

A pseudopotential study of molecular spectroscopy in rare gas matrices: absorption of NO in argon

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Abstract. We present a pseudopotential method to study the absorption spectroscopy of NO in an argon matrix modeled by a large albeit finite cluster. The excited states of NO are described with the virtual orbitals of a NO⁺ Hartree-Fock calculation plus a core-polarization operator to account for the electron-NO⁺ correlation. The argon atoms of the matrix are replaced by pseudopotentials for the repulsive contributions and core-polarization operators to account for matrix polarization and correlation with the excited electron. The model is shown to account for the matrix-induced transition shifts and also for the cut-off of the Rydberg series for $n > 3$ reported in absorption experiments from the ground state.

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1 Introduction

The spectroscopy of elementary systems such as atoms, molecules or small clusters trapped in matrices has been the object of continuous investigations until now [1–14]. From a theoretical point of view, the determination of spectroscopic properties still remains a challenge for *ab initio* calculations due to the difficulty to provide a correct description of the interaction of the excited states with the numerous electrons of the surrounding inert atoms.

Among the simple models used to deal with Rydberg series in matrices, one may cite the Wannier exciton model [2] and the quantum defect model [10,11]. Both models assume a simple coulombic interaction and an effective dielectric constant to represent the matrix. Such models of the matrix are however actually not adequate to provide a correct microscopic description of the interactions and to account for the discrete structure of the perturbing atoms. In particular, none of them does account for the cut-off of the Rydberg series in the matrix nor can quantitatively predict the observed shifts. Empirical harmonic fits of the potential surfaces have been also used, especially to follow the post-excitation dynamics and the so-called electronic bubble propagation [13].

The diatomic in molecules model (DIM) is often a good candidate to provide a simplified albeit still quantum treatment of ground and excited molecular states in extended systems, such as for instance small van der Waals clusters like NaAr_{*n*} [15,16], HgAr_{*n*} [17] or I₂Ar [18], impurities in rare gas liquids [19] or in rare gas matrices [20].

The DIM scheme is however more adapted to valence excited states which can be reasonably well-approximated as combinations of atomic or diatomic localizable fragment wavefunctions showing weak overlap. Its use is less relevant in the case of semi-Rydberg or Rydberg states due to the (very) diffuse nature of the associated orbitals. Moreover, the diatomics fragment potential curves which constitute the data inputs for the construction of a DIM Hamiltonian are not necessarily available experimentally nor theoretically.

We describe and use in the present work a general method closer to *ab initio* Quantum Chemistry to study the absorption spectroscopy of small systems embedded in inert gas clusters or matrices and based on pseudopotential techniques. The methodology relies on the explicit description of the active system electrons and on the representation of the rare gas atoms (R_g) via pseudopotential techniques. Several authors have investigated with such scheme the excitation of active alkali atoms (single active electron) trapped in inert matrices [21–23]. A few applications to molecules were also achieved. Nemukhin *et al.* [22] have applied a local pseudopotential scheme to study the spectral shifts for a sodium dimer trapped in krypton in the framework of the Hartree-Fock approximation. They were able to reproduce theoretically shifts with opposite signs experimentally observed [24] for A–X and B–X transitions respectively. Very recently, we have introduced on a similar example, namely Na₂ embedded in argon, a scheme which accounts for explicit correlation effects (two active valence electrons for the sodium dimer) as well as the polarization of the passive system [23].

The present paper is dedicated to the theoretical study of the Rydberg states observed in absorption spectroscopy for the NO molecule trapped in argon, which can be

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considered as an experimental test case [12–14]. We first report the general theoretical framework and then develop its adaptation and application to the NO molecule.

2 General methodology

The general methodology [23] relies on a partition of the full system into

- (i) an active part, namely the trapped subsystem, the electrons of which are treated explicitly, *via* quantum chemical methods, Hartree-Fock and eventually Configuration Interaction(CI),
- (ii) the rare gas atoms of the matrix, the electrons of which are substituted by pseudopotentials.

