Quantum wave packet dynamics of the $1^3A''$ N(4$S$)+NO($\tilde{X}^2\Pi$) 
$\rightarrow$N$_2$($\tilde{X}^1\Sigma_g^+$)+O(3$P$) reaction

Pablo Gamallo, Miguel González, a) and R. Sayós
Department de Química Física i Centre de Recerca en Química Teòrica, Universitat de Barcelona,
C/Marti i Franquès 1, 08028 Barcelona, Spain

Carlo Petrongolo b)
Dipartimento di Chimica, Universita' di Siena, Via A. Moro 2, 53100 Siena, Italy

(Received 23 May 2003; accepted 16 July 2003)

We present the quantum dynamics of the title reaction using the Gray–Balint–Kurti wave-packet (WP) method, several NO vibro-rotational levels, product coordinates, and an asymptotic analysis. We calculate accurate reaction probabilities at $J=0$, estimate those at $J>0$ via a capture model, and discuss the reaction mechanism analyzing the WP time evolution. We also obtain cross sections and rate constants. The potential is barrier-less and thus both probabilities and cross sections do not have a collision-energy ($E_{\text{col}}$) threshold. The probabilities present many sharp resonances, due to the $E_{\text{col}}$ redistribution on the NNO-internal and N$_2$-product degrees of freedom. The reaction is stereo-specific and occurs via a bent abstraction mechanism. The cross sections decrease with $E_{\text{col}}$, in agreement with the expected behavior for threshold-less reactions. The present values of the rate constant support previous and less accurate calculations, and are in excellent agreement with laboratory experimental data. This confirms the accuracy of the present $1^3A''$ PES. © 2003 American Institute of Physics. [DOI: 10.1063/1.1606672]
sions with damped Chebyshev recursions, and it is an extension to scattering processes of the work by Chen and Guo.

Using reactant or product coordinates, reaction probabilities are obtained via asymptotic or flux analysis. In this study, the initial WP is defined in reactant Jacobi coordinates \( R, r, \) and \( \gamma \) and is then transformed to the product ones \( R', r', \) and \( \gamma' \) for the subsequent time-propagation and asymptotic analysis. We thus take into account the \( ^{14}\text{N}_2 \) permutation and nuclear-spin symmetries, which require that \( ^{14}\text{N}_2 (\Sigma_g^+, \nu, j') \) vibro-rotational states with \( j' = \text{even} \) or \( \text{odd} \) have nuclear statistical weights equal to \( 2/3 \) or \( 1/3 \), respectively. Reaction probabilities resolved on the vibro-rotational reactant state \((v,j)\) at total angular momentum quantum number \( J \) and \( E_{\text{col}} \) are thus equal to

\[
P_{v'j'}(E_{\text{col}}) = \sum_{v} \left\{ \frac{2}{3} \sum_{j'' = ev} \epsilon_p p_{v'j''; vj}(E_{\text{col}}) \right. \\
+ \left. \frac{1}{3} \sum_{j'' = od} \epsilon_p p_{v'j''; vj}(E_{\text{col}}) \right\},
\]

where \( ev \) and \( od \) are even and odd \( j' \) quanta, respectively, and \( p_{v'j''; vj}(E_{\text{col}}) \) are state-to-state probabilities.

Accurate probabilities at \( J = 0 \) are calculated for \( v = 0 \) and \( 1, j = 0 \) to 10 \( (2) \), and \( E_{\text{col}} \approx 1 \) eV with the parameters of Table I. A propagation converges the probability in 40,000 steps, requiring \( \sim 2.14 \) CPU days on a Compaq Alpha DS20E/667 work station. On the other hand, probabilities at \( J > 0 \) are estimated via a capture model (CM) following an idea by Gray et al.\(^{27} \) The collision involves indeed three heavy nuclei, and both exact and centrifugal-sudden calculations at \( J > 0 \) are very CPU-time demanding. Because the reaction occurs without potential barrier and the PES is attractive, the present CM assumes that the early dynamics, before product formation, is dominated by the effective potentials

\[
V_{J\gamma}^{\prime\prime}(R) = \min_{r, \gamma} V(R, r, \gamma) + [J(J+1) + j(j+1) - 2K^2]/2\mu_R R^2, \quad r \leq 2.31 a_0.
\]

