Low-lying Adiabatic Electronic States of NO: a QMC Study[†]

Luigi Giannelli[a] and Claudio Amovilli[b,*]

[a]*Dipartimento di Fisica "E. Fermi", Università di Pisa, Largo Bruno Pontecorvo 3, I-56127 Pisa, Italy*
[b]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy*

Abstract. Using Diffusion Monte Carlo in the fixed node approximation (FN-DMC) we have computed the electronic energy curves for some low lying doublet and quartet adiabatic states of NO. By starting with compact trial wave functions, we obtained accurate results in a wide range of internuclear distances. We have also been able to compute some spectroscopic properties and to interpret UV and visible absorption and emission spectra of NO in the gas phase by computing the Franck-Condon factors in the Born-Oppenheimer approximation. The comparison with available theoretical and experimental data is good.(doi: 10.5562/cca2302)

Keywords: fixed-node diffusion Monte Carlo, excited states, potential energy curves, Born-Oppenheimer approximation, UV-Vis spectra

INTRODUCTION

With Quantum Monte Carlo (QMC) we intend a methodology which employs stochastic techniques to solve problems of quantum mechanics.[1–3] In particular there are methods designed to solve the Schrödinger equation for a system of interacting particles (bosons or fermions). When we refer to the electrons of an isolated molecule, we typically resort to the variational Monte Carlo (VMC) and to the fixed-node diffusion Monte Carlo (FN-DMC).[4] In VMC, the wave function is explicitly written and it is optimized to get the best electronic energy while in FN-DMC a trial wave function is projected over the best wave function with the same nodes. In DMC the final wave function is unknown but the expectation value of the energy is normally very close to the exact one, including in this way much of the electron correlation. The quality of the results depend on how much the nodal structure of the trial wave function approaches the exact one. Klein and Pickett[5] pointed out that the exact position of the boundary between positive and negative domains, namely the aforementioned fermionic nodes, is unknown and is determined by the quantum many-body physics. DMC is among the most accurate methods to compute the ground state energy of a system of electrons. In the last decade, there has been published a significant number of papers in which also excitation energies have been calculated at the FN-DMC level (see, for example Ref. 6). In this cases, the application of DMC to the lowest energy state of a given

symmetry is straightforward while to all other states is still possible provided that the nodes of the trial wave function are consistent with the state under study. The construction of such trial wave functions is one of the most challenging aspects of the present development of DMC.

In this work we present a study of the low-lying electronic adiabatic states of nitric oxide (NO). NO is an interesting substance, it is an important intermediate in chemical industry, is produced in combustion processes and in electrical discharges but is also important in biological processes being an important cellular signaling molecule in mammals and is also active at various levels in many physiological processes. In 1992, NO was proclaimed "Molecule of the Year".[7] From a pure chemical point of view, NO is a radical and is less stable than nitrogen (N_2) and oxygen (O_2), although this conversion is very slow at ambient conditions in absence of a catalyst.

NO is a good system to test a strategy for the construction of trial wave functions for FN-DMC calculations. In spite of the relatively small dimensions, NO presents some characteristics that are important for excites states, namely it is an open shell system, it is made of two different atoms and it contains multiple bonds (unsaturations). For these reasons, NO has several electronic states in a relatively small interval of energies above that of the ground state at equilibrium distance. For this system, there are benchmark calculations and also UV and visible absorption and emission spectra which provide several data for comparison.

[†] Dedicated to Professor Douglas Jay Klein on the occasion of his 70th birthday.
[*] Author to whom correspondence should be addressed. (E-mail: amovilli@dcci.unipi.it)

COMPUTATIONAL DETAILS

The key step of this work is the construction of FN-DMC potential energy curves for some selected adiabatic states of NO. To this end it is crucial to find each trial wave function by avoiding any contamination that could compromise the projection over the best wave function during the simulation in the fixed node approximation. The trial wave functions are thus constructed in a multideterminant spin free Slater-Jastrow form[8] in which the determinantal component is given by