In the most general formulation, the Hamiltonian can thus be expressed as

$$\begin{aligned}
 H = & \sum_i \left\{ -\frac{\Delta_i}{2} + \sum_A^M \left(-\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \hat{W}_A(i) + \hat{V}_A^{pol}(i) \right) \right. \\
 & + \sum_{\mu}^{Rg} \left(\hat{W}_{\mu}(i) + \hat{V}_{\mu}^{pol}(i) \right) \left. \right\} + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\
 & + \sum_{A < B}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \sum_A^M \sum_{\mu}^{Rg} V_{ARg}(\mathbf{R}_A, \mathbf{R}_{\mu}) \\
 & + \sum_{\mu < \nu}^{Rg} V_{RgRg}(|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|) \quad (1)
 \end{aligned}$$

where the sums refer to the active electrons \mathbf{r}_i of the trapped system (M), its nuclear coordinates \mathbf{R}_A , and the coordinates \mathbf{R}_{μ} of the rare gas atoms (R_g). Z_A is the net charge on nucleus A.

The first bracketed term of the above expression represents the Hamiltonian of the active electrons in the field of the nuclei of the molecule and the rare gas atoms replaced by pseudopotentials \hat{W}_{μ} . The inner electrons of the active molecule can themselves be substituted by standard atomic core pseudopotentials \hat{W}_A (usual semi-local or non-local Hartree-Fock extracted valence atomic pseudopotentials). The \hat{W}_{μ} pseudopotentials describe the repulsive interaction between the active electrons and the rare gas electrons as induced by the exclusion Pauli principle. They were also determined in semi-local and non-local form. The \hat{V}_A^{pol} and the \hat{V}_{μ}^{pol} are the so-called core polarization operators which allow to go beyond the frozen core approximation, both for the atomic cores and the rare gas atoms. They describe the static and dynamical polarization of the initially frozen part, the atoms of the matrix, and the atomic inner cores. The second term represents the correlation of the explicit electrons of the active system. The three last terms includes the interaction between the frozen part, respectively atomic core-atomic core Coulomb repulsion, atomic core-rare gas repulsion and rare gas-rare gas interactions. The repulsive atomic core-rare gas contributions are negligible in the usual

range of distance, whereas the rare-gas rare-gas cohesion forces will be kept constant in the present study not investigating matrix relaxation.

The $e-R_g$ pseudopotentials \hat{W}_{μ} and \hat{V}_{μ}^{pol} cannot be extracted from stable atomic configurations and must be fitted in order to reproduce electron-atom differential elastic scattering cross-sections as early illustrated in the context of model potential [25–27] or pseudopotential [28] studies of alkali-rare gas and long distance rare gas-rare gas diatomics. The forms of the pseudopotentials used here were recently developed in the context of excitations in homogeneous rare gas clusters [29,30].

The core-polarization operators may be defined in a scalar scheme [31]

$$V^{pol} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} \mathbf{f}_{\lambda} \cdot \mathbf{f}_{\lambda} \quad (2)$$

where the sum runs over all polarizable systems λ not represented explicitly (inner core electrons and rare gas atoms). α_{λ} is the dipole polarizability and \mathbf{f}_{λ} the electrostatic field at center λ produced by the explicit electrons (resulting field \mathbf{e}_{λ}) and the net nuclear charges of all other centers (resulting field \mathbf{E}_{λ}). The electronic contribution is damped by a cut-off function $F_{\lambda}(r)$ which is introduced to avoid divergency of the integrals at the origin of the polarizable centers.

$$\mathbf{f}_{\lambda} = \mathbf{e}_{\lambda} + \mathbf{E}_{\lambda} = \sum_i \frac{\mathbf{r}_{i\lambda}}{r_{i\lambda}^3} F_{\lambda}(r_{i\lambda}) - \sum_{\lambda' \neq \lambda} \frac{\mathbf{R}_{\lambda\lambda'}}{R_{\lambda\lambda'}^3}, \quad (3)$$

The polarization operator may also be expressed within a semi-local scheme [32] using l -dependent cut-off radii $F_{\lambda l}$. In the present work, we have used the l -independent version and the $F_{\lambda}(r)$ factors were taken as spherical step-functions with cut-off at radius $\rho_{\lambda c}$.

