

# A Theoretical Study for the Valence–Rydberg Interaction in Diatomic Molecules. Application to the NO $\beta$ Band System

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A detailed description of the  $\beta$  band system of the NO molecule has been achieved by calculating electronic transition moments, Einstein coefficients, and radiative lifetimes. The known strong interaction of the B<sup>2</sup> $\Pi$  valence state with Rydberg states of <sup>2</sup> $\Pi$  symmetry is treated through a vibronic interaction matrix. This actually implies an extension of the molecular quantum defect orbital (MQDO) methodology in the study of vibronic levels of diatomic molecules. The MQDO approach has recently led to rather good results in the study of the 3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\gamma$  band), 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\epsilon$  band), and 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ) transitions.

## I. Introduction

B<sup>2</sup> $\Pi$ , the lowest excited doublet valence state of NO, is found in a number of environments, including air afterglows and shock-heated air. Along with the 3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ) state, it is the longest wavelength NO absorption system, and several authors have measured the absorption oscillator strengths involving these states.<sup>1–4</sup>

For NO, several different band systems are observed: 3p $\pi$ –(C<sup>2</sup> $\Pi$ )–3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ), 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ), 3p $\pi$ (C<sup>2</sup> $\Pi$ )–X<sup>2</sup> $\Pi$  ( $\delta$  band), 3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\gamma$  band), 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\epsilon$  band), B<sup>2</sup> $\Pi$ –X<sup>2</sup> $\Pi$  ( $\beta$  band), and b<sup>4</sup> $\Sigma^-$ –a<sup>4</sup> $\Pi$  (Ogawa band). The  $\beta$  band system of NO is prominent in air and nitric oxide discharges and is excited in a number of chemical luminescent processes, most notably in the three-body recombination of oxygen and nitrogen atoms. Surprisingly, the quantitative spectroscopic aspects of this system have not been well characterized.<sup>5</sup> Although this system has been known for many years,<sup>6</sup> it was only recently that the Einstein coefficients and radiative lifetimes were accurately determined experimentally.<sup>7</sup>

A very important parameter in this context is the radiative lifetime of the B<sup>2</sup> $\Pi$  state, because of its relationship to the absorption strength and to the balance between radiative and quenching effects. It is somewhat surprising to find a lack of consensus concerning the above radiative lifetime,<sup>8–17</sup> which is related to the fact that a clean preparation of the B<sup>2</sup> $\Pi$  state is not as simple as that of Rydberg states such as 3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ), 3p $\pi$ –(C<sup>2</sup> $\Pi$ ), and 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ ). This has been explained on the basis of the relative large displacement between the ground state and the B<sup>2</sup> $\Pi$  state potentials, such that the optical pumping to B<sup>2</sup> $\Pi$  from  $v = 0$ , the lowest vibrational level of the ground state, involves very small Franck–Condon factors for the lowest vibrational levels of B<sup>2</sup> $\Pi$ . And for the higher levels, the transition wavelengths are inconveniently short for one-photon laser induced fluorescence.

Considering that accurate experimental lifetimes are now available,<sup>5,14,17</sup> it seemed worthwhile to reinvestigate the transi-

tion moments for the  $\beta$  band system of NO. The calculations are complicated by the fact that the B<sup>2</sup> $\Pi$  state undergoes an avoided crossing with the 3p $\pi$ (C<sup>2</sup> $\Pi$ ) Rydberg state. In fact, the  $v' = 7$  level of B<sup>2</sup> $\Pi$  and the  $v' = 0$  level of 3p $\pi$ (C<sup>2</sup> $\Pi$ ) are nearly degenerate. Since the 3p $\pi$ (C<sup>2</sup> $\Pi$ )–X<sup>2</sup> $\Pi$  electronic transition is much stronger than the one corresponding to the B<sup>2</sup> $\Pi$ –X<sup>2</sup> $\Pi$  system, the latter gains in intensity by mixing some Rydberg character into the B<sup>2</sup> $\Pi$  state. Previous theoretical studies<sup>18,19</sup> have shown that high levels of theory are required to properly describe valence–Rydberg mixing. The  $\beta$  system of NO is the only one for which the valence–Rydberg mixing occurs at internuclear distances,  $R$ , that fall within the Franck–Condon region of the  $\beta$  band system. In the present work, we deal with the coupling among the valence and Rydberg states through a vibronic matrix, as described in the next section. The description of the Rydberg states is achieved through the molecular quantum defect orbital (MQDO) approach.<sup>20</sup> In this way, the treatment of the vibrational levels for diatomics is an extension of the recent MQDO studies for the nonperturbed bands 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ ), 3p $\pi$ (C<sup>2</sup> $\Pi$ )–X<sup>2</sup> $\Pi$  ( $\delta$  band), 3s $\sigma$ (A<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\gamma$  band), and 3p $\sigma$ (D<sup>2</sup> $\Sigma^+$ )–X<sup>2</sup> $\Pi$  ( $\epsilon$  band), which have yielded excellent results.<sup>2,21</sup>

Our main goal in the present study is to shed some light on the existing uncertainties concerning the  $\beta$  band of NO as well as to test the adequacy of the MQDO procedure to describe the vibronic levels of a valence state that is subject to the interaction with a Rydberg state (3p $\pi$ (C<sup>2</sup> $\Pi$ )–B<sup>2</sup> $\Pi$ ) or, more generally, of the Rydberg–valence states of NO.