Here \( V(R, r, \gamma) \) is the PES, \( \gamma \) is the projection of \( J \) along \( R \), \( \mu_R \) is the reduced mass associated with \( R \), and the upper limit on \( r \) avoids the opening of the \( N_2 + O \) product channel. The second term in the rhs member of Eq. (2) is the centrifugal potential, and these effective potentials present centrifugal barriers that depend on the three quantum numbers. We, therefore, estimate \( J > 0 \) probabilities as

\[
P_{v'j'}(E_{\text{col}}) \approx P_{v'j'}^0(E_{\text{col}} - E_{J\gamma}),
\]

where the energy shifts \( E_{J\gamma} \) are equal to

\[
E_{J\gamma} = \max_R V_{J\gamma}^{\prime\prime}(R) - \max_{\gamma} V_{J\gamma}^0(R).
\]

In Eq. (2) we minimize the PES with respect to \( r \) and \( \gamma \), and for \( N + NO \) this is a better choice than Eq. (13) of Ref. 27, because the corresponding \( V_{J\gamma}^{\prime\prime}(R) \) present only shoulders as functions of \( J \) and \( K \). As an example, Fig. 2 shows two effective potentials for \( j = 8, J = 0 \) or 50, and \( K = 0 \) or 4, respectively. We clearly see the centrifugal barriers at \( R = 5.11 a_0 \), giving \( E_{5A} = 0.075 \) eV, and the minima at \( -0.758 \) and \( -0.565 \) eV and at \( R = 3.20 a_0 \).

Initial-state-resolved cross sections \( \sigma_{v'j'}(E_{\text{col}}) \) are obtained via the usual partial wave sums, and rate constants \( k_{v'j'}(T) \) and \( k(T) \) are calculated as Boltzmann averages in the 100–2000 K range. The thermal rate constant \( k \) is obtained by estimating the rates \( k_{v'j'} \) for odd \( j \approx 9 \) with linear interpolations and those for \( j \approx 10 \) via extrapolations, and including both spin–orbit (SO) \( ^2\Pi_{1/2} \) and \( ^2\Pi_{3/2} \) NO states with their energy difference \( \Delta R = 119.82 \) cm\(^{-1} \). Assuming that \( ^2\Pi_{1/2} \) correlates with the PES, the electronic population is thus equal to

\[
p^{\prime\prime}(T) = \frac{3}{4[2 + 2 \exp(-\Delta k_B T)]},
\]

where \( 3 \) and \( 4 \) are the degeneracies of \( NNO(^1A^\prime) \) and \( N(^3S) \), respectively, and the second term of the denominator is the NO electronic partition function. Note that \( p^{\prime\prime}(T) \) decreases with \( T \) from 3/8 to 3/16.
III. REACTION PROBABILITIES AND MECHANISM

Figure 3 shows three examples of reaction probabilities at $J = 0$, corresponding to $(v, j) = (0, 0)$, $(0, 8)$, and $(1, 0)$. Note that the $(0, 8)$ vibro-rotational level of NO is that most populated at room $T$ among those here considered, and that the $j'$ even and odd sums of Eq. (1) are nearly equal. The use of this equation is, therefore, not necessary in the present reaction.

The $1^3A''$ PES is without a reaction barrier, and thus the probabilities do not present an energy threshold and their average values increase from very low $E_{col}$ up to 1 eV. The probabilities are dominated by strong Feshbach resonances over the full energy range, i.e., the collision energy is transformed into internal energy owing to the minima of the effective potentials or the large reaction exoergicity. The role of the effective potentials should be more important at low $E_{col}$, when the centrifugal minima can trap part of the WP giving rise to quasi-bound NNO states and to a collision-to-internal energy redistribution. Because the sharpest resonance is that of $P_{0,8}$ at $E_{col} = 0.015$ eV, with a full width at half maximum of $\sim 69$ cm$^{-1}$, the lifetimes of these collision complexes should be as large as $\sim 77$ fs.