In fact, this partition can be further simplified in cases where one is uniquely interested in the Rydberg spectrum. It can then be reduced to a single active electron problem as shown below.

The molecular orbitals calculations are performed within the LCAO (Linear Combination of Atomic orbitals) expansion with Gaussian type basis functions and the present scheme implies the calculation of the matrix elements of the damped \mathbf{e}_{λ} and \mathbf{e}_{λ}^2 operators in the whole Gaussian basis set and at every site λ of the lattice.

3 Application and results

Pure solid argon as a van der Waals crystal has an fcc lattice structure. In our calculation, we modelize the infinite lattice by a finite sample cut from a full fcc crystal. The atom or molecule to be embedded, acting as a spectroscopic probe, is deposited into a vacancy at the center of the sample. Unlike the Na_2 molecule and even the Na atom in their ground state, the location of which in matrices is uncertain due to the large NaAr distance (about 9 bohr), NO forms a very small and compact molecule with

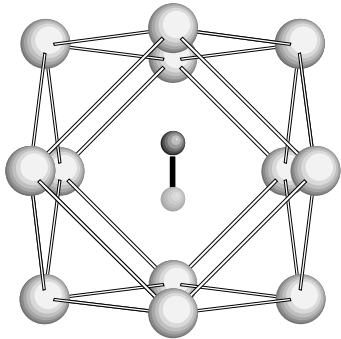


Fig. 1. Insertion site for NO in the matrix. Only the atoms closest to NO are displayed

an experimental interatomic distance of only 2.175 bohr and its location site in the matrix offers from an experimental point of view a more favorable situation. Accurate *ab initio* calculations are available for the electronic ground state of a NOAr trimer [33], keeping the NO distance fixed at its equilibrium value. Calculations also exist for some excited states [34]. In the ground state, the isoenergy contours for the argon atom around NO are not quite isotropic. The energy minimum occurs for the perpendicular configuration of the NOAr trimer. However, the deviation of these isoenergy surfaces from perfect spheres is very small. The energy barriers for a rotation of the argon atom around the N or O sites are of the order of 20 cm^{-1} . The mean distance of Ar from the center of the NO dimer is about 7 bohr, which is very close to the nearest-neighbour distance in the argon lattice. This means, that a NO molecule in its ground state may replace an atom in an argon crystal or cluster without inducing a large perturbation of its surrounding. In the present investigation of a matrix isolated NO molecule, we have simply inserted the dimer into a substitutional 12-coordinated site of a finite sample (O_h symmetry) of a fcc crystal (Fig. 1), without any further geometrical optimization. After insertion of NO, symmetry is reduced to C_{4v} .

The number of rare-gas shells around the probe was chosen sufficiently high to expect a direct transfer of the calculated results to the infinite crystal. In practice, we successively added shells until the energies of the ground and relevant excited states had converged up to a precision of about 100 cm^{-1} . Due to the different nature of the excited states, convergence was achieved much later for NO than in our previous study [23] dealing with Na and Na_2 . In the case of NO, eight shells were needed ranging from 6.979 bohr up to 19.740 bohr from the center of NO and the total number of argon atoms was 140.

Especially the Rydberg orbitals of NO but to a less extent also the excited states of Na are deformed by the repulsive pseudopotentials of the argon atoms. This deformation cannot be well-modeled by Gaussian basis functions centered on the spectroscopic probe (Na or NO) alone. We solved this problem by adding a small $3s1p$ Gaussian basis set on the inner shell matrix atoms. Unfortunately those functions located on Ar cannot be ob-

tained from atomic calculations, since there is no bound state for Ar^- . The exponents were thus optimized on another system, namely the single electron Na@Ar_{20} system (a sodium atom trapped in a dodecahedral argon cluster) which allows for rapid optimization since only one-electron integrals are necessary. The exponents (0.2, 0.07 and 0.02 for s functions, 0.09 for the p function) were then found to allow sufficient flexibility at the vicinity of the Ar centers and in particular to ensure a good representation of the wavefunction close to the repulsive region defined by the pseudopotential. This basis set was supposed to be essentially dependent on argon atoms and therefore transferable. The number of inner shell atoms necessarily depends on the type of the probe. In the case of NO with its very diffuse Rydberg states, it was necessary to use basis sets on the 42 argon atoms of the three first shells (at 6.979, 9.870 and 12.088 bohr) before convergence of the Rydberg excited states energies could be achieved. Including the NO basis set (see below), this means a total of 320 Gaussian type functions on the whole system. The other parameters defining the rare gas atoms are the dipole polarizability ($\alpha_{\text{Ar}} = 11.08 a_0^3$) and the cut-off radius ($\rho_c = 3.00$ bohr).

A preliminary task is to determine the Rydberg states of NO. Actually various accurate Configuration Interaction calculations do exist for the NO molecule [35,36], and it is not the scope of the present study to compete with those but to present a scheme which is compatible with an ulterior treatment of NO embedded in the matrix while remaining quantitative. The $1s$ electrons on NO were replaced by pseudopotentials of the Durand and Barthelat type [37,38]. On each atomic site (N and O), the Gaussian basis set was a valence uncontracted $4s4p$ basis set [38] augmented by two d -type polarization functions [35] and two diffuse s and p exponents [35] to describe the Rydberg states. The NO molecular orbitals are obtained self-consistently from the Fock operator corresponding to the NO^+ ion

$$\hat{f} = -\frac{1}{2}\Delta_i + \sum_A^{N,O} \left(-\frac{1}{R_{Ai}} + \hat{W}_A(i) \right) + \sum_{j \in \text{NO}^+} (2\hat{J}_j(i) - \hat{K}_j(i)) \quad (4)$$

where the Coulomb and Exchange operators run over the valence $2s$ and $2p$ orbital occupied in NO^+ , namely $3\sigma^2$, $4\sigma^2$, $5\sigma^2$ and $1\pi^4$. Although the $1\pi^*$ orbital occupied in the the NO ground state is a valence orbital, it appears here in the virtual space. The virtual one-electron energies for the Rydberg orbitals, (and even for the $1\pi^*$ orbital) already provide for isolated NO reasonable approximations of the energy levels and transitions between the ground state and the Rydberg states (Tab. 1). They can be further improved by considering the polarization and correlation of the Rydberg electron with the NO^+ core *via* a unique core-polarization operator \hat{V}_c^{pol} located at the center (C) of NO, assuming here a mean isotropic polarizability [40] $\alpha_c = 7.77a_0^3$ for NO^+ . If \mathbf{e}_c is the damped electric field created at C by the unique external electron,

$$\hat{V}_c = -\frac{1}{2}\alpha_c \mathbf{e}_c \cdot \mathbf{e}_c. \quad (5)$$

Table 1. Adiabatic transition energies from the ground state in NO without (T_e) and with (T_e^{pol}) polarization operator at the NO^+ core. All values in eV. Experimental data from Huber and Herzberg [41].

level	T_e	T_e^{pol}	T_e^{exp}
$3s\sigma$	4.91	5.31	5.45
$3p\pi$	5.85	6.41	6.46
$3p\sigma$	5.93	6.56	6.58
$4s\sigma$	6.97	7.58	7.52
$4p\pi$	7.30	7.99	7.99

This is a simple approximation since the anisotropic deviations may be non negligible. One then considers NO^+ as a frozen core and diagonalizes the one-electron operator resulting from the addition of the Fock and the core-polarization operator restricted to the basis of virtual molecular orbitals:

$$\hat{f}_{mn}^{pol} = \epsilon_m \delta_{mn} + \langle \phi_m | \hat{V}_c^{pol} | \phi_n \rangle \quad (6)$$

$$\hat{f}^{pol} | \phi_m \rangle = \epsilon_m^{pol} | \phi_m \rangle. \quad (7)$$