## II. Method of Calculation

The QDO formalism adapted to deal with molecular Rydberg transitions has been described in detail elsewhere.<sup>20</sup> We shall, thus, only give a very brief summary of this method here.

The QDO radial wave functions are the analytical solutions of a one-electron Schrödinger equation that contains a model potential of the form

$$V(r)_a = \frac{(c - \delta_a)(2l + c - \delta_a + 1)}{2r^2} - \frac{1}{r} \quad (1)$$

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where  $a$  represents the set of quantum numbers that define a given molecular electronic state, including a symmetry label. Solutions of this equation are related to the Kummer functions. The parameter  $\delta_a$  is the quantum defect, which varies with the electron's angular momentum, and  $c$  is an integer within a narrow range of values that ensures the normalizability of the radial orbitals and their correct nodal pattern. The number of radial nodes is equal to  $n - l - c - 1$ . The detailed MQDO algebraic expressions for the radial transition moment are given in ref 20.

The Einstein coefficients for spontaneous emission from a bound vibrational level  $v'$  of the upper electronic state into a vibrational level  $v''$  of the lower electronic state are given by<sup>23</sup>

$$A_{v'v''} = \frac{64\pi^4 e^2 a_0^2}{3h} \nu_{v'v''}^3 \frac{q_{v'v''} R_e^2}{g'} \quad (2)$$

where  $R_e^2$  is the square of the electronic transition moment in atomic units ( $ea_0$ ),  $A$  is expressed in  $s^{-1}$  and  $\nu$  in  $cm^{-1}$ ,  $g'$  is the statistical weight of the upper state, and  $\nu_{v'v''}$  is the wavenumber of the band origin. The  $q_{v'v''}$  factors are the Franck–Condon factors which for diatomic molecules are given by the squares of the overlap integrals of the vibrational states involved in the transition. The vibrational wave functions,  $\Psi_{v'}$  and  $\Psi_{v''}$ , depend on the internuclear distance,  $R$ :

$$q_{v'v''} = \left| \int \Psi_{v'} \Psi_{v''} dR \right|^2 \quad (3)$$

The derivation of accurate Einstein coefficients for vibrational bands depends on the availability of good-quality electronic transition moments (e.g., the ones supplied by MQDO calculations for Rydberg states) and on the use of accurate Franck–Condon factors for the transitions. In this work, we have adopted a Rydberg–Klein–Rees (RKR) methodology<sup>24</sup> to evaluate the potential energy surfaces (PES). Once the PES are obtained, the rotationless radial part of the Schrödinger equation for the motion of the nuclei is solved by the Numerov algorithm, and in this manner, the wave functions for the molecular vibration are evaluated. At this point, the Franck–Condon factors are immediately evaluated by solving the overlap integral given by eq 3.

The lifetime,  $\tau_{v'}$ , of a vibrational level  $v'$  is obtained from the emission coefficients calculated by means of eq 2 as follows:

$$1/\tau_{v'} = \sum_{v''} A_{v'v''} \quad (4)$$

where  $v''$  represents all vibronic states accessible from  $v'$  by spontaneous emission.

As mentioned in the Introduction, the Rydberg–valence interaction is solved by calculating the vibronic interaction matrix. The procedure is detailed below.

The transformation of the potential curves and properties from an adiabatic to a diabatic representation makes it possible to include the homogeneous interaction between the diabatic  $3p\pi$  ( $C^2\Pi$ ) and  $B^2\Pi$  states in the calculation of transition moments, transition probabilities, and radiative lifetimes.

The vibronic interaction matrix is constructed for the spin component  $\Sigma = 1/2$ . Its diagonal elements are written in the form

$$H_{v'v''}^{e'e''} = E_{v'v''}^{e'} \delta_{e'e''} \delta_{v'v''} \quad (5)$$

where  $E_{v'v''}^{e'}$  are the vibrational energies of the states introduced in the calculation.

**TABLE 1: Interaction Energies between the Electronic States a and b ( $E^{ab}$  in  $cm^{-1}$  and  $^2\Pi$  States of NO)**

a	b		
	$3p\pi(C^2\Pi)$	$4p\pi(K^2\Pi)$	$5p\pi(Q^2\Pi)$
$B^2\Pi$	1382.6	803.9	594.6
$L^2\Pi$	549.0	$-250 \pm 50$	200

The perturbation produced by every single vibrational level  $|e'',v''\rangle$  to another level  $|e',v'\rangle$  gives rise to off-diagonal elements, that take the form:

$$H_{v'v''}^{e'e''} = E_{v'v''}^{e'e''} S_{v'v''}^{e'e''} (1 - \delta_{e'e''}) \quad (6)$$

where  $E_{v'v''}^{e'e''}$  are the interaction energies of the  $e'$  and  $e''$  electronic states. In this work, we have adopted the interaction energies reported by Galluser and Dressler<sup>25</sup>, as listed in Table 1. The notation for the Rydberg states, in this and the remaining tables, consists of that of the atomic orbital to which the molecular Rydberg orbital can be correlated followed by its molecular orbital (MO) character and by the symbol of the irreducible representation to which the Rydberg MO belongs within the molecular symmetry group (in parentheses).  $S_{v'v''}^{e'e''}$  is the vibronic overlap matrix element. The complete diagonalization process may be written in the usual compact form