$$\Phi = \sum_K D_K^\uparrow D_K^\downarrow d_K, \qquad (1)$$

where $D_K^\uparrow$ and $D_K^\downarrow$ are the Slater determinants constructed from the occupied orbitals of spin-up and spin-down electrons, respectively, and d_K are the mixing coefficients. In our QMC calculations, such sums are multiplied by a Jastrow correlation factor containing electron-nucleus, electron-electron and electron-electron-nucleus terms.[8] We used Burkatzki *et al.*[9] effective core potentials. These pseudopotentials include relativistic effects and should be used with their own sets of contracted Gaussian atomic functions. In this work, we employed the supported VTZ basis set that we have augmented by adding diffuse s, p and *d* Gaussian functions on each atom.[10] Orbitals, determinant coefficients and Jastrow factor parameters have been optimized at the VMC level[11] at all internuclear distances. The determinant set has been chosen by truncating a given CI function extracted from an extended CASSCF wave function. For this truncation we used a threshold over the CI coefficients chosen in order to fix the sum of the square of the CI coefficients to be 0.96, the complete sum being unity. A threshold of 0.95 has already been used for some state specific VMC calculations on the nitrogen N_2 molecule[12] but without the full reoptimization of the truncated wave function at the QMC level. This procedure is sufficient to define compact QMC wave functions constructed by a relatively small number of determinants even for excited states. The CASSCF truncation for the selection of the determinants has been done only once for each state at its experimental equilibrium distance. This choice, in combination with the VMC optimization, allows to avoid unexpected kinks in the resulting potential energy curves. We then used both state-specific and state-average procedures to set up the wave function. In particular, the state average procedure is applied to perform the calculation of the trial wavefunction of excited states with the same symmetry of the ground state or, more generally, to study different electronic states of the same symmetry. As stated by Schautz *et al.*,[13] the DMC energy in such cases could be not variational. On the other hand, it

should be noted that, in our calculations, the trial wavefunctions for the excited states are taken in correspondence of given roots of a CI problem solved in the VMC step. For this reason, such wavefunctions have a nodal structure consistent with that of the excited states under investigation. This nodal structure is then preserved during the FN-DMC calculation leading to reliable results if the global VMC setup is performed in an accurate way. Standard CASSCF and CISDT calculations have been executed by using the program GAMESS-US[14] while VMC and DMC computations have been done by using CHAMP.[15] For the DMC calculations we used a time step of 0.05 a.u. and the pseudopotentials have been treated beyond the locality approximation.[16]

DMC calculated energies have been fitted against the NO internuclear distance by using a function resulting from a combination of at most two Morse potentials in the form

$$E(R) = c_0(R) + c_1(R)E_1(R) + c_2(R)E_2(R) \qquad (2)$$

where

$$E_j = D_j \left[1 - e^{-a_j(R - R_{0j})} \right]^2 + E_{0j} \quad (j = 1, 2) \qquad (3)$$

and

$$
\begin{aligned}
c_0(R) &= \left(\frac{H}{A} \right) \frac{\exp(R - X)/A}{\left[\exp(R - X)/A + 1 \right]^2} \\
c_1(R) &= \frac{1}{\exp(R - X)/A + 1} \\
c_2(R) &= 1 - c_1(R).
\end{aligned}
\qquad (4)
$$

where R is the internuclear distance and all other constants are fitting parameters. Finally, with these potential energy functions we have calculated the vibrational states in the Born-Oppenheimer approximation by using the truncated interval approach described in the work of Taşeli.[17]

RESULTS AND DISCUSSION

In this Section we present the adiabatic energy curves for the selected electronic states of NO. In all cases we started from a CASSCF(11,12) in which we have distributed the 11 valence electrons in 6 orbitals of σ symmetry and 3 pairs of π orbitals. The leading ground state determinant has configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1$.

In Table 1 we report the parameters for all the energy curves reproduced according to equation (2). For comparison purposes, in Figure 1 we show the fitted

Table 1. Fitting parameters for the NO FN-DMC electronic energy curves for the states considered in this work. Resulting energies are in Hartree while the internuclear distance R is in Å

parameter	$X^2\Pi$	$A^2\Sigma^+$	$(B,C)^2\Pi$	$D^2\Sigma^+$	$a^4\Pi$	$b^4\Sigma^-$
D_1	0.289(1)	0.422(5)	0.386(19)	0.340(4)	0.103(3)	0.128(2)
α_1	2.466(1)	2.63(1)	2.758(60)	2.835(15)	2.29(2)	2.57(2)
R_{01}	1.1496(1)	1.0595(2)	1.0565(3)	1.0619(2)	1.4174(5)	1.2837(4)
E_{01}	−25.9263(1)	−25.7249(1)	−25.6868(1)	−25.6824(1)	−25.7479(1)	−25.7149(1)
D_2	0.2690(2)		0.163(12)			
α_2	6.310(95)		1.929(70)			
R_{02}	1.127(1)		1.4074(10)			
E_{02}	−25.9507(2)		−25.7089(1)			
X	2.086(10)		1.186(1)			
A	0.228(3)		0.0048(6)			
H	0		−0.00010(2)			
R interval	[0.7–3.0]	[0.8–1.35]	[0.8–1.7]	[0.8–1.3]	[0.9–1.7]	[0.9–1.6]

electronic energy curve for all the states considered in this work with some of the points calculated at the FN-DMC level of the theory.

