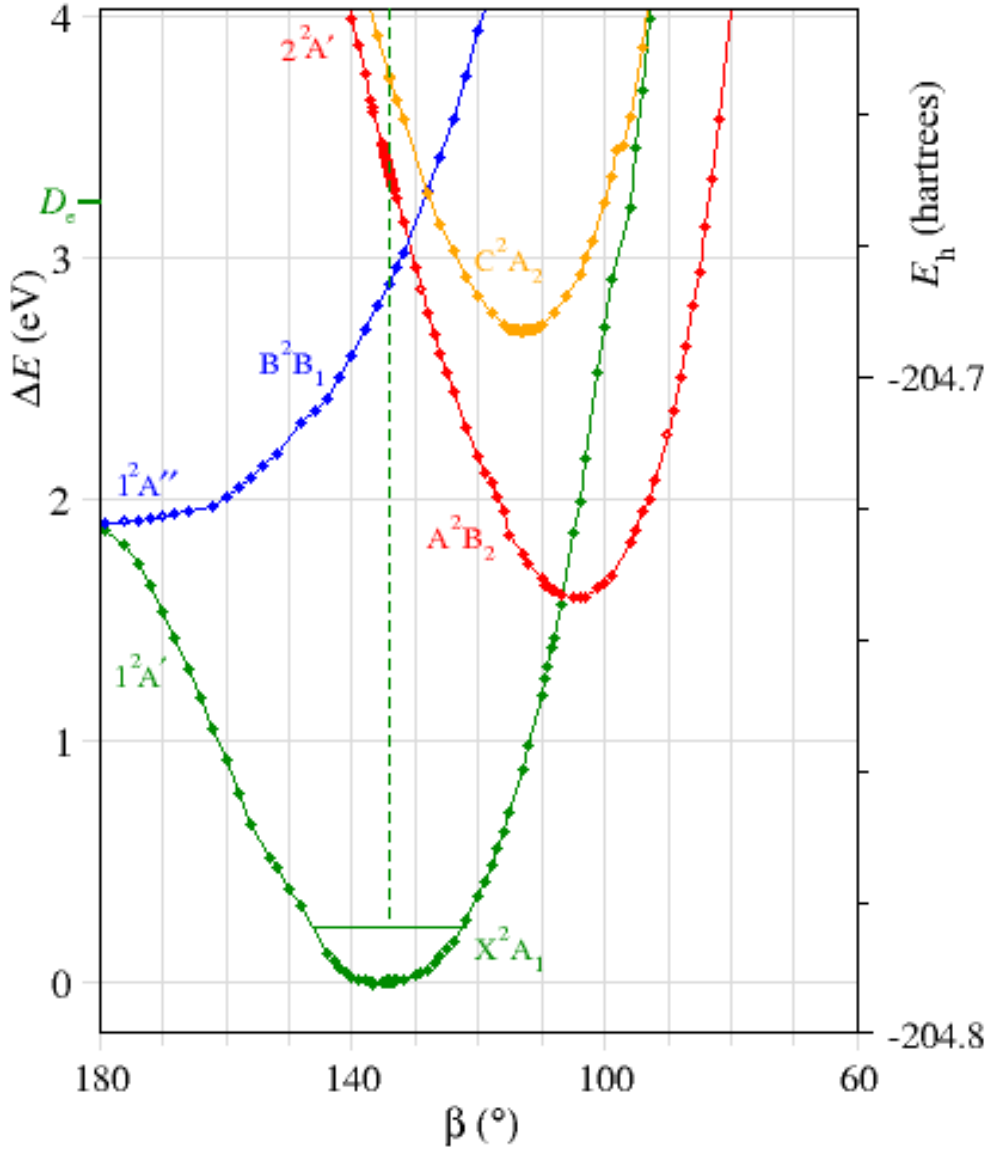
C_s $(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(1a'')^2(2a'')^2(9a')^2(10a')^1$