$$\mathbf{\Lambda} = \mathbf{C}^{-1} \mathbf{H} \mathbf{C} \quad (7)$$

where  $\mathbf{\Lambda}$  is the resulting diagonal matrix containing the eigenvalues and  $\mathbf{C}$  is the matrix of the associated eigenvectors. The wave functions of the states obtained by diagonalization of the interaction matrix, eq 7, will be the appropriate linear combinations  $|e_0, \nu_0\rangle$  of the original vibronic wave functions  $|e, \nu_e\rangle$ ,

$$|e_0, \nu_0\rangle = \sum_{e=1}^{ne} \sum_{\nu_e=0}^{\nu_{e,\max}} |e, \nu_e\rangle C_{\nu_e, \nu_0} \quad (8)$$

where  $ne$  is the number of electronic states considered in the mixing and  $\nu_{e,\max}$  is the highest vibrational level of the electronic state  $e$ . Consequently, if the wave functions given by eq 8 are adopted for the calculation of the vibronic transition moment matrix element from a generic nonperturbed state  $|X, 0\rangle$  to the mixed  $|e_0, \nu_0\rangle$  state, we have the following expression:

$$\langle M_{\nu_0, 0} \rangle = \sum_{e=1}^{ne} \sum_{\nu_e=0}^{\nu_{e,\max}} C_{\nu_e, \nu_0}^* R_e S_{\nu_e, 0}^{e,X} \quad (9)$$

where  $\langle M_{\nu_0, 0} \rangle$  is the resultant vibronic transition moment. By introducing this result as a new vibronic transition moment in eq 2, we are able to yield transition probabilities involving mixed states:

$$A_{\nu_0, 0} = \frac{64\pi^4 e^2 a_0^2}{3h} \nu_{\nu_0, 0}^3 \frac{\left[ \sum_{e=1}^{ne} \sum_{\nu_e=0}^{\nu_{e,\max}} C_{\nu_e, \nu_0}^* R_e S_{\nu_e, 0}^{e,X} \right]^2}{g'} \quad (10)$$

### III. Results and Analysis

The electronic configuration of the NO molecule may be considered to be “intermediate” between those of  $N_2$  and  $O_2$  and leads to an open-shell ground state:

$$\dots(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^1 X^2\Pi$$

**TABLE 2: Electronic Energies, Molecular Constants (Both in  $\text{cm}^{-1}$ ) and Number of Vibrational Levels for the States of NO Considered<sup>a</sup>**

	$X^2\Pi^b$	$3s\sigma(A^2\Sigma^+)^b$	$B^2\Pi^c$	$L^2\Pi^c$	$3p\pi(C^2\Pi)^c$	$4p\pi(K^2\Pi)^c$	$5p\pi(Q^2\Pi)^c$
$T_{00}$	948.67	44140.83	45503.0 <sup>d</sup>	62515.0 <sup>d</sup>	52418.0 <sup>d</sup>	64336.0 <sup>d</sup>	68674.0 <sup>d</sup>
$\omega_e$	1904.405	2374.307	1042.4	952.0	2381.3	2438.3	2340.0
$\omega_e\chi_e$	14.1870	16.1060	-7.7726	-11.28	-15.702	-48.38	-8.9
$\omega_e\gamma_e$	2.400 (-2)	-4.645 (-2)	1.1596 (-1)				
$\omega_e z_e$	-9.3 (-4)		-3.9577 (-3)				
$B_e$	1.70427	1.99478	1.1244	1.132	2.0155	2.034	2.034
$\alpha_e$	-1.7128 (-2)	-1.8328 (-2)	-1.3433 (-2)	-2.21 (-2)	-3.244 (-2)	-5.60 (-2)	-4.0 (-4)
$\gamma_e$	-3.7 (-5)		2.991 (-5)				
$Y_{31}$			-3.177 (-6)				
$v_{\max}$	16	16	37	11	9	4	3

<sup>a</sup> The quantities  $A$  ( $b$ ) represent  $A \times 10^b$ . <sup>b</sup> Engleman et al.<sup>27</sup> <sup>c</sup> Galluser and Dressler.<sup>25</sup> <sup>d</sup> Huber and Herzberg.<sup>26</sup>

**TABLE 3: Nonperturbed Electronic Transition Moments (au)**

	MQDO <sup>a</sup>	theor <sup>b</sup>
$X^2\Pi-B^2\Pi$	-0.08	-0.08
$X^2\Pi-L^2\Pi$	0	0
$X^2\Pi-3p\pi(C^2\Pi)$	0.3422	0.31
$X^2\Pi-4p\pi(K^2\Pi)$	0.1370	0.18
$X^2\Pi-5p\pi(Q^2\Pi)$	-0.08221	-0.12
$A^2\Sigma^+(3s\sigma)-B^2\Pi$	0	
$A^2\Sigma^+(3s\sigma)-L^2\Pi$	0	
$A^2\Sigma^+(3s\sigma)-3p\pi(C^2\Pi)$	4.4505	
$A^2\Sigma^+(3s\sigma)-4p\pi(K^2\Pi)$	0.4414	
$A^2\Sigma^+(3s\sigma)-5p\pi(Q^2\Pi)$	-0.2134	

<sup>a</sup> MQDO, this work. <sup>b</sup> Galluser and Dressler.<sup>25</sup>

where the molecular orbital and state notations correspond to a  $C_{\infty v}$  symmetry.