The total energies of the excited states of NO are then obtained as the sum of the energy of the $^1\Sigma^+$ ground state of NO^+ and of the one-electron levels involving core-polarization

$$E_m(R) = E_{\text{NO}^+}(R) + \epsilon_m^{pol}(R). \quad (8)$$

Rather than using the Hartree-Fock NO^+ energies of the present calculation, we have taken the accurate CI potential energy curve data $E_{\text{NO}^+}(R)$ of Chambaud and Rosmus [39] including all-electron correlation, complemented through cubic spline interpolation by values at any necessary internuclear distance. The cut-off radius was determined in order to fit the ionization potentials of the different states. However, due to the fact that the $X^2\Pi$ of NO with its $1\pi^*$ orbital close to the core is actually not a Rydberg state, the present cut-off value ($\rho_c = 2.126$ bohr) turns out to be a necessary compromise to obtain all states in a same calculation with a unique cut-off. The adiabatic ground state ionization potential is found to be 9.16 eV instead of 9.23 eV (experimental value [41] lowered by the 0.03 eV difference in the zero point energies between NO and NO^+). The adiabatic transition energies from the ground state are listed in Table 1. The equilibrium distance of the ground state in this model is 2.26 bohr, somewhat larger than the experimental value of 2.175 bohr. This is, however not too surprising since as previously mentioned the treatment of that state through of a one-electron model is somewhat questionable. All the other states have their equilibrium distance almost identical to that of NO^+ (2.010 bohr). If one looks at the adiabatic transitions, namely $X^2\Pi \rightarrow 3s\sigma^2\Sigma^+$, $X^2\Pi \rightarrow 3p\pi^2\Pi$, $X^2\Pi \rightarrow 3p\sigma^2\Sigma^+$, $X^2\Pi \rightarrow 4s\sigma^2\Sigma^+$ and $X^2\Pi \rightarrow 4p\pi^2\Pi$, one sees a remarkable agreement with experiment. In particular, the values without core-polarization correction are in error by 0.5–0.7 eV and are significantly improved in the final calculation. The satis-

factory result obtained for NO shows that polarization operators, which have been essentially used on atoms within the theory of pseudopotentials can also be extended to reproduce Rydberg states of molecules. The present quasi-spherical approximation is the simplest possible version. We do not report here $3d$ states since they cannot be described in the present calculation (the two Gaussian d -type functions used here are essentially valence polarization functions, not diffuse enough to represent Rydberg states).

We have used in the matrix the same reduction scheme as for NO. Defining now a one-electron operator including the electronic part of the polarization pseudopotentials for the NO^+ core and the rare gas atoms

$$\hat{f}_{mn}^{pol} = \epsilon_m \delta_{mn} + \langle \phi_m | \hat{V}_c^{pol} | \phi_n \rangle - \sum_{\mu}^{Rg} \frac{1}{2} \alpha_{\mu} \langle \phi_m | \mathbf{E}_{\mu} \cdot \mathbf{e}_{\mu} + \mathbf{e}_{\mu}^2 | \phi_n \rangle \quad (9)$$

where the ϵ_m are the virtual levels of the NO^+ Fock operator including the \hat{W}_{μ} repulsion pseudopotentials located on the argon atoms, the total energy for a state in the matrix is

$$E_m(R) = E_{\text{NO}^+}(R) - \sum_{\mu}^{Rg} \frac{1}{2} \alpha_{\mu} \mathbf{E}_{\mu}^2 + \epsilon_m^{pol}. \quad (10)$$

The second term in the latter expression accounts for the energy lowering (1.218 eV for the present sample) corresponding to the static polarization energy of the lattice by the NO^+ charge.

We first examine the wavefunctions. Contour plots of the matrix-embedded $3s\sigma$ (Fig. 2) and $3p\pi$ (Fig. 3) orbitals in a plane perpendicular to NO are displayed. One sees at first that the orbitals, although still resembling globally those of free NO, are strongly perturbed and exhibit avoidance at the argon sites, especially the first shell of nearest neighbours but also the second shell. A consequence of the deformation is also that, due to norm conservation of the wavefunctions, the electron density in the allowed region is increased with respect to the density of free NO orbitals. This should have importance on the transition dipole moments.

The exclusion defined by the repulsive potential range around the rare gas atoms causes a strong blue shift in the transitions, the compact ground state being almost unaffected, whereas the diffuse Rydberg states are shifted towards higher energies. The data concerning the adiabatic transitions are listed in Table 2. It should be clear that the transitions referred here as adiabatic do not imply any matrix relaxation. They are adiabatic with respect to the NO coordinate in the sense that the transitions are taken between the minimum of the $X^2\Pi$ state at 2.26 bohr and the minimum of the Rydberg states at $R = 2.010$ bohr. They can actually be compared to the (0,0) absorption transitions of the work of Chergui *et al.* [12]. If polarization contributions are neglected, the effect is such actually that the cut-off of the Rydberg series is drastic and only

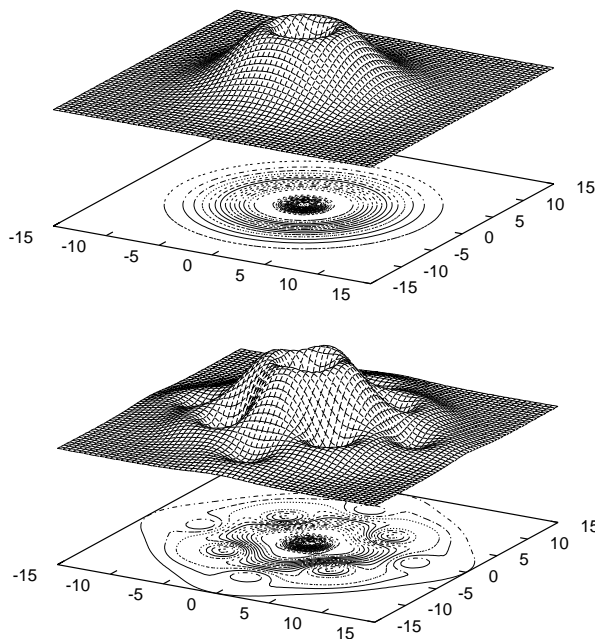


Fig. 2. Amplitude of the $3s\sigma$ orbital of free NO (above) and matrix embedded NO (below) in a plane perpendicular to the molecule axis. The distance range extends in the interval $[-15 \text{ bohr}, 15 \text{ bohr}]$ around the center of NO.

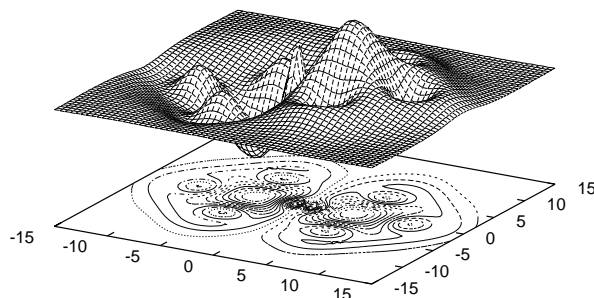


Fig. 3. Amplitude of the $3p\pi$ orbital of matrix embedded NO in the plane perpendicular to the molecule axis. The distance range extends in the interval $[-15 \text{ bohr}, 15 \text{ bohr}]$ around the center of NO.

the $3s\sigma$ state remains bound (Tab. 2). Its adiabatic transition energy from the ground state is now 6.871 eV shifted by 1.96 eV with respect to the same value (T_e of Tab. 1) in free NO. All the upper excited states lie above the ionization threshold at that approximation level. However, repulsion to the argon electrons is not the only effect. Polarization and correlation with the implicit electrons of argon atoms *via* the core-polarization operators play a crucial role. Table 2 also shows the transitions obtained with the core-polarization operators on the rare gas centers. Once the core-polarization effects are included, three excited levels are now obtained as bound states, namely $3s\sigma$, $3p\pi$, $3p\sigma$ whereas the upper states are still rejected in the continuum. This proves at the microscopic level that the number and position of bound levels result from a subtle balance between repulsive exclusion and polar-

Table 2. Adiabatic transition energies from the ground state for matrix trapped NO without and with polarization operator for the argon atoms. All values in eV. The experimental values are obtained from the (0,0) transitions of Chergui *et al.* [12] corrected by the differences in the zero point energies taken from gas phase.

level	T_e	T_e^{pol}	T_e^{exp}
$3s\sigma$	6.871	6.11	6.30
$3p\pi$	-	7.41	7.29
$3p\sigma$	-	7.57	7.43

ization/correlation. All the levels above those three turn out to be at positive energies, namely above the ionization threshold in the matrix. These results are in good agreement with the findings in absorption spectroscopy of Chergui *et al.* [12] who found a cut-off of the Rydberg series for $n \geq 4$ in the case of NO in argon. Moreover, the calculated transition shifts (0.80, 1.00 and 1.01 eV) between free NO and NO in the matrix are in satisfactory correspondence with the measurements of Chergui *et al.* (0.857, 0.832 and 0.852 in an argon matrix). One may notice however that the calculated shifts tend to slightly increase for $3p$ states *versus* $3s$ states, whereas they are remarkably stable in the experimental data for all three transitions $X \ ^2\Pi \rightarrow 3s\sigma \ ^2\Sigma^+$, $X \ ^2\Pi \rightarrow 3p\pi \ ^2\Pi$, and $X \ ^2\Pi \rightarrow 3p\sigma \ ^2\Sigma^+$. It would be interesting to check the influence of using l -dependent core-polarization operators on the matrix atoms. Optimization of the vacancy around NO in the ground state might also bring some improvement.

4 Conclusion

The general formalism presented in Section 2 introduces an encouraging framework to study with a microscopic point of view the interaction of excited states of atoms and molecules or eventually small clusters with inert environment, cages or matrices. We have demonstrated here its possibility in a situation which is almost reducible to a one-electron case. Although the present calculation provides results in consistency with the experimental data, it would be interesting to investigate the possible improvement brought by the use of l -dependent cut-off functions. Their use on NO should introduce more flexibility to describe simultaneously the ground state and the Rydberg states of free NO. Their use on the argon atoms may influence the matrix polarization.

Within this quasi one-electron picture, an immediate continuation will consist in obtaining the behaviour of the potential energy curves of the Rydberg states as a function of R_{NO} , as well as their spectroscopic constants and dipole transition moments corresponding to absorption spectroscopy from the ground state, that is keeping the matrix unrelaxed. A further investigation would be to consider the relaxation of the matrix in the excited states, namely the situation occurring in fluorescence experiments. Indeed, very recently by means of fluorescence

depletion techniques, Zerza *et al.* [14] have succeeded in observing intra-Rydberg transitions of NO in an argon matrix and higher members of Rydberg series with $n \geq 4$ could be observed. This was interpreted as the result of matrix relaxation after the $3s\sigma^2\Sigma^+$ state is populated and the possibility in the relaxed configuration for more Rydberg members to exist.

From a methodological point of view the present scheme is very flexible. Indeed in the present example, and since we wanted to study essentially the Rydberg states, we have determined the orbitals of NO^+ core through an explicit valence Hartree-Fock calculation and we have afterwards reduced the problem to the external electron only. One further simplification is to build a pseudopotential describing the whole NO^+ core which would define from the start the problem as a one-electron situation. This would be mostly efficient for determining matrix relaxation in the upper state since one-electron integrals only will be needed.

An extension in an actual many-electron context would be necessary to investigate Rydberg-valence interactions. It is known that at longer R_{NO} distance, one has crossings between the Rydberg and the valence states of NO. The study of such crossings implies the use of the general methodology with Configuration Interaction including all the valence electrons of NO. However, the CI size is the same as for free NO (with however eventually reduced symmetry). The main difficulty is the dimension of the basis set for the molecule in the matrix due to the necessary Gaussian functions on the argon atoms and the burden of the two-electron integral transformation. This technical difficulty can however be circumvented either by directly freezing the highest molecular orbitals in the CI or probably better by complementing the physical orbitals (those corresponding to physically bound levels) of the matrix problem by the non-redundant virtual ones of the isolated NO fragment using projection techniques.

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