$X^2\Pi$ Ground State

For this state we started from the orbitals of the CASSCF step and we selected the configuration state functions (CSFs) by truncating the relevant CISD wave function obtained from excitations performed on the leading configuration. We used the rule that the sum of the square of the selected determinant coefficients is 96 percent of the sum over all the CISD determinants. In this case this is obtained by taking 16 determinants. Such determinants are able to account for a large fraction of static correlation. Dynamical correlation is then included at the QMC level of the calculation by multiplying the above truncated CI wave function by the Jastrow factor. Orbitals, determinant coefficients and Jastrow parameters have been optimized at the VMC level in energy minimization. Finally, the resulting VMC wave function has been used as the trial wave function for the DMC calculation. Although not precisely the same, this recipe for the construction of the DMC trial wave function for NO ground state is very similar to the QMC generalized valence bond scheme recently introduced by Fracchia *et al.*[18] in their J-LGVB3 form. The J-LGVBn theory is based on a new class of multideterminantal Jastrow-Slater wave functions constructed with localized orbitals. It is inspired by the generalized valence bond formalism and it uses a coupling scheme between electron pairs which progressively includes new classes of excitations in the determinantal component of the wave function. When n = 3, it includes single and double excitations between bonding and corresponding antibonding orbitals within each pair and double excitations constructed as pair of

single excitations from bonding to corresponding antibonding orbitals. In the present NO ground state case, we have already two-centre orbitals and our truncated CISD QMC wavefunction contains certainly the J-LGVB3 wave function which, as shown by Fracchia et
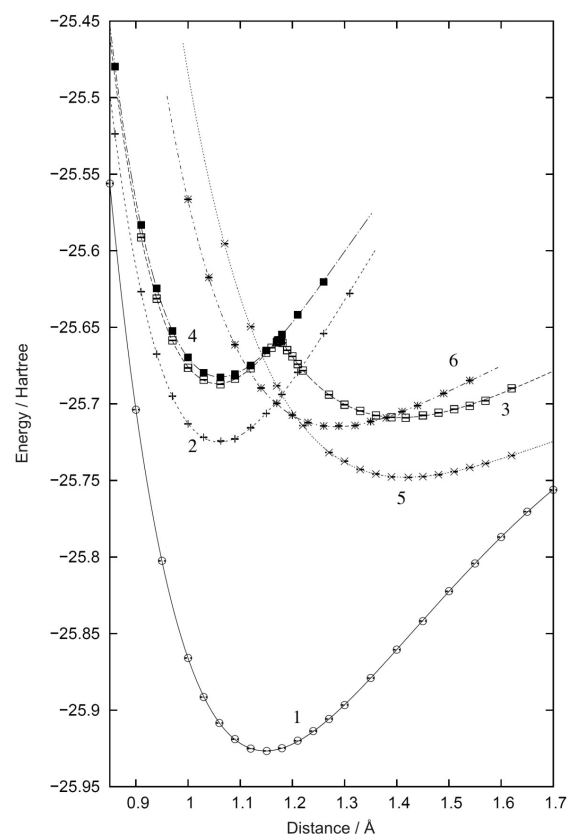

Figure 1. Plot of the NO FN-DMC fitted electronic energy curves for the states considered in this work. Curve numbering is as follows: 1 − $X^2\Pi$, 2 − $A^2\Sigma^+$, 3 − $(B,C)^2\Pi$, 4 − $D^2\Sigma^+$, 5 − $a^4\Pi$, 6 − $b^4\Sigma^-$.

al in their study,[18] is the leading term in such a CI expansion. In order to construct the energy curve we have varied the internuclear distance between 0.8 and 3.0 Å including completely the potential well and reaching the dissociation limit. The DMC estimate for the atomization energy leads to the value of 153.4 kcal/mol which is in good agreement with existing theoretical and experimental data (see, for example, Fracchia and Amovilli[19]). In particular, the experimental atomization energy is 152.4 kcal/mol,[20,21] only 1 kcal/mol below our DMC result. The interval of internuclear distances considered for this electronic states is sufficient to simulate the visible and UV emission and absorption spectra within the Born-Oppenheimer approximation as done in Section 4 by computing the Franck-Condon factors.

$A^2\Sigma^+$ Excited States

This state is the first Rydberg state of NO which is seen as corresponding to the excitation of the π^* unpaired electron to a 3s atomic orbital. The equilibrium distance occurs at a bond length smaller than that of the ground state. In our calculation we used 9 determinants obtained by truncating the CASSCF wave function in a way for which the sum of the square of CSF coefficients is 96 % of the complete sum. We explored only the electronic energies around the minimum of the distances in order to consider only the most important vibrational states in relation with fine structure of UV and visible emission and absorption spectra of NO.