At higher collision energy, these resonances are probably due to the opening and closing of several $N_2$ vibro-rotational product channels, owing to the flow of the collision energy of the approaching N atom into these $N_2$ modes.

Note also that the NO rotational excitation enhances the reaction probabilities, mainly at low collision energy, whereas the NO vibrational excitation has a little effect on the reactivity. As in Refs. 27 and 31, we explain these $(v, j)$ effects analyzing the effective interaction-centrifugal potentials

$$V^\text{int-cent}_{vj}(R) = \langle \phi^\text{NO}_{vj}(r)L_j(\gamma) \rangle |V(R, r, \gamma) - V^\text{NO}(r)| \phi^\text{NO}_{vj}(r)L_j(\gamma)\rangle, \gamma + j(j + 1)/2\mu R^2,$$

where $\phi^\text{NO}_{vj}$ and $L_j$ are NO states and normalized Legendre polynomials, respectively. The barriers of these potentials are in general lower increasing the NO $j$ quanta, showing that this probability enhancement is due to a lower effective interaction potential [first term of the rhs member of Eq. (6)] in spite of the increase of the second centrifugal term. There-
fore, stereo-specific effects due to proper alignment of the N atoms along the MEP, and inferred from Fig. 1, overcome the larger centrifugal barrier.

As for N\textsubscript{1}O\textsubscript{2}, expectation values of the reactant co-ordinates \( \langle R \rangle, \langle r \rangle, \) and \( \langle \gamma \rangle \), and snapshots of the WP at various times give qualitative insights into the reaction mechanism. We thus plot in Fig. 4 the radial trajectory and in Fig. 5 the \( \gamma \)-averaged probability density for \( (v,j)=(0,8) \) at 0, 130, 285, and 605 fs. These results are superimposed on the plot of the PES at \( \gamma=50^\circ \) whose deep hole corresponds to a part of the N\textsubscript{2}+O product channel. In the first \( \sim 100 \) fs, the WP moves in a narrow N+NO reactant channel, reaching the interaction region with \( \langle r \rangle \) nearly unperturbed. This confirms the role of the mutual orientation of the reactants we mentioned by discussing Fig. 1 and Eq. (6). Between \( \sim 130 \) and \( \sim 285 \) fs, the repulsive wall of the PES reflects back part of the WP towards the reactant channel, and both \( \langle R \rangle \) and \( \langle r \rangle \) increase. At larger times, part of the WP eventually enters the N\textsubscript{2}+O product channel and spreads on a wide \( (R,r) \) space, whereas \( \langle r'(N_2) \rangle \) decreases. On the overall, the WP density is negligible at \( R\approx0 \), and \( \langle \gamma \rangle \) decreases from 90\(^\circ\) at 0 fs up to \( \sim60^\circ \) at the end of the reaction. This is a quantum description of a bent abstraction mechanism, which can be contrasted with the H\textsubscript{2}+O(\(^1\)D) insertion reaction.\textsuperscript{33}

It is useful to contrast this reaction with that similar between N and O\textsubscript{2},\textsuperscript{31} which was investigated with the same method here employed, has \( \tilde{X}^2A' \) and \( \tilde{a}^4A' \) reaction barriers of 0.30 and 0.65 eV, and is exoergic by 1.41 eV. Owing to the potential barriers, the N\textsubscript{1}O\textsubscript{2} probabilities have collision energy thresholds that depend on the initial \( (v,j) \) level of O\textsubscript{2} and decrease in general at high \( j \), and the probability resonances are less sharp than the present ones, owing to the smaller exoergicity.