At equilibrium geometry of $\widetilde{X}$

Bending Adiabatic A′ & A″

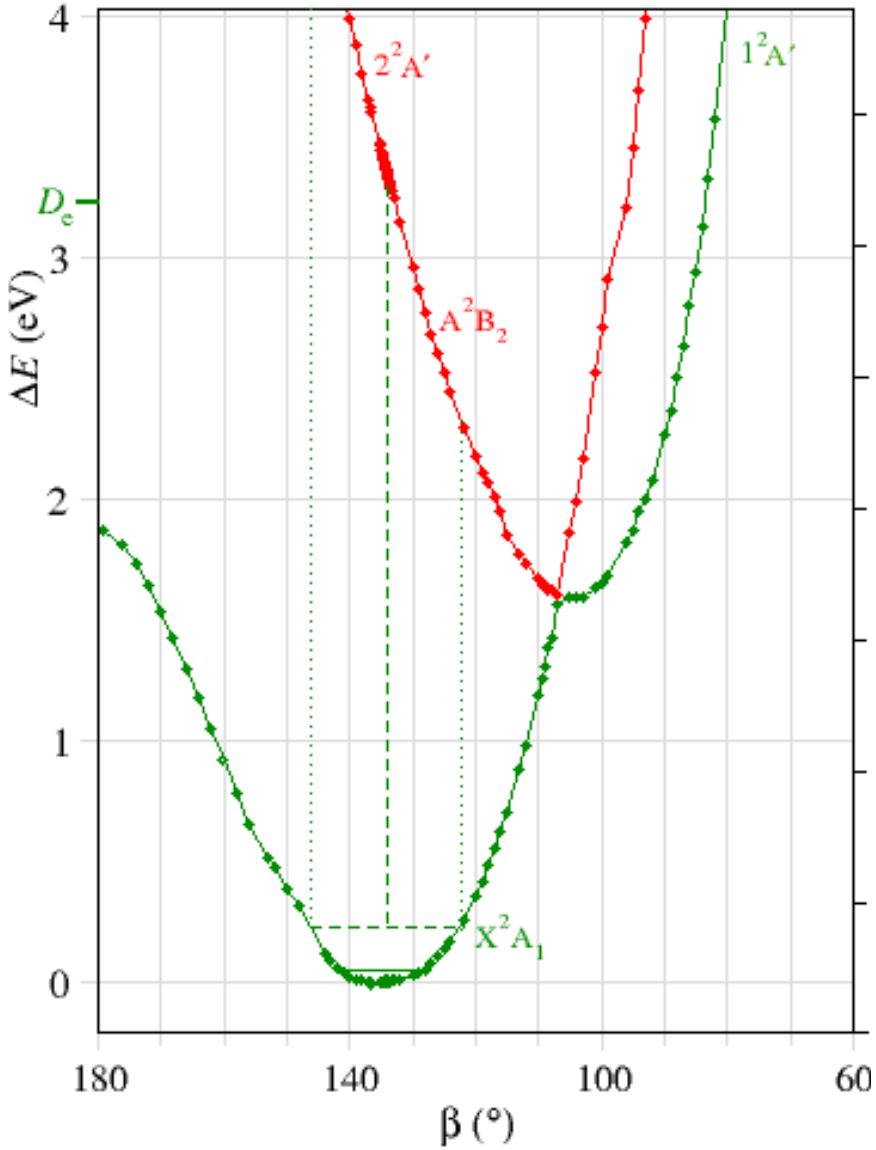
Diabatic

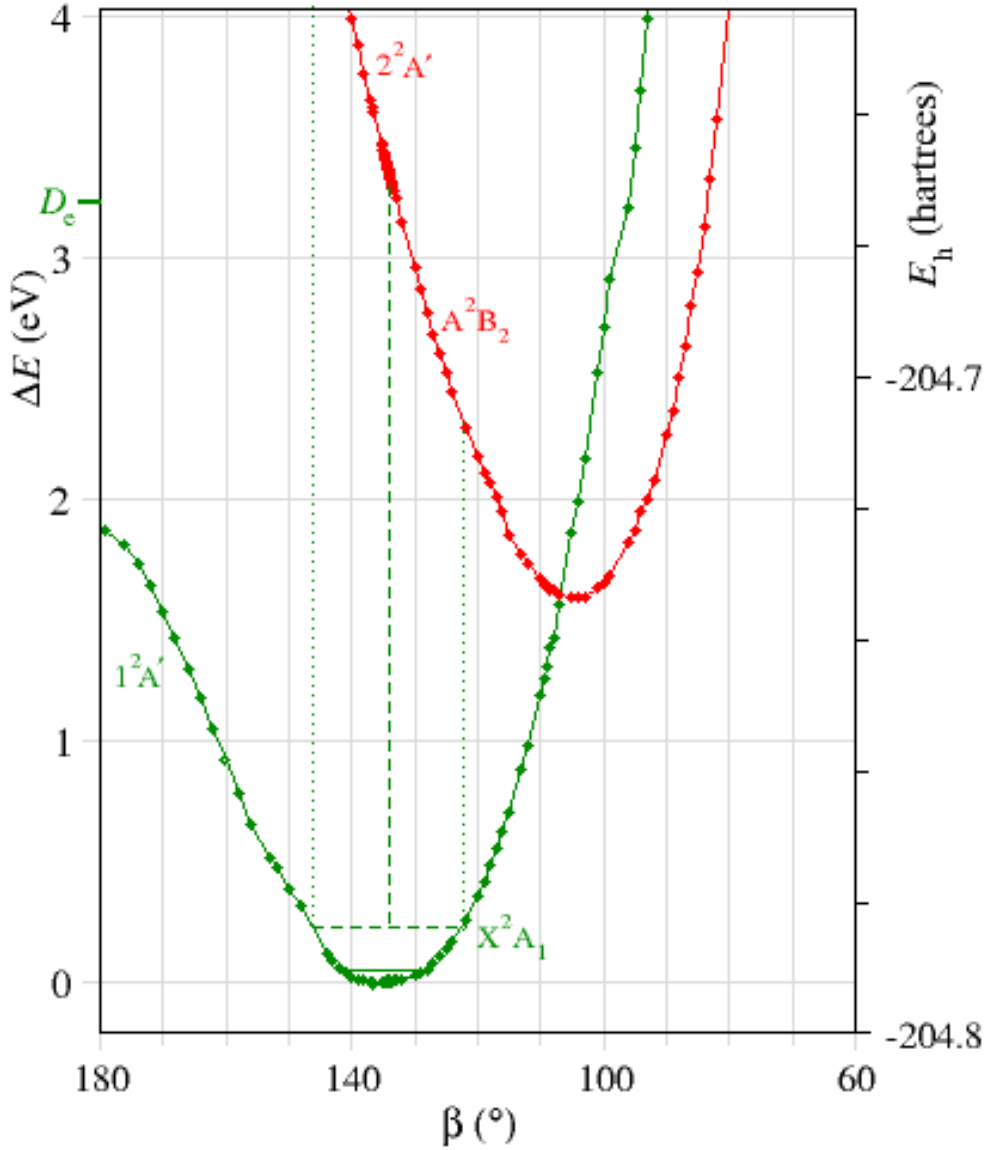




Bending Adiabatic A′

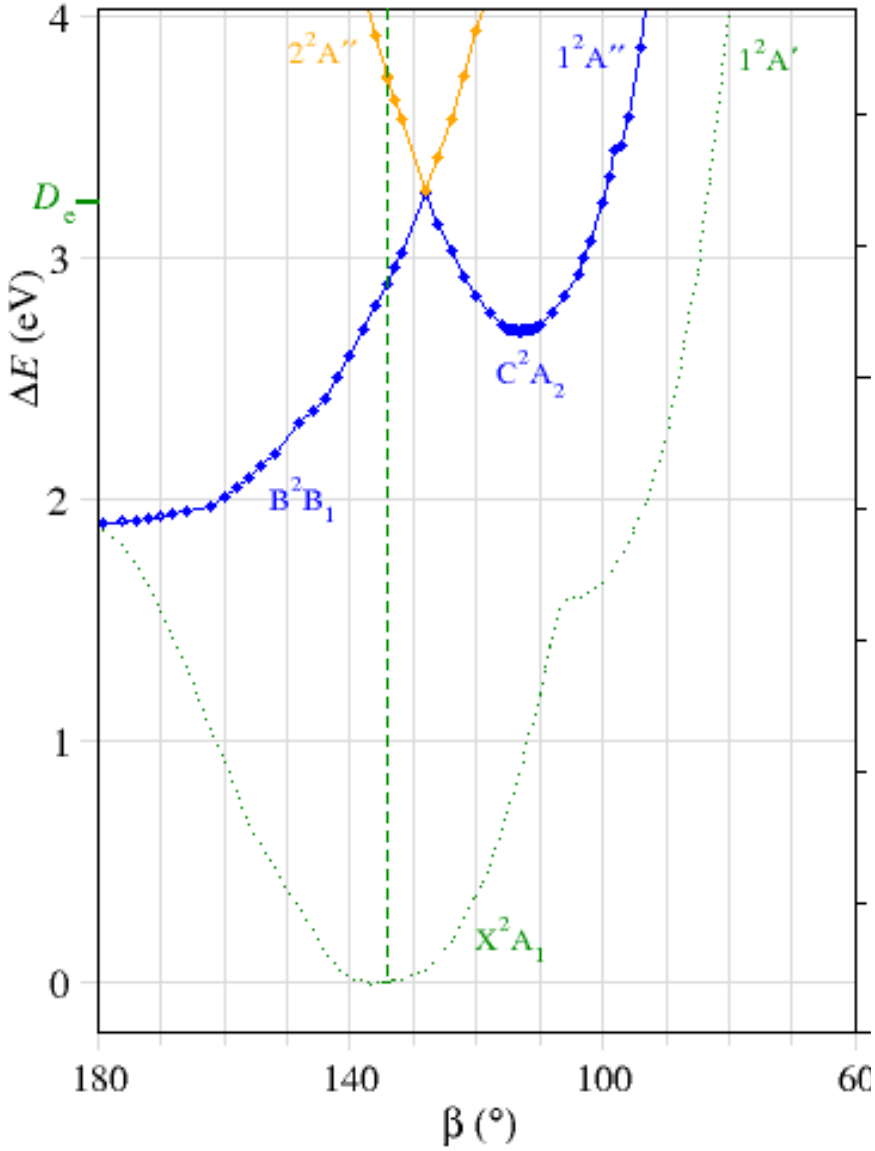
Diabatic

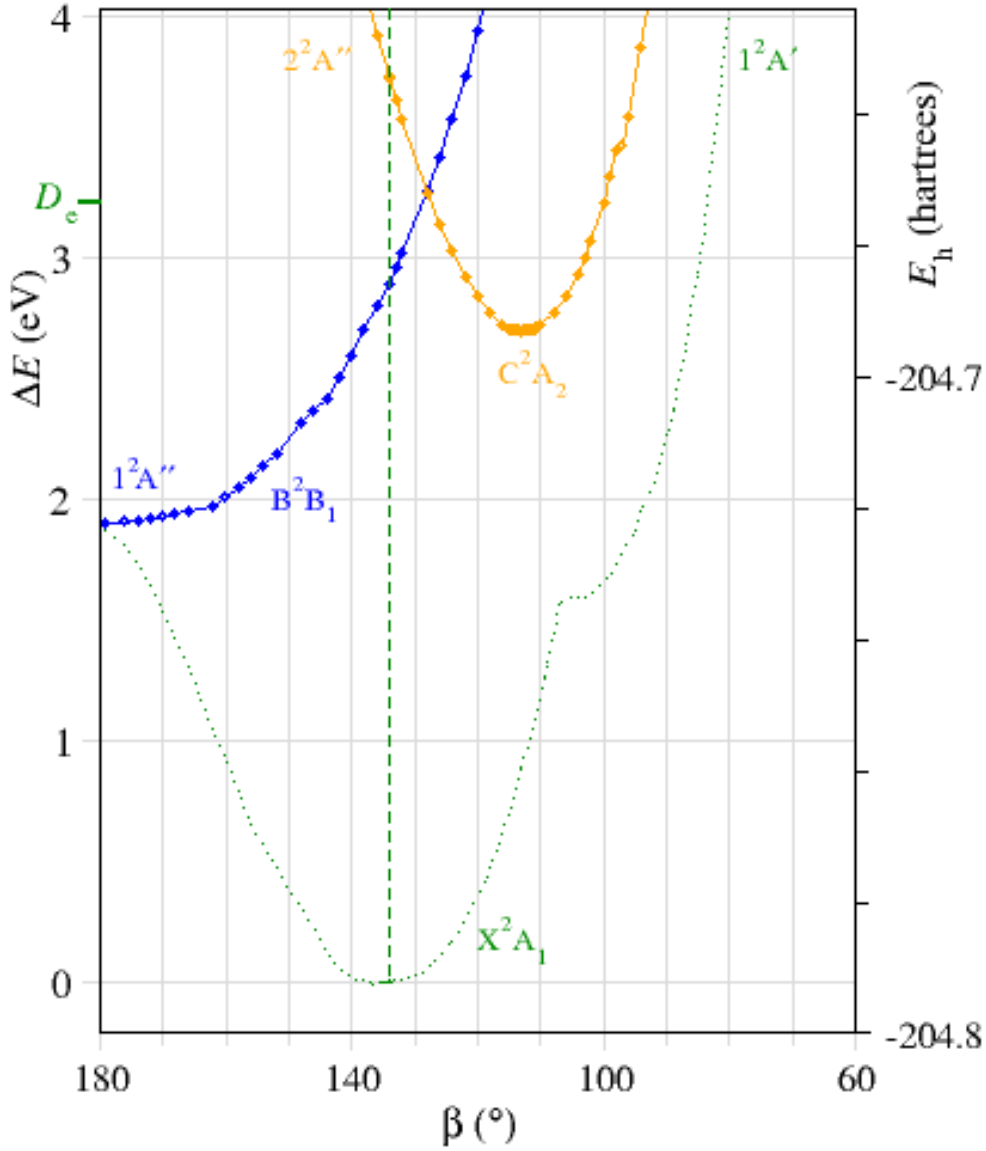




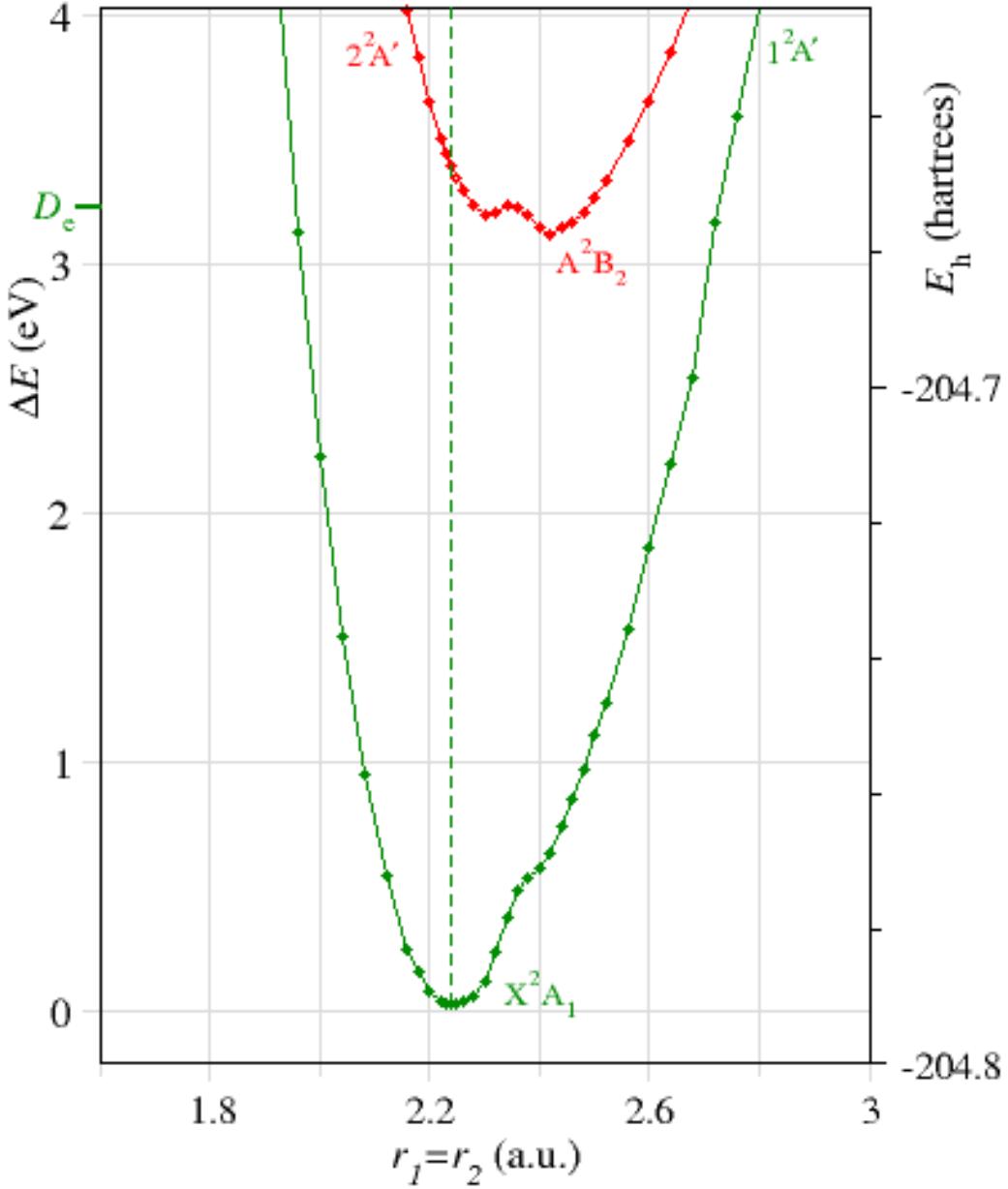
Bending Adiabatic A″

Diabatic

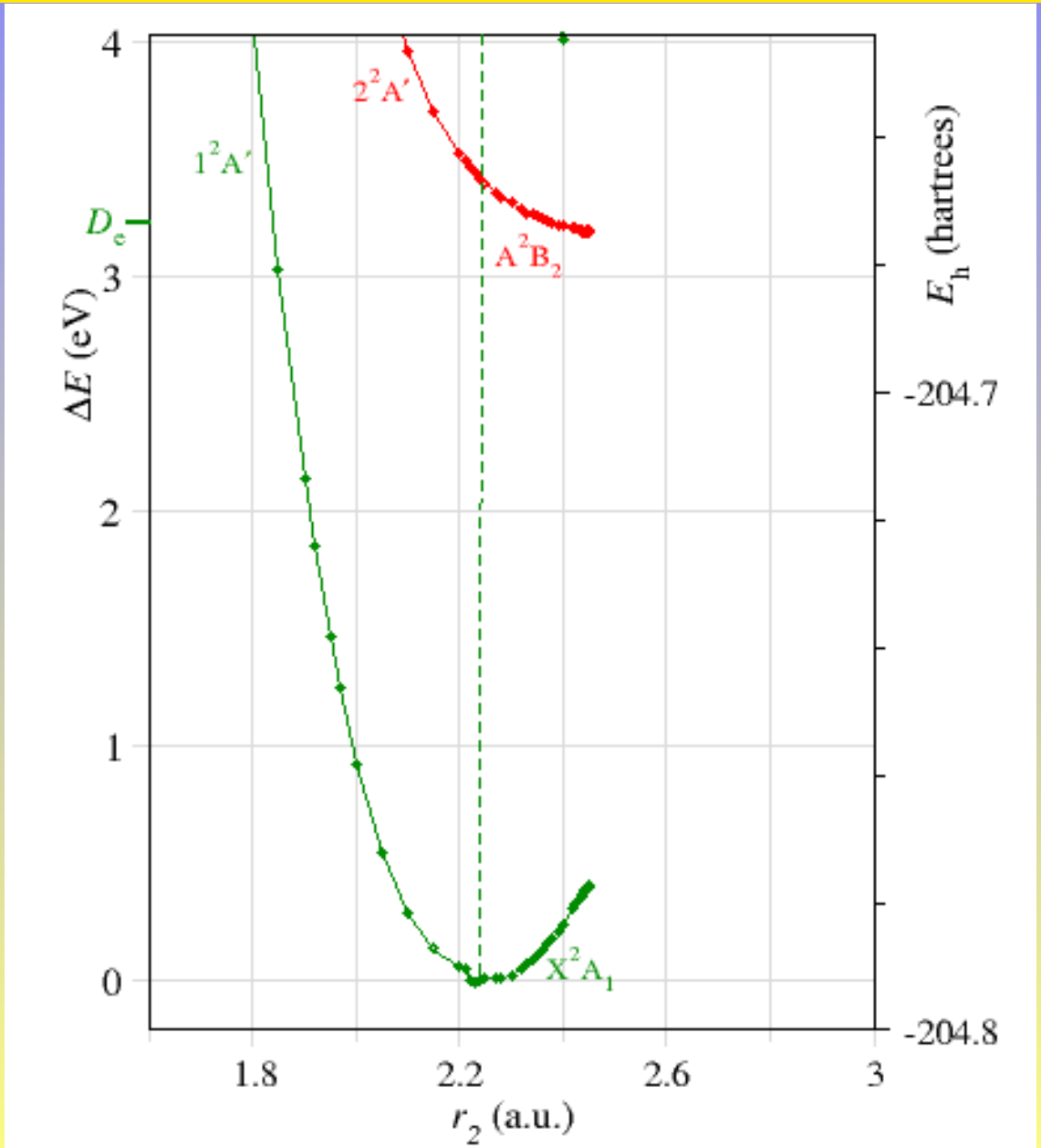




Symmetric stretch $^2A'$ states

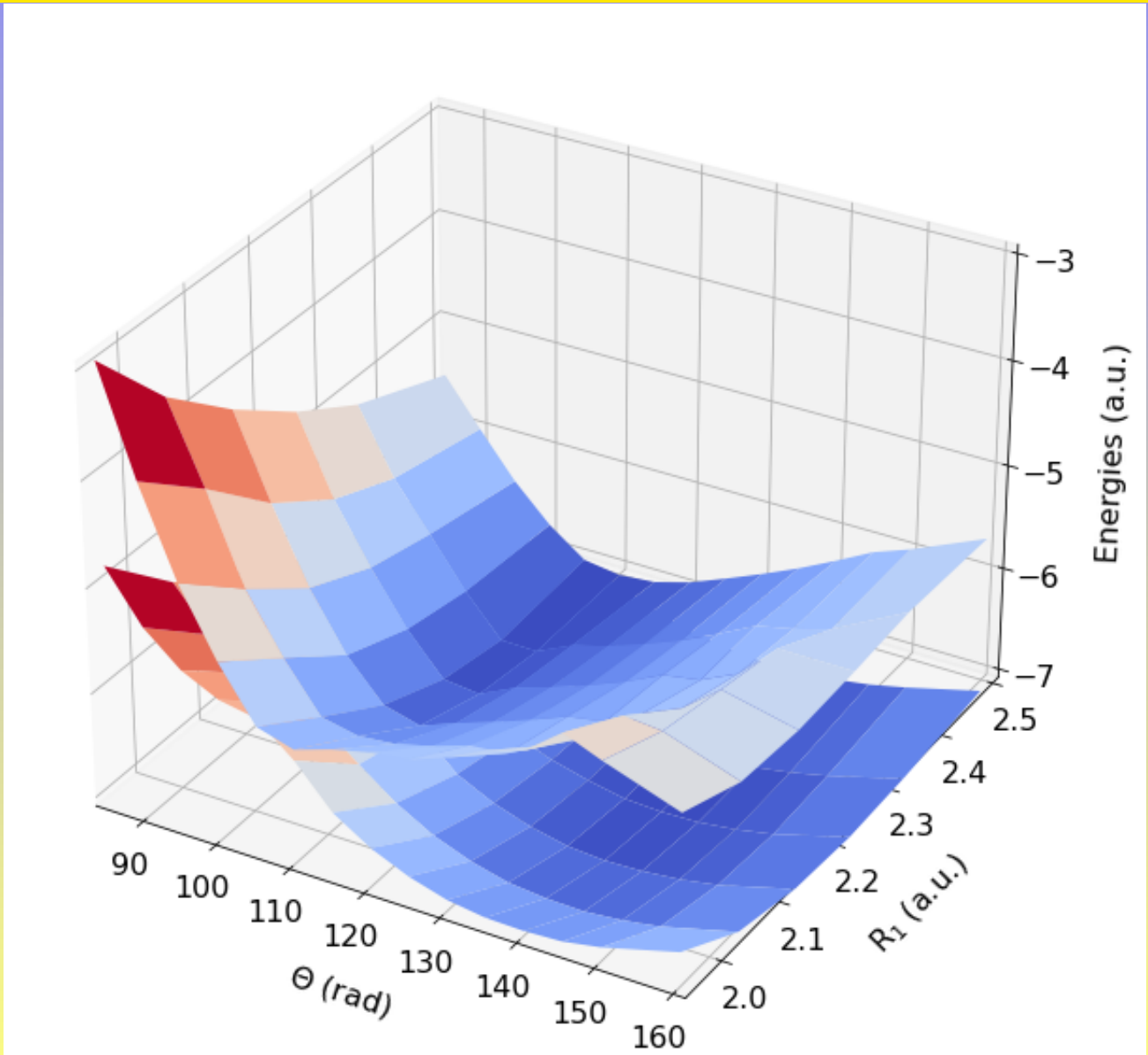


Asymmetric stretch $^2A'$ states