Avoided Crossing between $B^2\Pi$ and $C^2\Pi$ Excited States

$B^2\Pi$ is the second Rydberg state of NO resulting from the excitation of the π^* unpaired electron to a $3p\pi$ atomic orbital while $C^2\Pi$ is a valence state interpreted as a π to π^* transition. These two states have the same symmetry and therefore give rise to an avoided crossing occurring at a NO internuclear distance close to that of the ground state equilibrium distance. The electronic adiabatic state shows two minima. To perform QMC calculation we merged two sets of determinants, one for each state. The total number of determinants resulted in 36 with the sum of the square of CASSCF coefficients ranging from 93 % to 95 % of the total at all N−O distances considered in this case. Orbitals and Jastrow parameters have been optimized in State Averaged (SA) VMC. In order to compare the subsequent DMC energy with that of the ground state obtained as the best for the Π symmetry, we considered different weights for the first three states of this symmetry. Looking at our results, we can say that those coming from the choice (0.1/0.8/0.1) are accurate enough to compare the energy of the excited adiabatic $^2\Pi$ state with the best obtained for the ground state. We have
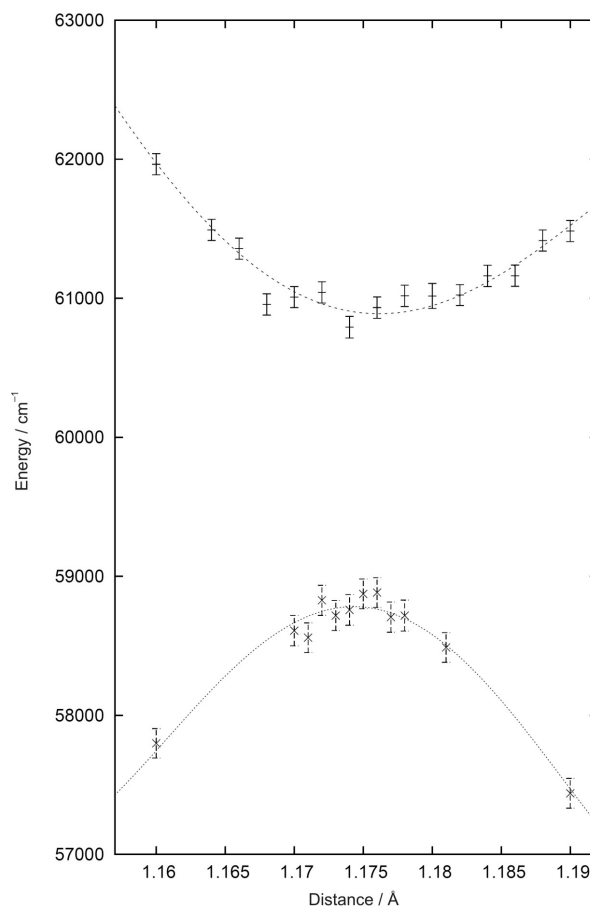

Figure 2. View of the avoided crossing between $B - C^2\Pi$ states of NO computed in this work at FN-DMC level.

also attempted to estimate the energy gap at the avoided crossing point. Our bond length at the avoided crossing point is 1.175 Å which is in quantitative agreement with literature data[22, 23] which report values between 1.17 and 1.18 Å. Our adiabatic energy center and adiabatic energy gap are respectively 59760 and 2040 cm^{-1} which instead differ more significantly from the best reported in the literature,[22] namely 57623 and 2634 cm^{-1} respectively. The main reason of such discrepancy should be ascribed to the weights we used to perform the SA calculation which where unbalanced in order to get the best energy for the second adiabatic state of Π symmetry. An image enlargement of this avoided crossing resulting from our DMC calculation is shown in Figure 2. At this scale it is possible to view the statistical noise of our data.

With the above QMC setting we have then computed the electronic energy of the first excited adiabatic $^2\Pi$ state in the interval of NO internuclear distances between 0.8 and 1.7 Å embracing, in this way, the two minima. This is sufficient to gain the relevant information about the interpretation of the visible and UV absorption and emission spectra. This will be illustrated below.

Table 2. Equilibrium distance (r_e in Å), adiabatic transition energy (T_e in cm^{-1}) and vibrational frequency (ω_e in cm^{-1}) calculated for the electronic states considered in this work and comparison with experimental[21,24] and theoretical[22,25] data from literature

state	r_e	r_e(exp)	r_e(calc)	T_e	T_e(exp)	T_e(calc)	ω_e	ω_e(exp)	ω_e(calc)
$X^2\Pi$	1.150	1.151	1.159	-	-	-	1866	1904	1862
$A^2\Sigma^+$	1.060	1.063	1.071	44444	43966	43558	2407	2374	2344
$B^2\Pi$	1.408	1.417	1.427	47780	45914	44803	1096	1037	1108
$C^2\Pi$	1.057	1.062	1.068	52564	52126	51808	2412	2395	2328
$D^2\Sigma^+$	1.062	1.062	1.074	53552	53085	52492	2327	2324	2323
$a^4\Pi$	1.417	1.422	1.421	39220	38711	38190	1036	1016	1027
$b^4\Sigma^-$	1.284	1.289	1.290	46594	46492	46089	1298	1262	1266

$D^2\Sigma^+$ Excited State

The $D^2\Sigma^+$ excited state is the third most important Rydberg state and formally it corresponds to the excitation of the π^* unpaired electron to a 3pσ atomic orbital. The interatomic distance of the minimal electronic energy for this state is lower than that of the ground state. We have performed the calculations at various distances between 0.8 and 1.3 Å. Due to the same symmetry of the previous $A^2\Sigma^+$ Rydberg state, we have prepared the trial wave function for the FN-DMC calculation at the VMC level in a SA framework by imposing the same weights. To achieve a good energy for the $D^2\Sigma^+$ state, we used 22 determinants.