The electronic energy data chosen for our calculations on the Rydberg states have been the experimental values found in the literature.<sup>26,27</sup> The molecular constants for the noninteracting states are those reported in ref 25. All these data are collected in Table 2 together with the highest quantum numbers of the vibrational levels included in each electronic state. For the ionization energy, we have adopted the value of  $74\,721.7 \pm 0.4 \text{ cm}^{-1}$  determined by Reiser et al.<sup>28</sup> by zero kinetic energy (ZEKE) spectroscopy.

We have recently reported several studies of the vibronic and continuous transitions of  $\text{NO}^{21,22,29}$  which indicated that the outermost molecular orbital of the ground state,  $2\pi$ , resembles closely a “united atom”  $3d\pi$  orbital of reduced size with a smaller  $2p\pi$  contribution, because of the asymmetry of the molecule.<sup>30</sup>

The presently calculated nonperturbed electronic transition moments are collected in Table 3 along with those reported by Galluser and Dressler.<sup>25</sup> We have not found comparative results for transitions where the initial state is  $3s\sigma(A^2\Sigma^+)$ . The comparative values for transitions from the ground state are those reported in ref 25 and obtained by fitting 69 experimental vibrational energy levels. There is a general good accord between those<sup>25</sup> and the MQDO results.

The transition probabilities for the  $\beta$  band system calculated with the values of the nonmixed transition moments and the Franck–Condon factors derived from the RKR curves generated with the molecular constants collected in Table 2 are listed in Table 4. Since they are derived from nonperturbed transition moments, they cannot be directly compared with the available experimental data. However, as these results are the basis for the valence–Rydberg coupling calculation, eq 9, we have considered it appropriate to display them in Table 4.

The Einstein coefficients obtained with the perturbed transition moments are collected in Tables 5 and 6. In Table 5, the

**TABLE 4: MQDO Einstein Coefficients ( $\text{s}^{-1}$ ) for  $v' = 0-6$  and  $v'' = 0-16$  Vibronic Transitions Belonging to the  $\beta$  Band System ( $B^2\Pi \leftarrow X^2\Pi$ ) of NO with Unperturbed Transition Moments<sup>a</sup>**

$v''$	$v'$						
	0	1	2	3	4	5	6
0	1.892 (1)	1.594 (2)	7.043 (2)	2.175 (3)	5.279 (3)	1.073 (4)	1.901 (4)
1	2.448 (2)	1.724 (3)	6.330 (3)	1.614 (4)	3.205 (4)	5.282 (4)	7.505 (4)
2	1.494 (3)	8.507 (3)	2.492 (4)	4.976 (4)	7.561 (4)	9.228 (4)	9.281 (4)
3	5.720 (3)	2.524 (4)	5.556 (4)	7.969 (4)	8.099 (4)	5.832 (4)	2.651 (4)
4	1.544 (4)	4.971 (4)	7.462 (4)	6.439 (4)	2.944 (4)	2.857 (3)	4.538 (3)
5	3.122 (4)	6.712 (4)	5.697 (4)	1.693 (4)	2.183 (2)	1.932 (4)	4.182 (4)
6	4.915 (4)	6.090 (4)	1.752 (4)	1.276 (3)	2.660 (4)	3.922 (4)	2.029 (4)
7	6.168 (4)	3.311 (4)	6.714 (1)	2.516 (4)	3.315 (4)	8.465 (3)	1.659 (3)
8	6.270 (4)	6.457 (3)	1.583 (4)	3.118 (4)	5.279 (3)	5.605 (3)	2.585 (4)
9	5.217 (4)	8.340 (2)	3.042 (4)	8.365 (3)	5.426 (3)	2.475 (4)	1.246 (4)
10	3.576 (4)	1.353 (4)	2.036 (4)	1.237 (3)	2.214 (4)	9.385 (3)	1.504 (3)
11	2.025 (4)	2.687 (4)	3.125 (3)	1.588 (4)	1.191 (4)	1.404 (3)	1.778 (4)
12	9.481 (3)	2.889 (4)	1.775 (3)	1.862 (4)	2.840 (0)	1.548 (4)	7.916 (3)
13	3.659 (3)	2.121 (4)	1.286 (4)	5.503 (3)	9.638 (3)	9.922 (3)	1.168 (3)
14	1.158 (3)	1.152 (4)	1.995 (4)	2.876 (2)	1.439 (4)	1.508 (0)	1.241 (4)
15	2.978 (2)	4.776 (3)	1.709 (4)	8.176 (3)	4.399 (3)	8.033 (3)	6.300 (3)
16	6.161 (1)	1.538 (3)	9.878 (3)	1.514 (4)	4.012 (2)	1.059 (4)	3.878 (2)

<sup>a</sup> The quantities  $A$  ( $b$ ) represent  $A \times 10^b$ .

transition probability values from the  $v' = 0-5$  levels of the  $B^2\Pi$  electronic state to the  $v'' = 0-16$  vibrational levels of the ground state,  $X^2\Pi$ , are listed together with those supplied by Luque and Crosley<sup>14</sup> and by Piper et al.<sup>5</sup> In Table 6, the same types of data are collected but exclusively referring to transitions from the  $v' = 6$  level of  $B^2\Pi$  to the  $v'' = 0-16$  vibrational levels of the ground electronic state. The data found in the literature, those reported by Piper et al.,<sup>5</sup> by Gadd and Slanger,<sup>17</sup> by Laux and Kruger,<sup>13</sup> and by Langhoff et al.,<sup>7</sup> have also been included in Table 6 for comparative purposes.