3D plots of the ground (lower) and first excited states of NO_2

Displaying the A–X conical intersection



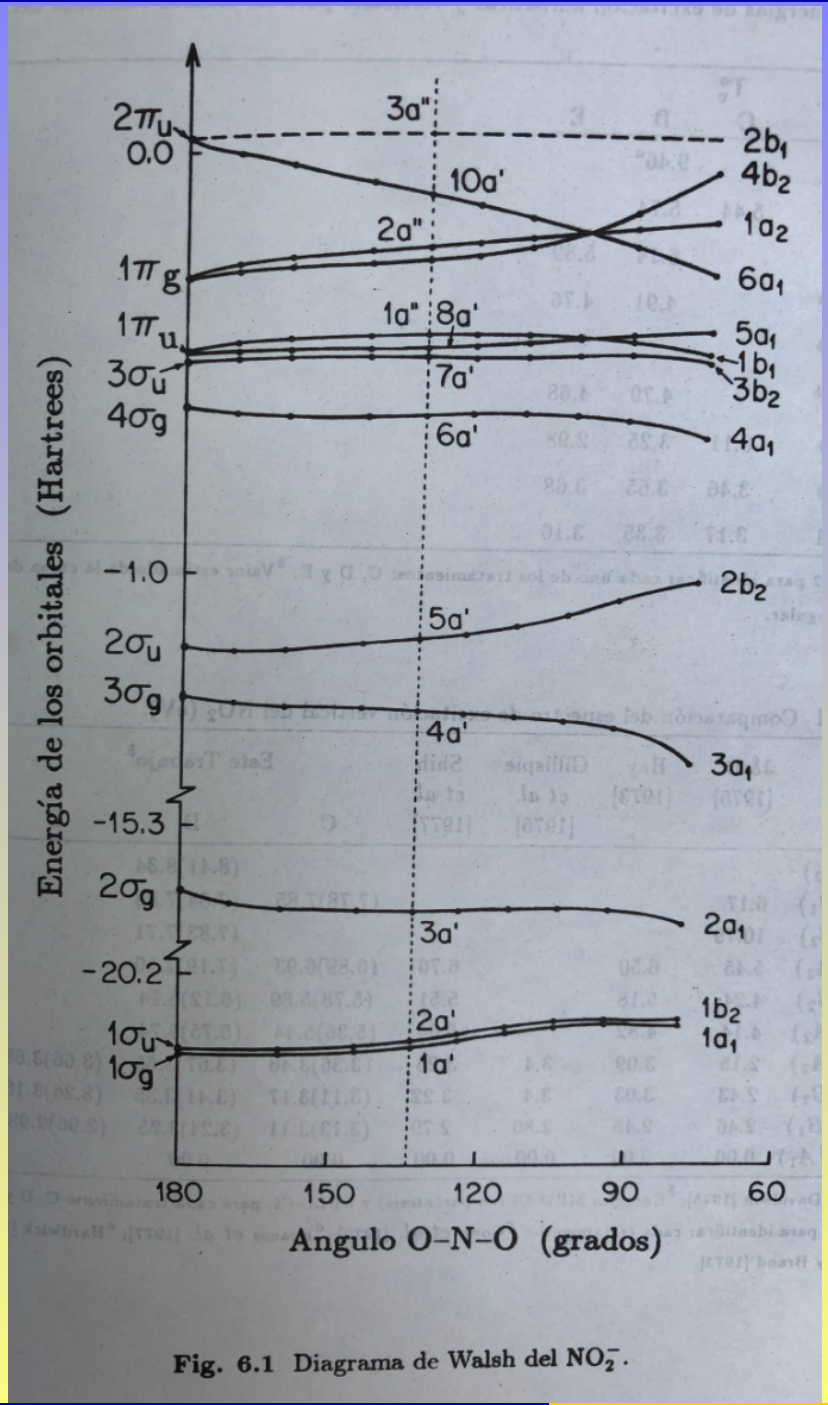


Fig. 6.1 Diagrama de Walsh del NO_2^-.

The $6a_1$ ($10a'$) drops steeply as the O–N–O angle decreases

This singular behaviour of $6a_1$ modifies the relative ordering of the upper MOs ...

This, in turn, determines the lowest-energy arrangements/occupancy of the electrons, *i.e.*, the configurations with lowest-energy

... and, ultimately, the *Order* of the electronic states.