**IV. CROSS SECTIONS AND RATE CONSTANTS**

Figure 6 shows that the cross sections for \( (v,j) = (0,0), (0,8), \) and \( (1,0) \) decrease as the collision energy increases from \( \sim 0.015 \) to \( \sim 0.20-0.40 \) eV, depending on the initial NO rotational level. This is consistent\textsuperscript{29} with a barrierless reaction and with a long-range potential \( V(R) \approx -C_1/R^2 \) that dominates the dynamics at low \( E_{\text{col}} \). For example, a linear fit to \( \log(\sigma_{0,8}/\text{Å}^2) \) for \( 0.015<E_{\text{col}} <0.40 \) eV, gives

![FIG. 5. \( \gamma \)-averaged WP density for \( v=0 \) and \( j=8 \). See the Fig. 4 caption for further details.](image-url)
log $\sigma_{0,0}(E_{\text{col}}) = (0.82 \pm 0.01) - (0.30 \pm 0.01) \log E_{\text{col}},$ \hspace{1cm} (7)

with standard deviation equal to 0.03. From this equation and from Eq. (2.58) of Ref. 29, we estimate that $s \approx 6.67,$ and $C_s = 1.58 \text{ eV} \times \text{Å}^{6.67}.$

Increasing the collision energy, the cross sections become nearly constant because more N$_2$ + O product channels are now opened. At low $E_{\text{col}}$ and $j,$ some cross-section resonances survive the partial wave sum, with $\sigma_{0,0} < \sigma_{0,8}$ and $\sigma_{0,0} \approx \sigma_{1,0},$ in agreement with the probability results.

The WP initial-state-resolved cross sections are rather similar to the $^3A''$ one of Ref. 9. However, the agreement is quite fortuitous because $\sigma$ of Ref. 9 was obtained via a semi-empirical PES, using a QCT method and a Boltzmann distribution at 500 K of the NO vibro-rotational states. Unlike the N+NO results, the N+O$_2$ cross sections$^{31}$ are zero up to a threshold energy and increase with $E_{\text{col}},$ like the reaction probabilities and owing to the potential barriers.

Figure 7 shows initial-state-resolved rate constants $k_{v,j}(T)$ at 300 and 2000 K as functions of the NO $(v,j)$ quanta. They oscillate somewhat with $j,$ with a minimum at $j = 2,$ are rather constant at high $j,$ save $k_{1,j}(300)$ that decreases, and are reduced by $v,$ mainly at 300 K and high $j.$ Moreover, these rates increase moderately with $T$ (up to about two times for $k_{1,10}$), because in their expression$^{29}$ the decrease of $\sigma$ with $E_{\text{col}}$ reduces the enhancement of the Boltzmann factor with $T.$ This behavior is due to the absence of any potential barrier and reaction threshold, and is very different from that of N+O$_2.$$^{31}$ Owing to the $X^2A'$ and $A^2A'$ potential barriers of the latter reaction, its $k_{v,j}(T)$ are indeed orders of magnitude smaller and are very sensitive to the O$_2(v,j)$ level at room $T$ and to the temperature.

Table II and Fig. 8 contrast the calculated WP and ICVT/µ OMT-SO$^2$ thermal rate constants $k(T)$ with the experimental recommended$^{14,15}$ and laboratory$^{10,12}$ values between 100 and 2000 K. The reviews of Refs. 14 and 15 are based on other laboratory data.$^{11,13}$ The experimental rates are given as upper and lower bounds in Table II and as analytical fits of the data in Fig. 8. WP rates in cm$^{-3}$s$^{-1}$ were also calculated in this temperature range in steps of 100 K and best-fitted to the equation

$$k(T) = A T^x \exp(B/T),$$ \hspace{1cm} (8)

finding $A = (1.15 \pm 0.06) \times 10^{-11},$ \hspace{1cm} $x = 0.15 \pm 0.01,$ \hspace{1cm} and \hspace{1cm} $B = 79.97 \pm 3.99.$ Note the small value of $x$ and the negative value of the “activation” energy.

Because the reaction occurs without a collision energy threshold, $k$ varies very few with $T,$ even less than the initial-state-resolved $k_{v,j}$ do, decreasing by $\sim 16\%$ from 100 up to 600 K, and then increasing by only $\sim 9\%$ up to 2000 K. The behavior up to 600 K is due to the decrease of the electronic population $\rho_x$ of Eq. (5), because omitting this term the rate increases in the full $T$ range, from $13.04 \times 10^{-11}$ cm$^3$s$^{-1}$ at 100 K to $19.48 \times 10^{-11}$ cm$^3$s$^{-1}$ at 2000 K. The subsequent change of slope at higher $T$ reflects the moderate increase of $k_{v,j}$ shown in Fig. 7. The low and high $T$ behaviors of the rate constant are described by the exponential and $T^x$ terms of Eq. (8), respectively.