Luque and Crosley<sup>14</sup> have excited the levels  $v' = 0-3$  with a tunable dye laser, obtaining a function for the transition moment through a nonlinear regression. Piper et al.<sup>5</sup> followed a branching-ratio procedure to determine the variation of the electronic transition moment with the internuclear separation in the region  $2.4a_0 \leq R \leq 3.02a_0$ . Gadd and Slanger<sup>17</sup> used a laser-induced fluorescence (LIF) technique to measure the zero-pressure radiative lifetimes for  $v' = 0-6$ . The work of Langhoff et al.<sup>7</sup> is a theoretical determination of the transition moment functions (TMFs) using a state-averaged (SA) complete-active-space self-consistent field (CASSCF) multireference configuration interaction (MRCI) method. These authors report two sets of values in Figure 3 of their paper.<sup>7</sup> The ones denoted as MRCI<sup>1</sup> in Table 6 have been determined with their TMFs after scaling them with a factor of 1.376 in order to bring their lifetimes into better agreement with the experiment.<sup>17</sup> The ones denoted as MRCI<sup>2</sup> in Table 6 were obtained by shifting the TMFs to larger  $R$  values by  $0.045a_0$ , in order, again, to reproduce the experimental lifetime data. However, the Einstein coef-

**TABLE 5: Einstein Coefficients ( $s^{-1}$ ) for  $v' = 0-5$  and  $v'' = 0-16$  Vibronic Transitions Belonging to the  $\beta$  Band System ( $B^2\Pi \leftarrow X^2\Pi$ ) of  $NO^a$** 

$v''$	$v'$								
	$0^b$	$0^c$	$0^d$	$1^b$	$1^c$	$1^d$	$2^b$	$2^c$	$2^d$
0	4.334 (1)	5.342 (1)	5.269 (1)	3.889 (2)	4.869 (2)	4.746 (2)	1.802 (3)	2.233 (3)	2.286 (3)
1	5.035 (2)	6.065 (2)	6.029 (2)	3.707 (3)	4.560 (3)	4.503 (3)	1.395 (4)	1.789 (4)	1.783 (4)
2	2.715 (3)	3.287 (3)	3.290 (3)	1.605 (4)	1.977 (4)	1.986 (4)	4.769 (4)	6.109 (4)	6.182 (4)
3	9.389 (3)	1.136 (4)	1.138 (4)	4.270 (4)	5.239 (4)	5.297 (4)	9.435 (4)	1.202 (5)	1.227 (5)
4	2.275 (4)	2.283 (4)	2.280 (4)	7.578 (4)	9.345 (4)	9.454 (4)	1.144 (5)	1.444 (5)	1.481 (5)
5	3.887 (4)	5.236 (4)	5.216 (4)	8.623 (4)	1.154 (5)	1.167 (5)	7.371 (4)	9.915 (4)	1.021 (5)
6	5.013 (4)	7.676 (4)	7.608 (4)	6.024 (4)	9.648 (4)	9.748 (4)	1.456 (4)	2.693 (4)	2.815 (4)
7	5.814 (4)	9.029 (4)	8.914 (4)	2.732 (4)	4.834 (4)	4.899 (4)	9.583 (2)	2.744 (2)	2.229 (2)
8	6.316 (4)	8.640 (4)	8.513 (4)	6.224 (3)	8.431 (3)	8.770 (3)	1.607 (4)	2.441 (4)	2.382 (4)
9	5.343 (4)	6.786 (4)	6.692 (4)	7.372 (2)	1.371 (3)	1.211 (3)	2.894 (4)	4.242 (4)	4.197 (4)
10	3.427 (4)	4.394 (4)	4.356 (4)	1.536 (4)	1.792 (4)	1.729 (4)	2.107 (4)	2.609 (4)	2.610 (4)
11	2.021 (4)	2.349 (4)	2.353 (4)	2.665 (4)	3.301 (4)	3.238 (4)	2.447 (3)	3.504 (3)	3.643 (3)
12	9.626 (3)	1.036 (4)	1.054 (4)	2.795 (4)	3.331 (4)	3.313 (4)	2.356 (3)	2.394 (3)	2.251 (3)
13	3.375 (3)	3.758 (3)	3.901 (3)	2.184 (4)	2.301 (4)	2.326 (4)	1.259 (4)	1.498 (4)	1.479 (4)
14	1.244 (3)	1.115 (3)	1.185 (3)	1.068 (4)	1.173 (4)	1.210 (4)	2.092 (4)	2.153 (4)	2.174 (4)
15	2.712 (2)	2.979 (2)	2.927 (2)	4.802 (3)	4.559 (3)	4.812 (3)	1.647 (4)	1.721 (4)	1.777 (4)
16	5.798 (1)	5.129 (1)	5.816 (1)	1.499 (3)	1.362 (3)	1.478 (3)	9.601 (3)	9.194 (3)	9.735 (3)