Changes at the MO level, translate into changes at the electronic state level !

Plot from C. Godoy, M. Sc. Thesis, 1992

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity of the NO_2 NIR–Vis–UVA spectrum

Various factors contribute to the complexity :

i) Notice first that only few triatomics, *e.g.*, compounds made up of second-row atoms, exhibit transitions in the IR (H-III, page 1).
The NO_2 NIR spectrum is thus unusual, an exception to the rule

ii) Four electronic states below 4 eV, namely, three excited species A^2B_2, B^2B_1 and C^2A_2, in addition to the ground state X^2A_1

iii) Strong non–adiabatic effects due to two conical intersections, between A and X (A′s), and between B and C (A″s)

iv) Fine structure due to the spin angular momentum $s = \frac{1}{2}$ of the unpaired electron

v) Hyperfine structure due to the nuclear spin angular momentum $I = 1$ of ^{14}N

vi) Renner-Teller (RT) interaction between B^2B_1 and X^2A_1, as both, states arise from, or correlate to, the linear doubly-degenerated $1^2\Pi_u$ state at 180°

vii) Predissociation. The dissociation energy of the $^{14}N^{16}O_2$ GS to the first dissociation limit, $O(^3P) + NO(^2\Pi)$, is $D_0 = 25,128.56\,cm^{-1}$ (3.115 eV) and $D_e = 26,051.17\,cm^{-1}$ (3.229 eV).
The Zero-Point Energy (ZPE) is $1871.05\,cm^{-1}$ (0.231 eV).

Hence, above 3.115 eV, all four states X, A, B and C are open energetically to predissociate into $O(^3P) + NO(^2\Pi)$

On the complexity . . .

viii) Dissimilar geometrical traits of A and X.
The geometries (β_e, r_e) of A and X are rather different.

The A and X minima are shifted appreciably with respect to each other.
The bending equilibrium angles, for instance, are $\beta_e(A) = 101.9^\circ$ and $\beta_e(X) = 134.1^\circ$.

Also, a singular feature of A is that it drops steeply as the bending angle decreases.
The shifted A vis-à-vis X minima and the steepness of A are at the origin of the long bending vibrational progressions observed in the A $\leftarrow$ X transition.