We see that the WP and ICVT/µ OMT-SO$^2$ rates are in qualitative agreement in the full temperature range, although they are somewhat quantitatively different. Indeed, for $T \leq 300$ K the statistical rate seems too large, and the opposite holds above 600 K where it changes slope at $\sim 1000$ K. Note
that the weight of the excited $1 \, ^3A'$ PES to the thermal rate constant is negligible up to 2000 K, where it is maximal and equal to 7%.\textsuperscript{2} The WP rates confirm those QCT calculated in Ref. 6 up to 1000 K, when Eq. (5) is employed,\textsuperscript{2} although the PESs and the theoretical treatments are quite different as we mentioned above.

Like previous and less accurate calculations,\textsuperscript{2,6} the WP rate is in excellent agreement with laboratory\textsuperscript{11–13} and recommended\textsuperscript{14,15} values, in particular with the constant value of Ref. 12. Note also that the theoretical error bounds of Eq. (8) are lower than the experimental ones. On the other hand, both the present results and those of Refs. 2, 6, 11–15 do not support the oldest experimental value.\textsuperscript{10} As in Refs. 2 and 6, the WP rate is different from those inferred in models of planetary atmospheres,\textsuperscript{16,17} so that these models are incorrect and/or the planetary populations of the reactants are different from the laboratory thermal one.\textsuperscript{6} The comparison with the N+O$_2$ $k(T)$\textsuperscript{15} confirms the very different behavior of the initial-state-resolved rates of these two reactions. In conclusion, these WP results point out the accuracy of the present $1 \, ^3A''$ PES.

### ACKNOWLEDGMENTS

We thank Dr. S. K. Gray and P. Defazio for many discussions, suggestions, and assistance. P.G. thanks the Universities of Barcelona and Siena for pre-doctoral research grants. This work was supported by the Spanish Ministry of Science and Technology (Projects BQU2002-03351 and BQU2002-04269-C02-02), by MIUR, University of Siena, and IPCF-CNR of Pisa, Italy.

\begin{table}[h]
\centering
\caption{Theoretical WP and VTST rate constants $k \times 10^{11}$ in cm$^3$ s$^{-1}$, versus experimental recommended and laboratory upper and lower bounds.}
\begin{tabular}{cccccc}
\hline
T/K & WP & VTST & Recomm.$^a$ & Recomm.$^b$ & Lab.$^c$ & Lab.$^d$
\hline
100 & 4.15 & & & & & \\
200 & 3.87 & 6.52 & 2.3–5.4 & & 2.4–4.6 & \\
300 & 3.65 & 4.68 & 2.2–3.8 & & 1.2–3.7 & \\
400 & 3.54 & 3.79 & 1.9–3.8 & & 1.8–4.6 & \\
600 & 3.49 & 3.20 & & & 2.8–5.9 & \\
1000 & 3.61 & 3.05 & & & & \\
1500 & 3.77 & 3.11 & & 2.7–6.7 & & \\
2000 & 3.81 & 3.29 & & 3.0–7.6 & & \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Reference 2, ICVT/$\mu$ OMT-SO, including both $1 \, ^3A'$ and $1 \, ^3A''$ PESs.

\textsuperscript{b}Reference 15.

\textsuperscript{c}Reference 14.

\textsuperscript{d}Reference 12. The rate is constant in the full temperature range.

\textsuperscript{e}Reference 10.

FIG. 8. Thermal rate constants. Calculated: WP (full line) and ICVT/$\mu$ OMT-SO (dashed line with ref. number) with full circles. Experimental: Dotted lines with ref. numbers and open circles. Reference 12 with the error bar. See Table II for other experimental error bars.
26 G. Herzberg, *Molecular Spectra and Molecular Structure* (Krieger, Mala-
29 R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and 
30 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure 