Intensities of Vibronic Transitions for the Main Bands Observed in the Electronic Spectrum of Atmospherically Relevant Nitric Oxide

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Absorption oscillator strengths for the $\gamma(A^2\Sigma^+-X^2\Pi)$, $\delta(C^2\Pi-X^2\Pi)$, and $\epsilon(D^2\Sigma^+-X^2\Pi)$ bands of NO, which are relevant to the study of atmospheric processes are reported. We have calculated both electronic and vibronic transition probabilities with the molecular-adapted quantum defect orbital (MQDO) method, which has proved, in previous applications, to be an adequate theoretical tool in the context of Rydberg spectra. The results appear to be in good accord with the available experimental values and, with some exceptions, conform fairly well with theoretical data derived from rather more sophisticated methods.

I. Introduction

Rydberg states of molecules have recently received a good deal of attention from the experimental spectroscopists, possibly motivated, in part, by the development of very sensitive spectroscopic techniques, which are able to probe these high-lying electronically excited states. The bound Rydberg states of the NO molecule have attracted much attention for many years. Apart from its relevant atmospheric implications, the simplicity of its electronic structure may have encouraged the theoreticians. This simplicity is mostly due to the fact that the first electronic excitation energy of NO^+ is rather high (6.5 eV),[1] and as a consequence, the Rydberg series converging to the excited NO^+ states do not mix with the series converging to the ground state of the cation. In addition, the high ionization energy of NO (9.26 eV)[2] facilitates the presence of low-*n* members of the Rydberg series.

Nitric oxide is a minor, but significant, neutral constituent of the thermosphere.[3] It has been found to play a very important role in the physics and chemistry of the Earth's upper atmosphere.[4] The reason for its importance in atmospheric chemistry is the fact the production and loss mechanisms for NO are strongly dependent on the interaction of the major constituents of the upper atmosphere (mainly N_2 and O_2) with solar radiation and energetic charged particles.

In addition, NO is known to be a catalyst in the destruction of ozone[5,6] at lower altitudes. It is also important in the thermal balance of the Earth's atmosphere, because its rotational−vibrational transitions in its vibrationally excited ground electronic state ($X^2\Pi$) efficiently produce infrared radiation.[7]

Good-quality oscillator strengths for the $\gamma(A^2\Sigma^+-X^2\Pi)$ absorption bands of nitric oxide bear directly upon atmospheric science through processes such as the measurement of NO column densities in the mesosphere,[8] or the interpretation of emissions in a strong aurora. Proper NO $\gamma(A^2\Sigma^+-X^2\Pi)$ transition probabilities are also needed to calculate the gain for various transitions in the optically pumped NO $\gamma(A^2\Sigma^+-X^2\Pi)$ laser.[9] But the availability of accurate NO $\gamma(A^2\Sigma^+-X^2\Pi)$ transition probabilities affects a wider range of studies. Because they are easy to excite, the NO γ bands are often used to establish the relative spectral response of monochromators in the ultraviolet.[10,11]

Nevertheless, the use of NO emissions as a diagnostic tool in atmospheric processes is complicated because both the molecular spectroscopy and spectral emission characteristics of this molecule are relatively poorly known compared to those of N_2 and O_2. For example, the optical transition moments corresponding to both the β and γ bands, extensively used as NO diagnostics, are still the subject of both experimental and theoretical studies.

Below 8 eV, the valence shell excitation spectrum of nitric oxide consists mainly of discrete transitions belonging to the $\gamma(A^2\Sigma^+-X^2\Pi)$, $\beta(B^2\Sigma^+-X^2\Pi)$, $\delta(C^2\Pi-X^2\Pi)$, and $\epsilon(D^2\Sigma^+-X^2\Pi)$ spectral series. In this work, we have undertaken the calculation of absorption oscillator strengths for the $\gamma(A^2\Sigma^+-X^2\Pi)$, $\delta(C^2\Pi-X^2\Pi)$, and $\epsilon(D^2\Sigma^+-X^2\Pi)$ bands of NO which are relevant in areas such as atmospheric sciences[8,12] and the development of lasers.[9] We have not studied the $\beta(B^2\Sigma^+-X^2\Pi)$ band system because the $B^2\Sigma^+$ state does not have a Rydberg character, unlike the states involved in the transitions that give rise to all the other bands that are the object of the present study. Our calculations have been performed with the molecular-adapted quantum defect orbital (MQDO) method, as its adequacy for yielding Rydberg transition intensities of good quality in a variety of molecular species has been proven (see for example refs 13−17) where satisfactory results for oscillator strengths and partial cross sections have been obtained with the MQDO procedure. To further test the scope of this methodology, in the present work we have dealt with vibronic transitions for the first time. The correctness of the present results has been established with the help of experimental and theoretical data available in the literature.

One of the goals of the present work was to assess the performance of our procedure in the description of relevant features in the discrete region of the spectrum of NO before undertaking studies related to the photoionization of this molecule.

II. Method of Calculation

The QDO formalism adapted to deal with molecular Rydberg transitions has been described in detail elsewhere.[13] We shall, thus, only give here a very brief summary of this method.

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TABLE 1: Values of Non-zero Angular Factors $Q\{A \rightarrow B\}$ of NO Molecule, for $C_{\infty v}$ Symmetry and for $l = 0, 1, 2$

$Q\{np\pi(\Pi) \rightarrow ns\sigma(\Sigma^+)\} = 1/3$
$Q\{np\pi(\Pi) \leftrightarrow nd\pi(\Pi)\} = Q\{nd\pi(\Pi) \rightarrow np\sigma(\Sigma^+)\} = 1/5$

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

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

where a represents the set of quantum numbers that define a given molecular state, including a symmetry label. Solutions of this equation are related to Kummer functions. The parameter δ_a is the quantum defect, which varies with the electron's angular momentum (i.e., differs from one Rydberg series to another), and c is an integer with a narrow range of values that ensure the normalizability of the orbitals and their correct nodal pattern. The number of radial nodes is equal to $n - l - c - 1$. The angular part of the molecular Rydberg orbitals is a linear combination of spherical harmonics, so that the Rydberg MO's form bases for the different irreducible representations of the molecular symmetry group.

The quantum defect, δ_a, corresponding to a given state, is related to the energy eigenvalue through the following equation,

$$E_a = T - \frac{1}{2(n_a - \delta_a)^2} \qquad (2)$$

where T is the ionization energy. Both T and E_a are expressed here in Hartrees.

The absorption oscillator strength for an electronic transition between two states a and b may be expressed as follows,

$$f(a \rightarrow b) = \frac{2}{3}(E_b - E_a)Q\{a \rightarrow b\}|R_{ab}|^2 \qquad (3)$$

where $Q\{a \rightarrow b\}$, referred to as the *angular factors*, result from the angular integration of the transition matrix element, and the radial part of the transition moment is denoted as

$$R_{ab} = \langle R_a(r)|r|R_b(r)\rangle \qquad (4)$$

The detailed MQDO algebraic expressions for the radial transition moment are given in ref 13.

We find it relevant to mention here that with the quantum defect orbitals, all the radial transition integrals have closed-form analytical expressions. This makes the calculations of transition intensities to be free from numerical errors and convergence problems, which is, in our view, an important computational advantage.

The values of $Q\{a \rightarrow b\}$ for the symmetry group $C_{\infty v}$, to which the Rydberg states of nitric oxide involved in the presently studied γ, δ, and ϵ bands belong, are collected in Table 1. In this and the remaining tables we are employing a notation for the molecular Rydberg states that is commonly found in the literature. The *nl* symbol of the atomic orbital to which the molecular Rydberg orbital can be correlated is followed by its MO character, and by the symbol of the irreducible representation to which the Rydberg orbital belongs within the molecular symmetry group (in parentheses).

The oscillator strength for a vibronic transition may be expressed as follows:[18]

$$f_{v'v''} = \frac{8\pi^2 mc}{3he^2 g''} \nu_{v'v''} q_{v'v''} R_e^{\,2}(\bar{r}_{v'v''}) \qquad (5)$$

where v' and v'' refer to upper- and lower-state vibrational quantum numbers, respectively, g'' is the statistical weight of the lower state, $q_{v',v''}$ is the Franck−Condon factor, $\nu_{v'v''}$ is the wavenumber of the band origin, and R_e is the electronic transition moment.

Nicholls and Steward[19] have emphasized the importance of taking into account the possible variation of the electronic transition moment as a function of the internuclear distance $\bar{r}_{v'v''}$. However, it is known that for transitions in which the vibrational energy is small compared with the electronic energy, and if no very high vibrational levels are involved, the range where $q(v',v'')$ has significant values is not too large. This happens in some transitions that occur in the ultraviolet region of the spectrum. For these, the magnitude of R_e can safely be assumed to be constant, and an effective electronic oscillator strength is defined by summing over a v'' progression,

$$f_{\mathrm{elec}} = \sum_{v'} f_{v'v''} \qquad (6)$$

By introducing the last expression into eq 5, we have

$$f_{\mathrm{elec}} = \frac{8\pi^2 mc}{3he^2 g''} R_e^{\,2} \bar{\nu} \qquad (7)$$

where $\bar{\nu} = \sum_{v'}[\nu(v',v'')\ q(v',v'')]$, may be taken as a mean wavenumber for the whole band system or, in other words, is the $q(v',v'')$-weighted average frequency of the transition.

It is then inferred from eq 7 and by taking into account eq 5, that the oscillator strength for a vibronic transition is related to the one corresponding to an electronic transition, in the following form:

$$f_{v'v''} = \frac{q_{v'v''}\nu_{v'v''}}{\bar{\nu}} f_{\mathrm{elec}} \qquad (8)$$

The derivation of accurate electronic oscillator strengths for vibrational bands depends on the availability of good-quality electronic oscillator strengths (e.g., the ones supplied by MQDO calculations), and on the use of accurate Franck−Condon factors for the transitions. In this work we have adopted the ones reported by Ory.[20,21]

The energy data and quantum defects used in the present calculations are discussed in the section that follows.

III. Results and Analysis

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

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

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

The energy data chosen for our calculations on the electronic Rydberg states have been the experimental values found in the literature.[22,23] For the ionization energy we have adopted the value of 9.26 eV, determined by Miesher[2] through an extrapolation of selected rotational lines from the absorption spectrum. All these data are collected in Table 2, together with the quantum defects for the molecular Rydberg states.

TABLE 2: Energy Levels and Quantum Defects for 3sσ(A$^2\Sigma^+$), 3pπ(C$^2\Pi$), and 3pσ(D$^2\Sigma^+$) Rydberg States of NO

state	energy (cm^{-1})	δ
3sσ(A$^2\Sigma^+$)	44 231.086[a]	1.10
3pπ(C$^2\Pi$)	52 417.548[a]	0.78
3pσ(D$^2\Sigma^+$)	53 292.40[b]	0.74
	IP = 74 721.5[c]	

[a] Brunger et al.[22] [b] Huber and Herzberg.[23] [c] Miescher.[2]

TABLE 3: Spectroscopic Constants (cm^{-1}) for the NO Ground State and the Excited 3sσ(A$^2\Sigma^+$), 3pπ(C$^2\Pi$), and 3pσ(D$^2\Sigma^+$) States

	ω_e	$\omega_e\chi_e$	$\omega_e\gamma_e$	$\omega_e\tau_e$	T_e
X$^2\Pi$[a]	1904.405	14.1870	0.02400	0.00093	
3sσ(A$^2\Sigma^+$)[a]	2374.307	16.1060	0.04645		43906.37
3pπ(C$^2\Pi$)	2395[b]	15[b]			52279.9[c]
3pσ(D$^2\Sigma^+$)	2327[d]	23[d]			53084.7[c]

[a] Engleman et al.[24] [b] Lagerqvist and Miescher.[25] [c] Huber and Herzberg.[23] [d] Barrow and Miescher.[26]

The vibrational energy levels of the ground and Rydberg electronic states (3sσ, 3pπ, and 3pσ) involved in the presently studied transitions have been determined with an anharmonic model. In our calculations, we have used the spectroscopic constants measured by Engleman et al.[24] for the ground and the 3sσ Rydberg states, and the ones reported by Lagerqvist and Miescher[25] and by Barrow and Miescher,[26] respectively, for the 3pπ and 3pσ states. All these data, together with the electronic binding energies are collected in Table 3.

Before carrying out the calculations on both the electronic and vibronic transitions that correspond to excitations from the ground state (X$^2\Pi$) to the 3sσ(A$^2\Sigma^+$), 3pπ(C$^2\Pi$), and 3pσ(D$^2\Sigma^+$) Rydberg states, known as the γ, δ, and ϵ bands of NO, respectively, as already remarked, we had to take into account the following considerations:

The 2π orbital in the ground state of NO (X$^2\Pi$) resembles closely a "united atom" 3dπ orbital of reduced size, with a smaller 2pπ contribution, because of the asymmetry of the molecule.[27] This 3dπ "hydrogenic" Rydberg orbital is neither orthogonal to all the orbitals occupied by the 14 electrons of the NO$^+$ core, nor to the 2π orbital occupied by the valence electron in the ground state of NO, which is rather concentrated to the core region. This results in a nonzero overlap integral with the core orbitals. Jungen[27] estimated the value of the overlap integral, S, between the Φ(2pπ) non Rydberg wave function and the Φ(3dπ) "hydrogenic" function, to be equal to 0.107. Then, the orthogonalized orbital could be expressed in the form $\Phi = (1 - S^2)^{-1/2}[\Phi^*(3d\pi) - S\Phi(2p\pi)]$. Two constants were defined as $C_{3d\pi} = (1/[1 - S^2])^{-1/2}$ and $C_{2p\pi} = (-S/[1 - S^2])^{-1/2}$, such that the singly occupied MO in the ground-state configuration of NO may be denoted as $C_{3d\pi}\Phi^*(3d\pi) + C_{2p\pi}\Phi(2p\pi)$.

In our calculations of radial transition moments (eq 3), we have adopted Jungen's[27] expression for the wave function of the ground state. Consequently, for the electronic transition from the ground state to the 3sσ Rydberg state, the expression that results for the radial integral is the following: $R_{X^2\Pi,3s\sigma} = C_{3d\pi}\langle R_{3d\pi}|r|R_{3s\sigma}\rangle + C_{2p\pi}\langle R_{2p\pi}|r|R_{3s\sigma}\rangle$.

Given the one-electron nature of the Rydberg states of NO (as is widely accepted for molecular Rydberg states), the molecular Rydberg electron retains an orbital angular momentum well-defined by the atomic orbital quantum number l (see, e.g., ref 18). Hence, the Laporte selection rule $\Delta l = \pm 1$ (in addition to symmetry constraints) applies to the transitions that involve Rydberg states in NO. This has the consequence that the above radial integral for the excitation from the ground state to the 3sσ Rydberg state of NO is simplified to the form corresponding to the 2pπ−3sσ radial integral, as defined by eq 4, multiplied by the $C_{2p\pi}$ coefficient. For the other bands that arise from excitations from the ground state to the 3pπ and 3pσ Rydberg states we have proceeded likewise. That is, the integrals of the form given by eq 4 that correspond to the 3dπ−3pπ and 3dπ−3pσ transitions have been multiplied by the $C_{3d\pi}$ coefficient.

In Table 4 we collect the MQDO calculated absorption oscillator strengths for the electronic transitions corresponding to the γ(3sσ(A$^2\Sigma^+$)←X$^2\Pi$), δ(3pπ(C$^2\Pi$)←X$^2\Pi$), and ϵ(3pσ(D$^2\Sigma^+$)←X$^2\Pi$) bands of NO, together with the experimental values found in the literature[28−32] and those by Ory,[21] which refer to the average value of the electronic oscillator strengths calculated from the vibrational measurements by Bethke.[28] The MQDO values conform well the comparative data with the exception of the measurements reported by Keck et al.[29] and by Flink and Welge,[32] which appear to be lower in magnitude than the rest of the experimental observations.

Tables 5−10 display the presently calculated oscillator strengths for the vibrationally resolved transitions belonging to the γ(3sσ(A$^2\Sigma^+$)←X$^2\Pi$), δ(3pπ(C$^2\Pi$)←X$^2\Pi$), and ϵ(3pσ(D$^2\Sigma^+$)←X$^2\Pi$) bands. Previously reported experimental and theoretical data available in the literature have also been included for comparative purposes.

The MQDO f-values for the (ν', $\nu'' = 0$) vibronic transitions within the γ band, as shown in Table 5, compare fairly well with the most recent measurements, performed by Chan et al.,[33] with a high-resolution dipole(e,e) technique, and more so if we take into account their estimated uncertainties of 5−10% for the strong, partially resolved peaks, and of 10−20% for the remaining peaks. A general good agreement with the rest of the experimental[28,34−37] values is apparent. The available theoretical data have been obtained by means of multireference configuration interaction (MRCI) procedures by de Vivie and Peyerimhoff[38] and by Langhoff et al.,[39] which are rather more complex than the MQDO calculations. However, our results and those reported by Langhoff et al.[39] are in better agreement with the experimental values than the calculations by de Vivie and Peyerimhoff.[38]