$a^4\Pi$ and $b^4\Sigma^-$ Low Lying Quartet Valence States

In this work, we have studied also the two low lying quartet valence states $a^4\Pi$ and $b^4\Sigma^-$. The energy calculations have been performed in state specific QMC because these are ground states of given symmetry. In particular, the $a^4\Pi$ is the first excited state if we compare the energy of the corresponding minimum to that of the ground state. For this reason, $a^4\Pi$ is an important reference. With the selected threshold for the CI truncation, we constructed very compact VMC wave functions for these two states, namely by combining only 5 determinants for $a^4\Pi$ and 10 for $b^4\Sigma^-$.

According to our calculations, the electronic energy of these two states cross at an internuclear distance of 1.208 Å and at an energy of 47780 cm^{-1} above the energy of the ground state minimum.

INTERPRETATION OF UV-VISIBLE ABSORPTION AND EMISSION SPECTRA OF NO

The comparison of computed data with corresponding experimental values is not an easy task when excited states are involved. The so-called vertical transition energy, for instance, is very well defined as the difference between the electronic energy of two different states taken at the same geometry, but this quantity cannot be obtained directly from an experimental absorption spectrum because observed transitions involve also vibrational states. The adiabatic transition energy (T_e) is instead a quantity that can be estimated from experiments. This property corresponds to the difference between the electronic energy at the geometry of equilibrium for a given state and the corresponding value for the ground state. T_e can be measured from high resolution absorption and emission spectra through the estimate of the vibrational zero point energy of ground and excited states. The derivation of zero point energy comes from the fine structure of spectral bands from which we have also the vibration frequencies (ω_e). It is important to remark that the vibration frequencies provide useful informations about the curvature of the electronic potential energy surface around the geometry of the minimum. A further spectroscopic parameter for diatomic molecules is the equilibrium distance itself (r_e). This length can be measured through the analysis of the fine structure due to rotational states in the vibrational spectra.

In Table 2, we compare our results from FN-DMC theory for the equilibrium distance, the adiabatic transition energy and the vibrational frequency with experimental data[21,24] and some of the best computed values from the literature.[22,25] Theoretical data for this comparison have been taken from MRCI+Q calculations[22] for the doublet states and CCSD(T) calculations for the quartet states.[25] If we refer to experiments, the mean absolute deviation (MAD) of our results is 0.004 Å for r_e, 643 cm^{-1} for T_e and 29 cm^{-1} for ω_e. The theoretical literature data of Table 2 give respectively 0.006 Å, 559 cm^{-1} and 32 cm^{-1}. This confirm that our FN-DMC calculations are among the best existing theoretical results for the electronic states of NO considered in this work. It should be noted that the present FN-DMC adiabatic transition energies are all overestimated while the corresponding theoretical values reported here are all underestimated.