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

Summary

- Ab initio MRD–CI electronic structure calculations of NO_2.
- PECs (bending, symmetric/asymmetric stretch) of the five states rooted in the NIR-Vis-UVA : X^2A_1, A^2B_2, B^2B_1, C^2A_2 and 2^2B_2.
- NO_2 is one of the smallest species displaying the complexity associated with the coupling of the electronic and nuclear motions and the break-down of the BO adiabatic approximation.
- These phenomena, which in NO_2 are already apparent in the NIR, become common at higher energies, notably in the visible, but chiefly in the UV region where Rydberg-valence interactions set in.
- We mentioned various non-adiabatic processes, e.g., conical intersections, RT interactions, relaxation of vibrational energy, electronic-to-vibrational (E-V) energy transfer, dynamics of photodissociation/predissociation & of photoionization/autoionization
- NO_2 has become a preferred testing ground for the study of such non-adiabatic processes
- Studies of the above processes in this 'simple' triatomic species can provide a detailed insight into the mechanisms of intramolecular energy redistribution in molecular systems

A few months ago

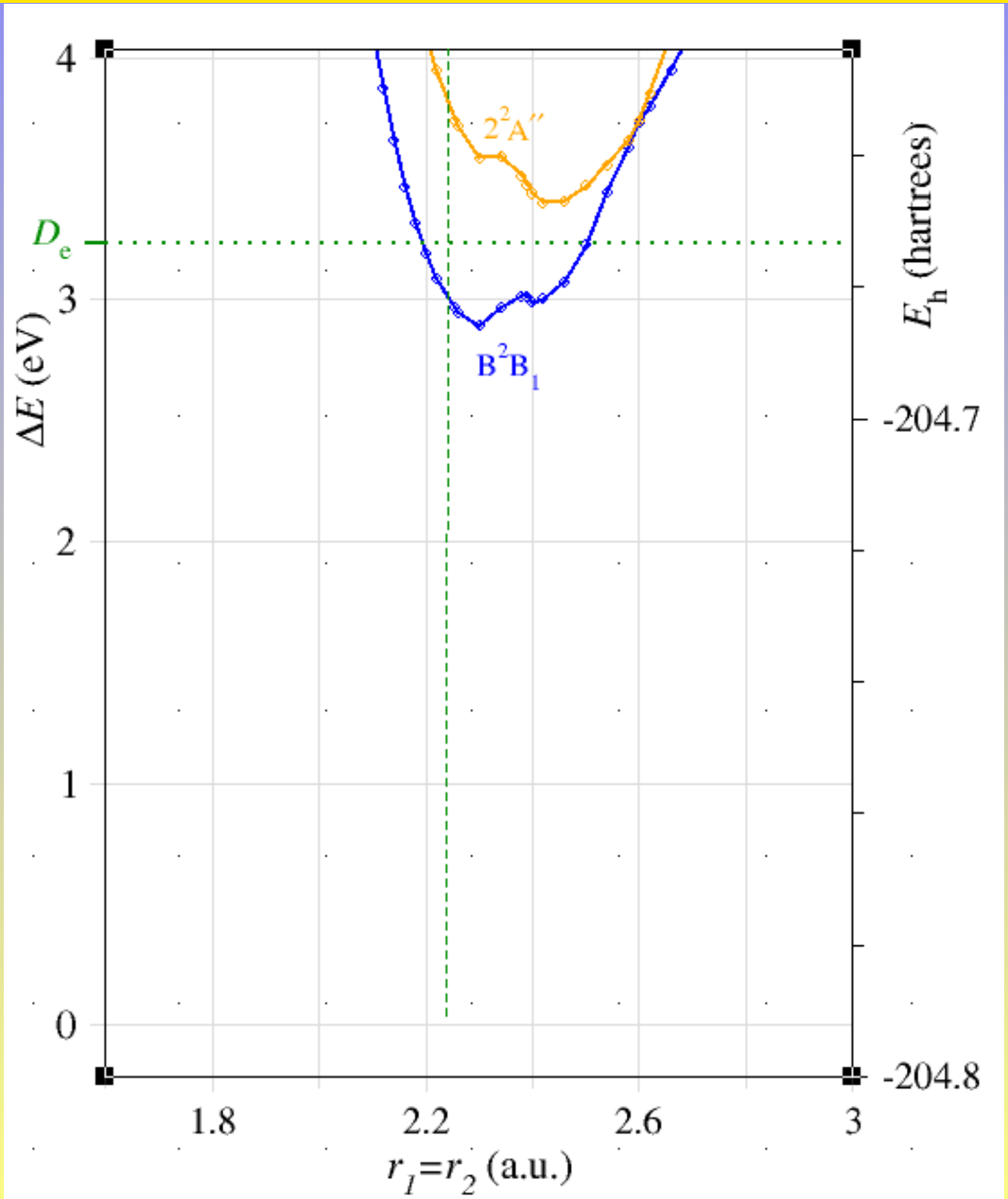
Emeritus Prof. Osman Atabek passed away suddenly.

In this posthumous contribution

the authors pay

Homage to the scientist, colleague and friend.

Symmetric stretch $^2A''$ states



Asymmetric stretch $^2A''$ states