$v''$	$v'$								
	$3^b$	$3^c$	$3^d$	$4^b$	$4^c$	$4^d$	$5^b$	$5^c$	$5^d$
0	5.858 (3)	7.836 (3)	7.665 (3)	1.541 (4)	2.077 (4)	2.026 (4)	3.533 (4)	4.632 (4)	4.495 (4)
1	3.632 (4)	4.881 (4)	4.873 (4)	7.492 (4)	1.039 (5)	1.039 (5)	1.303 (5)	1.836 (5)	1.837 (5)
2	9.584 (4)	1.285 (5)	1.308 (5)	1.483 (5)	2.050 (5)	2.102 (5)	1.869 (5)	2.610 (5)	2.693 (5)
3	1.338 (5)	1.765 (5)	1.845 (5)	1.342 (5)	1.854 (5)	1.943 (5)	9.412 (4)	1.322 (5)	1.415 (5)
4	9.702 (4)	1.260 (5)	1.318 (5)	4.222 (4)	5.507 (4)	5.970 (4)	2.756 (3)	3.030 (3)	4.090 (3)
5	2.141 (4)	2.777 (4)	2.991 (4)	4.446 (2)	1.349 (3)	1.143 (3)	2.783 (4)	4.564 (4)	4.523 (4)
6	3.016 (3)	2.251 (3)	2.895 (3)	3.280 (4)	5.117 (4)	5.123 (4)	4.317 (4)	7.204 (4)	7.445 (4)
7	3.022 (4)	4.251 (4)	4.220 (4)	3.232 (4)	5.384 (4)	5.512 (4)	5.223 (3)	1.143 (4)	1.251 (4)
8	2.880 (4)	4.653 (4)	4.684 (4)	3.568 (3)	6.621 (3)	7.128 (3)	7.372 (3)	1.163 (4)	1.112 (4)
9	6.862 (3)	1.077 (4)	1.113 (4)	6.152 (3)	9.522 (3)	9.095 (3)	2.284 (4)	3.832 (4)	3.834 (4)
10	1.504 (3)	1.176 (3)	1.980 (3)	2.281 (4)	3.152 (4)	3.116 (4)	9.172 (3)	1.170 (4)	1.205 (4)
11	1.707 (4)	2.128 (4)	2.074 (4)	1.101 (4)	1.474 (4)	1.485 (4)	2.135 (3)	2.808 (3)	2.596 (3)
12	1.863 (4)	2.261 (4)	2.242 (4)	6.282 (1)	6.299 (1)	5.361 (1)	1.628 (4)	2.095 (4)	2.054 (4)
13	4.587 (3)	5.958 (3)	6.044 (3)	1.040 (4)	1.237 (4)	1.209 (4)	8.827 (3)	1.137 (4)	1.138 (4)
14	3.687 (2)	4.453 (2)	4.391 (2)	1.414 (4)	1.635 (4)	1.632 (4)	2.870 (1)	6.300 (1)	6.043 (1)
15	8.933 (3)	9.006 (3)	9.085 (3)	4.021 (3)	4.336 (3)	4.433 (3)	8.638 (3)	9.753 (3)	9.673 (3)
16	1.529 (4)	1.498 (4)	1.549 (4)	5.923 (2)	5.164 (2)	5.086 (2)	1.048 (4)	9.753 (3)	1.135 (4)

<sup>a</sup> The quantities  $A$  ( $b$ ) represent  $A \times 10^b$ . <sup>b</sup> MQDO, this work, calculated with mixed transition moments. <sup>c</sup> Luque and Crosley.<sup>14</sup> <sup>d</sup> Piper et al.<sup>5</sup>

**TABLE 6: Einstein Coefficients ( $s^{-1}$ ) for  $v' = 6$  and  $v'' = 0-16$  Vibronic Transitions Belonging to the  $\beta$  Band System ( $B^2\Pi \leftarrow X^2\Pi$ ) of  $NO^a$** 

$v''$	MQDO <sup>b</sup>	exptl <sup>c</sup>	exptl <sup>d</sup>	exptl <sup>e</sup>	theor <sup>f</sup>	MRCI <sup>g</sup>	MRCI <sup>h</sup>
0	7.439 (4)	9.027 (4)	8.706 (4)	1.05 (5)	7.604 (4)	1.78 (5)	1.54 (5)
1	1.934 (5)	2.791 (5)	2.790 (5)	3.14 (5)	2.167 (5)	4.66 (5)	3.91 (5)
2	1.959 (5)	2.697 (5)	2.805 (5)	2.93 (5)	2.044 (5)	3.89 (5)	2.76 (5)
3	3.764 (4)	5.392 (4)	6.032 (4)	6.14 (4)	4.730 (4)	7.25 (4)	3.18 (4)
4	1.114 (4)	1.784 (4)	1.640 (4)	2.12 (4)	9.129 (3)	2.43 (4)	2.09 (4)
5	6.063 (4)	9.254 (4)	9.511 (4)	1.01 (5)	7.295 (4)	1.44 (5)	7.36 (4)
6	1.915 (4)	3.284 (4)	3.555 (4)	5.55 (4)	3.378 (4)	5.75 (4)	1.96 (4)
7	4.931 (3)	5.678 (3)	5.105 (3)	1.11 (4)	3.058 (3)	1.25 (4)	1.82 (3)
8	2.636 (4)	4.547 (4)	4.579 (4)	7.43 (4)	4.072 (4)	8.28 (4)	4.55 (4)
9	8.870 (3)	1.650 (4)	1.727 (4)	2.83 (4)	1.743 (4)	2.88 (4)	1.84 (4)
10	1.548 (3)	3.745 (3)	3.446 (3)	7.79 (3)	2.406 (3)	1.13 (4)	5.45 (2)
11	1.917 (4)	2.604 (4)	2.570 (4)	5.07 (4)	2.378 (4)	4.63 (4)	2.64 (4)
12	7.074 (3)	8.984 (3)	9.127 (3)	1.65 (4)	1.017 (4)	1.83 (4)	8.18 (3)
13	1.970 (3)	2.342 (3)	2.185 (3)	5.78 (3)	1.448 (3)	2.75 (3)	1.45 (2)
14	1.213 (4)	1.569 (4)	1.543 (4)	1.89 (4)	1.512 (3)	3.00 (4)	1.36 (4)
15	5.808 (3)	6.363 (3)	6.417 (3)	9.00 (3)	7.239 (3)	1.13 (4)	5.64 (3)
16	6.049 (2)	7.151 (2)	7.202 (2)	2.95 (3)	4.069 (2)	2.50 (2)	1.64 (2)

<sup>a</sup> The quantities  $A$  ( $b$ ) represent  $A \times 10^b$ . <sup>b</sup> MQDO, this work, calculated with mixed transition moments. <sup>c</sup> Luque and Crosley.<sup>14</sup> <sup>d</sup> Piper et al.<sup>5</sup> <sup>e</sup> Gadd and Slanger.<sup>17</sup> <sup>f</sup> Laux and Kruger.<sup>17</sup> <sup>g</sup> Langhoff et al.<sup>7</sup> (see text for explanations of MRCI<sup>g</sup> and MRCI<sup>h</sup>).

ficients reported for  $v' = 6$  obtained by using the shifted moment<sup>7</sup> differ more from the experiment than those obtained with the unshifted moment.<sup>7</sup> Both Langhoff et al.<sup>7</sup> and Piper et

al.<sup>5</sup> remark that there appears to be some systematic error in the Einstein coefficients reported by Gadd and Slanger,<sup>17</sup> that may be attributed to difficulties in calibrating the sensitivity of their instrument over a wide wavelength region. Finally, we have also introduced the values reported by Laux and Kruger<sup>13</sup> obtained by combining the ab initio TMFs of Langhoff et al.<sup>7</sup> with accurate spectroscopic constants, producing extensive arrays of data.

It can be noticed that the present MQDO results obtained with mixed transition moments resemble closely both the previously reported experimental and theoretical values for the spontaneous emission coefficients. It is evident that the interaction with Rydberg states (more specifically, with the  $3p\pi(C^2\Pi)$  state) enhances the probability of a transition from a valence state. This is proof of the need to introduce the Rydberg–valence interaction in the description of the  $B^2\Pi$  state of  $NO$ . Furthermore, the high quality of the MQDO transition moments has also been proved through their participation in the linear combinations of the wave functions that have led to the final values of the vibronic Einstein coefficients (eq 10).

Before carrying out the calculations of the radiative lifetimes of the  $\beta$  band system of  $NO$ , we took into account some considerations. The different nature of the nonperturbed  $B^2\Pi$  state (of valence character) and the  $3s\sigma(A^2\Sigma^+)$  state (of Rydberg type) does not allow for dipole transitions between them, as is reflected in Table 3, where the corresponding transition moments

**TABLE 7: Radiative Lifetimes for the Levels  $v' = 0-6$  of the  $B^2\Pi$  State ( $\mu\text{s}$ )**

$v'$	MQDO <sup>a1</sup>	MQDO <sup>a2</sup>	exptl <sup>c</sup>	exptl <sup>d</sup>	exptl <sup>e</sup>	theor <sup>f</sup>	MRCI <sup>g</sup>	MRCI <sup>g1</sup>	MRCI <sup>g2</sup>	MRCI <sup>i</sup>
0	2.72	2.85	2.00	2.02	2.00	2.12	3.70	2.12	1.99	5.52
1	2.33	2.76	1.77	1.75	1.82	1.95	3.40	1.93	1.79	4.49
2	2.03	2.72	1.56	1.54	1.52	1.78	2.94	1.76	1.60	3.66
3	1.90	2.78	1.39	1.36	1.46	1.63	2.67	1.60	1.41	2.85
4	1.80	2.80	1.24	1.22	1.19	1.49	2.47	1.45	1.23	2.18
5	1.63	2.71	1.11	1.11	1.07	1.36	2.31	1.31	1.05	1.70
6	1.46	2.72	0.99	1.00	0.85	1.24	2.16	1.17	0.87	1.34

<sup>a</sup> MQDO, this work, calculated with mixed transition moments. <sup>b</sup> MQDO, this work, calculated with nonmixed transition moments. <sup>c</sup> Luque and Crosley.<sup>14</sup> <sup>d</sup> Piper et al.<sup>5</sup> <sup>e</sup> Gadd and Slanger.<sup>17</sup> <sup>f</sup> Laux and Kruger.<sup>13</sup> <sup>g</sup> Vivie and Peyerimhoff.<sup>31</sup> <sup>h</sup> Langhoff et al.<sup>7</sup> (see text for explanations). <sup>i</sup> Cooper.<sup>6</sup>

are equal to zero. However, there exists a finite probability for a transition between the  $3p\pi(C^2\Pi)$  unperturbed Rydberg state and the  $3s\sigma(A^2\Sigma^+)$  state. In addition, the  $3p\pi(C^2\Pi)-B^2\Pi$  interaction lends some Rydberg character to  $B^2\Pi$ .<sup>7,18,19</sup> In this way, the final, mixed  $B^2\Pi$  state has a nonzero probability of undergoing a spontaneous transition to the  $3s\sigma(A^2\Sigma^+)$  state by a dipole mechanism. Obviously, the probabilities for these processes are very small, though nonnegligible in the calculation of radiative lifetimes. As it has been mentioned above, all allowed vibronic transitions had to be included in eq 4 to perform this evaluation. Mention of the quenching exerted by the  $3s\sigma(A^2\Sigma^+)$  Rydberg state on the  $B^2\Pi$  valence state has been made in previous works, such as that by Luque and Crosley.<sup>15</sup>

The present results and comparative values for radiative lifetimes, comprising the  $v' = 0-6$  levels of the  $B^2\Pi$  state of NO, are listed in Table 7. The first column, denoted as MQDO<sup>a1</sup>, contains our results achieved by explicitly considering the Rydberg–valence interaction. In the second column (MQDO<sup>a2</sup>) we give the results obtained with nonmixed vibronic transition moments. The need for an explicit account of the perturbation effects is again made apparent if one wants to bring lifetimes into agreement with the experiment.

The results reported by Langhoff et al.,<sup>7</sup> Vivie and Peyerimhoff,<sup>31</sup> and Cooper,<sup>6</sup> also included in Table 7, have been derived from ab initio calculations. The magnitude of the lifetimes obtained by Vivie and Peyerimhoff<sup>31</sup> and by Cooper<sup>6</sup> is larger than that obtained by Gadd and Slanger.<sup>17</sup> Langhoff et al.<sup>7</sup> remarked that the values calculated by Cooper<sup>6</sup> were not as accurate as their determinations due to limitations in his configuration interaction (CI) treatments. Vivie and Peyerimhoff<sup>31</sup> also followed a CASSCF MRCI method to yield a survey of many electronic transitions in the NO molecule, whereas Langhoff et al.<sup>7</sup> focused on the  $\beta$  system. Langhoff et al.<sup>7</sup> also reported two sets of values. Those denoted as MRCI<sup>g1</sup> in Table 7 were computed directly, and the ones denoted as MRCI<sup>g2</sup> in Table 7 were obtained by performing a shift on the TMFs. Piper et al.<sup>5</sup> used a branching-ratio technique together with the experimental values determined by Gadd and Slanger.<sup>17</sup> The determination of electronic transition moments by Luque and Crosley<sup>14</sup> made possible the calculation of Einstein emission coefficients, but their experiment only furnishes relative information. To derive absolute values for radiative lifetimes, Luque and Crosley<sup>14</sup> adopted the value of 2.00  $\mu\text{s}$  for the lifetime of the  $v' = 0$  level reported by Gadd and Slanger,<sup>17</sup> for normalization purposes. Laux and Kruger<sup>13</sup> also supplied lifetimes for the first vibrational level of the  $B^2\Pi$  state of NO. Given that the Einstein values of Laux and Kruger<sup>13</sup> resemble quite closely those calculated in the present work, we attribute the discrepancies in the lifetimes to differences in the extension of the vibrational basis set.

We emphasize that our calculated lifetimes, based on a rather simple approach, conform fairly well with the experimental

values. Our results agree in magnitude (both absolute and relative) as well as in trend with all the previously reported theoretical results, no matter that our methodology is computationally less expensive than the traditional ab initio methods. We interpret the existing discrepancies in lifetimes basically in terms of having constrained the perturbations suffered by the  $B^2\Pi$  valence state only to the one exerted by the  $3p\pi(C^2\Pi)$  Rydberg state, ignoring other potentially mixing Rydberg or intermediate states, but not to limitations in our methodology.

#### IV. Concluding Remarks

Transition moments belonging to the  $\beta$  band of NO, which are relevant to the study of atmospheric processes, have been calculated. The electronic transition moments have been determined with the MQDO approach. Our results agree fairly well with most of the experimental values, which make us confident in the proposed interaction scheme as well as in the vibronic matrix representation of the perturbations. The present results have been expressed in the form of Einstein coefficients and of radiative lifetimes, to compare them with previous results found in the literature.

The MQDO method has proved to be a useful tool to estimate transition intensities (given here in the form of transition probabilities), even for mixed states, confirming its potential as a basis for the representation of Rydberg molecular orbitals. The high ratio between the quality of results and the computational effort of this procedure is undoubtedly linked to its analyticity.

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