Table 6 collects the present and previous results for the δ (ν', $\nu'' = 0$) band. Our MQDO values are in good agreement with the experimental data for the vibronic transitions to $\nu' = 0$ and $\nu' = 1$ but are of a higher magnitude than the measurements for $\nu' = 2$. A reason may be the occurrence of perturbations that have been experimentally observed[25] for the C$^2\Pi$(ν'=2) and B$^2\Pi$(ν'=15) bands in the spectrum of NO. We have not accounted for such perturbations in our calculations. Galluser and Dressler[40] followed an electronic coupling proce-

TABLE 4: Oscillator Strengths (in Units of 100) for the X$^2\Pi$ → 3sσ(A$^2\Sigma^+$), $X^2\Pi$ → 3pπ(C$^2\Pi$) and $X^2\Pi$ → 3pσ(D$^2\Sigma^+$) Transitions of NO

	MQDO[a]	expt	expt[d]	expt[e]	expt[f]	expt[g]
$X^2\Pi$−3sσ(A$^2\Sigma^+$)	0.252	0.24 ± 0.01[b]	0.1 ± 0.05	0.34 ± 0.08	0.39 ± 0.15	0.12 ± 0.01
$X^2\Pi$−3pπ(C$^2\Pi$)	1.85	1.70 ± 0.17[c]				
$X^2\Pi$−3pσ(D$^2\Sigma^+$)	1.29	1.37 ± 0.14[c]				

[a] MQDO, this work. [b] Bethke.[28] [c] Ory.[21] [d] Keck et al.[29] [e] Daiber and Williams.[30] [f] Antropov et al.[31] [g] Flink and Welge.[32]

TABLE 5: Oscillator Strengths (in Units of 100) for the (v', $v'' = 0$) Vibronic Transitions Belonging to the $\gamma(3s\sigma(A^2\Sigma^+) \leftarrow X^2\Pi)$ Band of NO

v'	MQDO[a]	expt[b]	expt[c]	expt[d]	expt[e]	expt[f]	expt[g]	MRCI[h]	MRCI[i]
0	0.0383	0.039	0.0420	0.0404	0.0399	0.041	0.0364	0.0377	0.104
1	0.0804	0.082	0.0824	0.0829	0.0788	0.088		0.0731	0.247
2	0.0747	0.081	0.0730	0.0750	0.0673	0.067		0.0620	
3	0.0406		0.0356		0.0360				
4	0.0144								
5	0.00348								

[a] MQDO, this work. [b] Piper and Cowles.[34] [c] Chan et al.[33] [d] Mohlmann et al.[35] [e] Bethke.[28] [f] Weber and Penner.[36] [g] Phery-Thorne and Banfield.[37] [h] Langhoff et al.[39] [i] de Vivie and Peyerimhof.[38]

TABLE 6: Oscillator Strengths (in Units of 100) for the (v', $v'' = 0$) Vibronic Transitions Belonging to the $\delta(3p\pi(C^2\Pi) \leftarrow X^2\Pi)$ Band of NO

v'	MQDO[a]	expt[b]	expt[c]	theor[d]	theor[e]	MRCI[f]
0	0.262	0.229	0.214	0.220	0.223	0.249
1	0.570	0.601	0.578	0.610	0.545	0.481
2	0.551	0.308	0.274	0.259	0.529	0.456

[a] MQDO, this work. [b] Chan et al.[33] [c] Bethke.[28] [d] Galluser and Dressler[40] perturbed. [e] Galluser and Dressler[40] unperturbed. [f] de Vivie and Peyerimhoff.[38]

TABLE 7: Oscillator Strengths (in Units of 100) for the (v', $v'' = 0$) Vibronic Transitions Belonging to the $\epsilon(3p\sigma(D^2\Sigma^+) \leftarrow X^2\Pi)$ Band of NO

v'	MQDO[a]	expt[b]	expt[c]	expt[d]	MRCI[e]
0	0.200	0.263	0.19	0.242	0.196
1	0.441	0.461	0.40	0.460	0.245
2	0.400	0.367		0.332	
3	0.191	0.179			
4	0.0508				
5	0.00731				

[a] MQDO, this work. [b] Chan et al.[33] [c] Hesser.[41] [d] Bethke.[28] [e] de Vivie and Peyerimhoff.[38]

dure with a diabatic basis, in which coupling was performed with a vibronic interaction matrix. Nonperturbed and perturbed electronic state calculations were done. The resulting oscillator strengths are included in Table 6. It is apparent that when the perturbations were taken care of, by adjusting the transition moments, taking the photoabsorption data reported by Bethke[28] as a reference, the *f*-values obtained by these authors[40] (column d of Table 6) conform rather well with the experimental data, in particular with the *f*-value measured by Bethke.[28] We have not continued our calculations to higher v' levels transitions because they also seem to be subject to perturbations.[25]

The present and comparative data for the (v', $v'' = 0$) transitions belonging to the ϵ band are shown in Table 7, where a good accord of the presently calculated oscillator strengths and the experimental values[28,33,41] is observed. It is apparent that the MQDO *f*-value for the transition to the level with $v' = 1$ is in much better agreement to the measurements than the MRCI value reported by de Vivie and Peyerimhoff.[38]

In Tables 8−10 the oscillator strengths for ($v' = 0$, $v'' \geq 1$) transitions corresponding to the γ, δ, and ϵ bands, respectively, are given. The MQDO results for the γ band (Table 8) appear to be in good agreement with the more recent experimental data we have found in the literature, those reported by Piper and Cowles[34] (where branching rations are obtained from relative emission intensities) but are of a lower magnitude than the observations by Pery-Thorne and Banfield[37] with the hook technique. Our *f*-values also compare fairly well with those obtained with MRCI calculations by Langhoff et al.,[39] even though the latter are slightly higher in magnitude. The MRCI data by de Vivie and Peyerimhoff[38] appear to be of a much higher magnitude than the rest of the results. We have not found any experimental data of oscillator strengths in the literature for the δ band (Table 9). The MRCI theoretical values[38] are also included in Table 9.

TABLE 8: Oscillator strengths (in Units of 100) for the ($v' = 0$, $v'' \geq 1$) Vibronic Transitions Belonging to the $\gamma(3s\sigma(A^2\Sigma^+) \leftarrow X^2\Pi)$ Band of NO

v''	MQDO[a]	expt[b]	expt[c]	MRCI[d]	MRCI[e]
1	0.0584	0.0577	0.072	0.0620	0.198
2	0.0502	0.0516	0.078	0.0576	0.206
3	0.0322	0.0360	0.057	0.0402	0.164
4	0.0172	0.0216	0.03	0.0235	0.105
5	0.00817	0.0118	0.014	0.0122	0.0619

[a] MQDO, this work. [b] Piper and Cowles.[34] [c] Pery-Thorne and Banfield.[37] [d] Langhoff et al.[39] [e] de Vivie and Peyerimhoff.[38]

TABLE 9: Oscillator Strengths (in Units of 100) for the ($v' = 0$, $v'' \geq 1$) Vibronic Transitions Belonging to the $\delta(3p\pi(C^2\Pi) \leftarrow X^2\Pi)$ Band of NO

v''	MQDO[a]	MRCI[b]
1	0.419	0.568
2	0.377	0.636
3	0.253	0.463
4	0.141	0.251
5	0.0692	0.119

[a] MQDO, this work. [b] de Vivie and Peyerimhoff.[38]

TABLE 10: Oscillator Strengths (in Units of 100) for the ($v' = 0$, $v'' \geq 1$) Vibronic Transitions of the $\epsilon(3p\sigma(D^2\Sigma^+) \leftarrow X^2\Pi)$ Band of NO

v''	MQDO[a]	expt[b]	MRCI[c]
1	0.300	0.28	0.254
2	0.261	0.25	0.181
3	0.172	0.16	0.090
4	0.0956	0.09	0.022
5	0.0473	0.05	

[a] MQDO, this work. [b] Hesser.[41] [c] de Vivie and Peyerimhoff.[38]

A general good accord between the MQDO oscillator strengths for the ϵ band ($v' = 0$, $v'' \geq 1$) transitions dealt with and the experimental values by Hesser[41] is found by inspection of Table 10. The available MRCI theoretical values[38] are also slightly lower in magnitude, particularly for the transitions originated in the levels with $v'' = 2-4$.

IV. Concluding Remarks

Absorption oscillator strengths for electronic and vibronic transitions of the γ, δ, and ϵ bands of NO, which involve Rydberg states, have been calculated with the MQDO method. This procedure has been applied to the study of vibronic transitions for the first time. Our results conform rather well with most of the experimental data available to our knowledge. Our next objective is the photoionization spectrum of this molecule.

The MQDO method has proved, once more, to be a very useful tool to estimate transition intensities (given here in the form of oscillator strengths). The high ratio between the quality of results and computational effort of this procedure is undoubtedly linked to its analyticity.

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