In order to get a deeper insight about the quality of our potential energy curves, we have simulated the absorption and emission spectra of NO in the range of UV and visible radiation by computing the Franck-
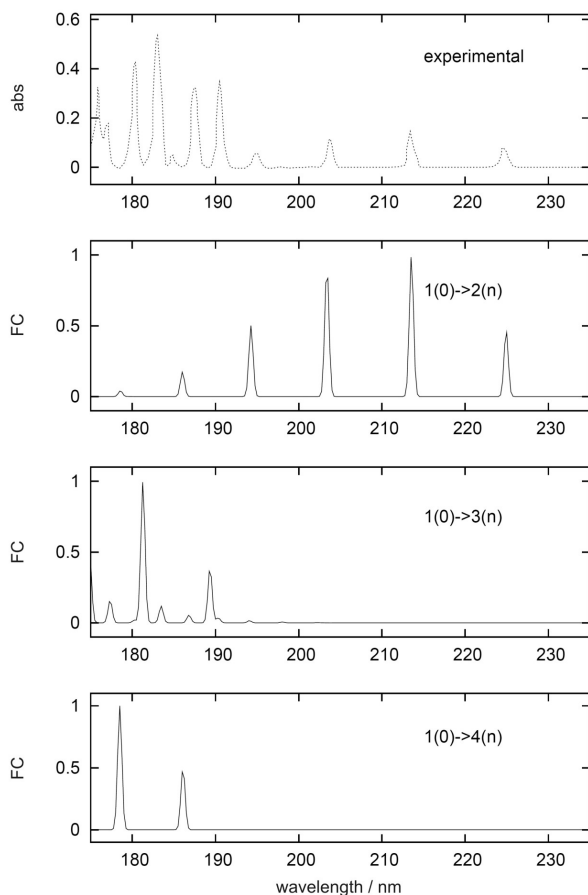
Figure 3. Comparison between the experimental UV absorption spectrum of NO, replotted from Ref. 26, and the Franck-Condon factors calculated in this work for transitions from the vibrational lowest state (0) of the electronic ground state to the n-th vibrational state (Born-Oppenheimer) of the low lying adiabatic excited states. State labeling is as follows: $1 - X^2\Pi$, $2 - A^2\Sigma^+$, $3 - (B,C)^2\Pi$, $4 - D^2\Sigma^+$.
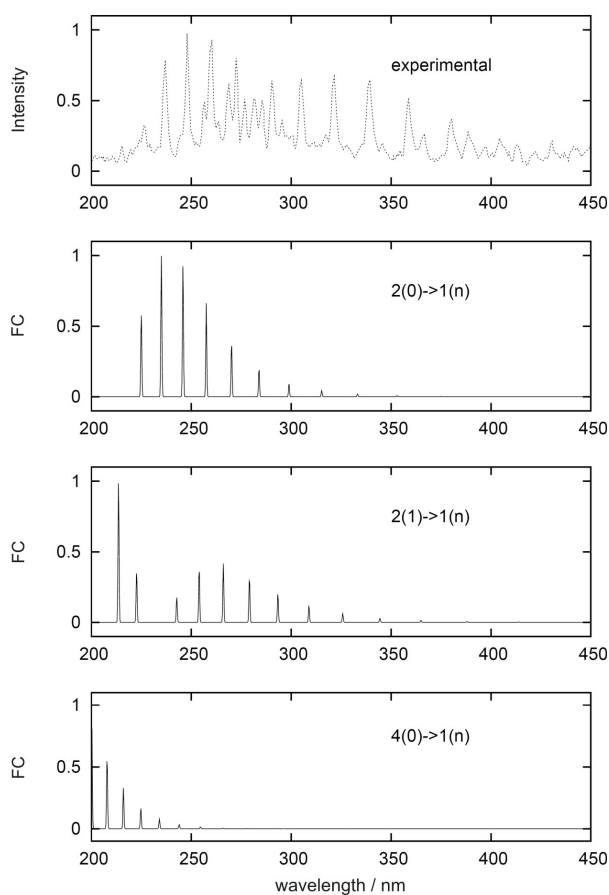

Figure 4. Comparison between the experimental UV emission spectrum of NO, replotted from Ref. 27, and the Franck-Condon factors calculated in this work for transitions from the vibrational lowest states (0 and 1) of the some low lying adiabatic excited state to the *n*-th vibrational state (Born-Oppenheimer) of the electronic ground state. State labeling is as follows:$1 - X^2\Pi$, $2 - A^2\Sigma^+$, $4 - D^2\Sigma^+$.

Condon factor between starting and final vibrational states. The vibrational states, for each adiabatic electronic state, have been computed in the Born-Oppenheimer approximation by using the truncated interval approach described in the work of Taşeli.[17] Following this procedure, the vibrational states are developed in terms of the basis functions

$$\phi_k(R) = \sqrt{\frac{2}{L}} \sin\left(\frac{k\pi}{L}\right) R, \tag{5}$$

with R in the interval [0, L], and are calculated by solving the one-dimensional Schrödinger equation

$$\left\{ -\frac{1}{2\mu} \frac{d^2}{dR^2} + E^{(i)}(R) \right\} \varphi_{im}(R) = E_{im} \varphi_{im}(R), \tag{6}$$

where $E(i)(R)$ is the potential energy function of the

electronic adiabatic state i, written according to equation (2), and μ is the nuclear reduced mass. The solutions take the form

$$\varphi_{im}(R) = \sum_k \phi_k(R) T_{k,im} \tag{7}$$

and, for a given $i \rightarrow j$ electronic transition, the relevant sequence of Franck-Condon factors is then computed from the expression

$$FC(im \rightarrow jn) = \left| \left\langle \varphi_{jn} \middle| \varphi_{im} \right\rangle \right|^2. \tag{8}$$

We have performed the calculation of the first 30 vibrational states for each of the fitted curves obtained from the parameters of Table 1 in the interval of distances between 0 and 2.5 Å (*L*). In Figures 3–5, the Franck-Condon factors are plotted as narrow Gaussian functions of the wavelength centered at $hc/|E_{jn} - E_{im}|$. The
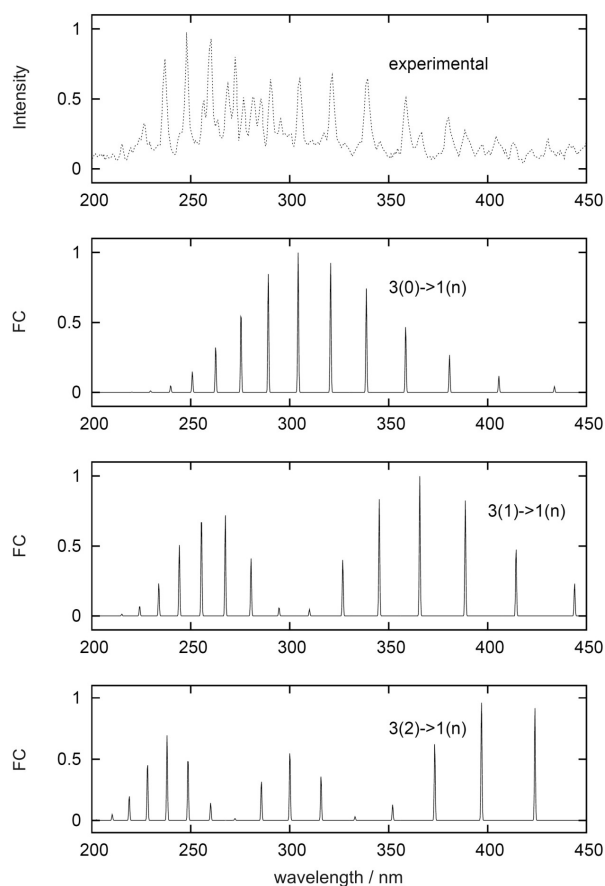
Figure 5. Comparison between the experimental UV emission spectrum of NO, replotted from Ref. 27, and the Franck-Condon factors calculated in this work for transitions from the vibrational lowest states (0, 1 and 2) of adiabatic $(B,C)^2\Pi$ (3) excited state to the n-th vibrational state (Born-Oppenheimer) of the electronic $X^2\Pi$ (1) ground state.

height of each of such Gaussian functions is shown relatively to that of the maximum value for each given sequence.

In Figure 3, we compare the gas phase experimental absorption UV spectrum, replotted from Figure 8 of Ref. 26, with the various sequences of Franck-Condon factors calculated for each adiabatic state considered in this work and starting from the lowest vibrational state of the $X^2\Pi$ potential energy curve. The spectrum was obtained[26] at room temperature and then we can neglect, in this case, the contribution from $X^2\Pi$ vibrational excited states. Looking at this Figure, it is relatively easy to make the qualitative assignment of the experimental absorption peaks to the computed wavelength for the various transitions. In this sense, our FN-DMC calculations allow the interpretation of the absorption spectrum in the wavelength range of 170–250 nm. The MAD is 0.8 nm for the peaks assigned to the electronic transition $X^2\Pi \rightarrow A^2\Sigma^+$, is 1.8 nm for the transition $X^2\Pi \rightarrow (B,C)^2\Pi$ and 2.3 nm for $X^2\Pi \rightarrow D^2\Sigma^+$.

The interpretation of emission spectra is, in general, more complicate because we can have transitions from many different starting Born-Oppenheimer vibroelectronic states. In Figures 4 and 5, we make the comparison with the experimental emission spectrum of gas phase NO in the range 200–450 nm now replotted from Figure 5 of Ref. 27. Due to this interval of UV and visible radiation, we have considered transitions from the first two vibrational states of $A^2\Sigma^+$ curve, the first three of $(B,C)^2\Pi$ and the first of $D^2\Sigma^+$ to all possible vibrational states of $X^2\Pi$. Again, looking at these Figures, the qualitative agreement between the emission spectrum and the partial decomposition in terms of the distribution of computed Franck-Condon factors is quite good and consistent with the common interpretation of the experiment. The overall MAD of the Franck-Condon peaks position with respect to the bands of the emission spectrum is about 1.5 nm.

CONCLUSION

In this work, we have computed the electronic energy of some low lying adiabatic electronic states of NO at various internuclear distances by means of the FN-DMC method. In order to exploit the capability of DMC of projecting over the best wave function with a given Fermion nodal structure, we have attempted the construction of the trial wave function independently for each state. We have been able to construct compact wave functions in a Slater-Jastrow form at VMC level. The QMC setup has been done by truncating appropriate CI wave functions made of Slater determinants constructed from CASSCF orbitals. For this selection, we used a threshold on the square of the CI coefficients. The sum of the square of coefficients of the selected configurations covered 96 % of the total sum. At the VMC level, orbitals, CI coefficients and Jastrow parameters have been reoptimized to achieve the best trial wave function for the DMC step. We have used both state specific and state average approaches. The main focus of this work is the assessment of the quality of the calculated DMC potential energy curves. In this case, other than comparing the usual spectroscopic properties like equilibrium distance, transition energy and vibrational frequency with available data, we have simulated both absorption and emission UV and visible electronic spectra of gaseous NO. This test is able to provide useful information about the curvature of the potential energy function in a wide range of internuclear distances. By computing vibrational states and Franck-Condon factors, we have found a substantial agreement with fine structure experimental spectra. A good agreement has been found also for the aforementioned spectroscopic properties by comparison with existing experimental and theoretical reference data.

As a result of this work, we can state that, at least for small molecules, FN-DMC is a very good method to construct potential energy surfaces of ground and low lying excited states. This is a field of great interest in computational chemistry due to the possibility of applying such studies to the geometry optimization in both ground and excited states, to conformational analysis of biomolecules, to molecular dynamics simulations and, in general, to any research which needs the knowledge of such an energy surface. QMC can be considered an emerging technique in computational chemistry because it offers new possibilities to design specific theoretical approaches (see, for example Refs. 6, 18, 28–32) and, very important, it is supported by new computer technologies being well-adapted for parallel computation.

REFERENCES

1. W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, *Rev. Mod. Phys.* **73** (2001) 33−83.
2. A. Lüchow, *WIREs Comput. Mol. Sci.* **1** (2011) 388−402.
3. B. M. Austin, D. Y. Zubarev, and W. A. Lester Jr., *Chem. Rev.* **112** (2012) 263−288.
4. P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, *J. Chem. Phys.* **77** (1982) 5593−5603.
5. D. J. Klein and H. M. Pickett, *J. Chem. Phys.* **64** (1976) 4811−4812.
6. O. Valsson and C. Filippi, *J. Chem. Theory Comput.* **6** (2010) 1275−1292.
7. D. E. Koshland Jr., *Science* **258** (1992) 1861−1861.
8. C. Filippi and C. J. Umrigar, *J. Chem. Phys.* **105** (1996) 213−226.
9. M. Burkatzki, C. Filippi, and M. Dolg, *J. Chem. Phys.* **126** (2007) 234105−234112.
10. We have added elementary Gaussian functions of s, p and d type on each atom with exponents $\alpha_s = 0.028$, $\alpha_p = 0.025$ and $\alpha_d = 0.015$ on nitrogen and $\alpha_s = 0.032$, $\alpha_p = 0.028$ and $\alpha_d = 0.015$ on oxygen.
11. C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, *Phys. Rev. Lett.* **98** (2007) 110201-1-110201-4.
12. F. A. Fayton Jr., A. A. Gibson, and J. A. W. Harkless, *Int. J. Quantum Chem.* **109** (2009) 43−49.
13. F. Schautz, F. Buda, and C. Filippi, *J. Chem. Phys.* **121** (2004) 5836−5844.
14. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14** (1993) 1347−1363.
15. CHAMP is a quantum Monte Carlo program package written by C. J. Umrigar and C. Filippi, and collaborators.
16. M. Casula, *Phys. Rev. B* **74** (2006) 161102−161105.
17. H. Taşeli, *J. Phys. A: Math. Gen.* **31** (1998) 779−788.
18. F. Fracchia, C. Filippi, and C. Amovilli, *J. Chem. Theory Comput.* **8** (2012) 1943−1951.
19. F. Fracchia and C. Amovilli, *Chem. Phys. Lett.* **521** (2012) 20−25.
20. JANAF Thermochemical Tables, 2nd ed., edited by D. R. Stull and H. Prophet, National Bureau of Standards, Washington DC, 1971.
21. K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV, Constant of Diatomic Molecules, Vand Nostrand, New York, 1979.
22. H. Shi and A. L. L. East, *J. Chem. Phys.* **125** (2006) 104311-1-104311-7.
23. R. de Vivie-Ridle, M. C. van Hemert, and S. D. Peyerimhoff, *J. Chem. Phys.* **92** (1990) 3613−3618.
24. K. P. Huber and M. Vervloet, *J. Mol. Spectrosc.* **129** (1988) 1−23.
25. O. V. Ershova and N. A. Besley, *Chem. Phys. Lett.* **413** (2011) 179−183.
26. L. Lagesson-Andrasko, V. Lagesson, and J. Andrasko, *Anal. Chem.* **70** (1998) 819−826.
27. S. Saupe, I. Adamovich, M. J. Grassi, and J. W. Rich, *Chem. Phys.* **174** (1993) 219−228.
28. F. R. Petruzielo, J. Toulouse and C. J. Umrigar, *J. Chem. Phys.* **136** (2012) 124116-1-124116-5.
29. F. M. Floris, C. Filippi, and C. Amovilli, *J. Chem. Phys.* **137** (2012) 075102-1-075102-12.
30. E. Coccia, O. Chernomor, M. Barborini, S. Sorella, and L. Guidoni, *J. Chem. Theory Comput.* **8** (2012) 1952-1962.
31. M. Barborini, S. Sorella, and L. Guidoni, *J. Chem. Theory Comput.* **8** (2012) 1260−1269.
32. S. Saccani, C. Filippi, and S. Moroni, *J. Chem. Phys.* **138** (2013) 084109-1-084109-5.