Time-dependent quantum dynamics calculations of product photofragment cross-sections

Mohammad Noh Daud
Department of Chemistry, University of Malaya
Kuala Lumpur 50603, Malaysia
mnoh@um.edu.my
www.um.edu.my

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A time-dependent quantum dynamics theory has been presented to interpret product partial cross-sections of the photofragmentation of triatomic molecule by treating correctly the coupling of angular momenta and taking fully into account the vector properties of the transition dipole moment and electric field of the exciting radiation. A model system of \(\text{N}_2\text{O}(X^1\Sigma^+) + h\nu \rightarrow \text{N}_2(X^1\Sigma^+) + \text{O}(^1\text{D})\) has been used to study the nuclear motion of N\(_2\) photofragments through the asymptotic dissociation channels which relies upon the transition dipole vector either lies parallel on the molecular plane \((^1\text{A}'\rightarrow ^1\text{A}')\) or perpendicular to the molecular plane \((^1\text{A}'\rightarrow ^1\text{A}^0)\).

Keywords: Quantum dynamics; cross-section; angular momentum; photofragmentation.

1. Introduction

We employed a time-dependent quantum dynamics method to interpret the absorption spectrum of product fragments in terms of its motion on the upper potential surface. The method relies on numerical solution of the time-dependent Schrödinger equation, involving only matrix vector multiplications and avoiding diagonalization of large matrices which are often required in the time-independent computations.\(^1\) Although time-dependent approaches involve an additional dimension (i.e. time) they have a great compensating advantage of immediately yielding the energy dependence of cross-sections and other physical observables.\(^1\)–\(^8\)

Nitrous oxide (N\(_2\)O) like all triatomic molecules with 16 valence electrons, is linear in its ground state and bent in its first, second and third excited states. In linear \(C_{\text{vir}}\) geometry it has electronic configuration \((1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4\) and in bent \(C_s\) geometry it has \((1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^2(7a'')^2(8a'')^2(2a''')^2(9a'')^2\). Singlet channel is the main dissociation pathway in
the first ultraviolet absorption band of N$_2$O, described by

$$\text{N}_2\text{O}(X^1\Sigma^+, v, J) + h\nu \rightarrow \text{N}_2\text{O}(1^1\Sigma^-(1^1A'')) + 1\Delta(2^1A', v', J')$$

$$\rightarrow \text{N}_2(X^1\Sigma^+_g, v'', j) + \text{O}(1^1\text{D}).$$

(1)

N$_2$O actively absorbs infrared radiation in the atmosphere and thereby contributes to greenhouse warming. Due to the importance of the electronically excited oxygen atom O(1D) in regulating the ozone layer and also due to its vast application in the kinetic and dynamics experiments, its photofragmentation processes have been the focus of several experimental investigations.$^{9-14}$ We studied in particular the effect of initial rovibrational state of N$_2$O on the N$_2$ partial cross-section. This study will demonstrate the close relation between the details topology of the potential energy and transition dipole moment surfaces ($2^1A'$ and $1^1A''$) on one hand and quantitatively different final product cross-sections on the other hand.

2. Theory

2.1. Hamiltonian operator

Using the standard Jacobi coordinates ($R, r, \theta$) in the body-fixed (rotating) frame, the nuclear Born–Oppenheimer Hamiltonian operator for a triatomic molecule can be expressed as$^{15,16}$

$$\hat{H} = -\left\{ \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_e} \frac{\partial^2}{\partial r^2} \right\} - \left( \frac{\hbar^2}{2\mu R^2} + \frac{\hbar^2}{2\mu_e r^2} \right) \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{K^2}{\sin^2 \theta} \right\}$$

$$+ V(R, r, \theta) + \left( \frac{\hbar^2}{2\mu R^2} \right) (J(J + 1) - 2K^2) - \frac{\hbar^2 C_{J,K}^{\pm}}{2\mu R^2} \left\{ -\frac{\partial}{\partial \theta} - K \cot \theta \right\},$$

(2)

where

$$C_{J,K}^{\pm} = [J(J + 1) - K(K \pm 1)]^{1/2},$$

$\mu = m_N m_O / m_{N_O}$, $\mu_e = m_e^2 / m_N$, $J$ is the total angular momentum quantum number, $K$ is the quantum number for the projection of $J$ on the body-fixed $z$-axis, and $V$ is the potential energy of electron–electron and electron–nucleus interactions.

2.2. Basis expansion

A wave function corresponding to a particular $J$ and its space-fixed $Z$ component can be expressed in terms of body-fixed coordinates in the following form$^{17,18}$

$$\psi_J^M(R, r, \theta, \omega) = \sum_{K=-J}^{J} \varphi_K^J(R, r, \theta) \sqrt{\frac{2J + 1}{8\pi^2}} D_{K,M}^J(\omega).$$

(3)
where $M$ is the quantum number for the projection of $J$ on the space-fixed $Z$-axis, $D_{K,M}^J$ is the rotation matrix of Wigner $D$-function, $\omega \equiv \alpha, \beta, \gamma$ are the Euler angles, defining the orientation of the body-fixed axes $(x, y, z)$ with respect to the space-fixed (non-rotating) axes $(X, Y, Z)$.

In addition to $J$ and $M$, there is a further good quantum number corresponding to the parity $p$ of the wave function which describes the property of the system under inversion of all the space-fixed coordinates. Furthermore, in Eq. (3) the $K$ and $-K$ terms together can be grouped to define a parity-adapted body-fixed angular momentum wave function,

$$F_{K,M}^{J,p}(\omega) = \sqrt{\frac{2J + 1}{8\pi^2}} \frac{1}{\sqrt{21}} \left[ D_{K,M}^J(\omega) - (-1)^{J+K+p} D_{-K,M}^J(\omega) \right], \quad (4)$$

where $p = 1$ corresponds to state of odd parity and $p = 2$ corresponds to state of even parity.

In general case, the eigenfunctions of the angular kinetic energy operator (in the second term in Eq. (2)) are known to be the normalized associated Legendre polynomials $P_j^K(\theta)$. Light et al. have discussed the grid representation based upon a Gauss–Legendre scheme, and this technique is used for the angular variable in the present work. By using the parity-adapted basis functions $F_{K,M}^{J,p}$, we can explicitly rewrite the total wave function in Eq. (3) which is simultaneously an eigenfunction of the parity operator to be

$$\psi_M^{J,p}(R, r, \theta, \omega) = \sum_{K=\lambda}^{J} \sum_{j=K}^{j_{\text{max}}} \varphi_K^{J,p}(R, r) \Theta_{j,K}(\theta) F_{K,M}^{J,p}(\omega), \quad (5)$$

where $\lambda$ is defined as

$$\lambda = \frac{1 - (-1)^{J+p}}{2} \quad (6)$$

and if an $N_\alpha$ Gauss–Legendre quadrature scheme is used, then the maximum value of $j$ in the associated basis representation is $j_{\text{max}} = (N_\alpha - 1)$.

### 2.3. Partial cross-section

Our method of extracting the partial cross-sections from the wave packet dynamics requires us to analyze the wave packet as it passes a plane in the asymptotic region. The partial cross-section is obtained from

$$\sigma_j(J', K, E) = \frac{4\pi^3 \nu k_j}{3\varepsilon_0\mu_r} |A_{J,K}(R_\infty, E)|^2, \quad (7)$$

where $J'$ is the final total angular momentum quantum number, $K$ is the quantum number which relates to the component of $j$ along the body-fixed $z$-axis, $R_\infty$ is
located in the asymptotic region of the potential, and \( k_j \) is the wave vector given by

\[
k_j = \frac{[2\mu_r(E - E_f)]^{1/2}}{\hbar},
\]

where \( E_f \) is the final energy.

The analysis of the wave packet as it passes the analysis plane yields the time-dependent coefficients \( C \),

\[
\phi_{j,K}(R_\infty, r, \theta, t) = \sum_j C_{j,K}(R_\infty, t)\Theta_{j,K}(\theta)\chi_j(r),
\]

where \( \chi_j(r) \) are the vibrational wave functions and the rotational wave functions are normalized associated Legendre polynomials \( \Theta_{j,K}(\theta) \).

The function \( A_{j,K}^{J_p} \) for the production of a particular diatomic rotational state at any energy can be calculated from a half Fourier transform of the coefficients\(^{16}\)

\[
A_{j,K}^{J_p}(R_\infty, E) = \frac{1}{2\pi} \int_0^\infty \exp\left(\frac{iEt}{\hbar}\right) C_{j,K}^{J_p}(R_\infty, t)dt.
\]

In fact, the heart of Eq. (7) relies on the time-dependent coefficient \( C_{j,K}^{J_p} \). The coefficients will be formulated in the following section based on the manner of the transition dipole moments oriented with respect to molecular plane.

2.4. Time-dependent coefficient

We begin by writing the explicit form of the initial wave packet on the excited state potential as

\[
\phi(R, r, \theta, \omega, t = 0) = \mathbf{d} \cdot \mathbf{\epsilon} \psi_{M}^{J_p}(R, r, \theta, \omega),
\]

where \( \mathbf{d} \) is the transition dipole moment vector in space-fixed frame, connecting the initial ground state and the final excited state potentials and \( \mathbf{\epsilon} \) is the polarization vector of the electric field of the light. Using relation\(^{17,18}\)

\[
d_m = d_{-1}D_{-1,m}^{1}(\omega) + d_0D_{0,m}^{1}(\omega) + d_1D_{1,m}^{1}(\omega),
\]

where \( D_{0,m}^{1}(\omega) \) is a Wigner rotation matrix element, \( d_m \) and \( d_q \) are the components of the transition dipole moment in the space-fixed and body-fixed frames, respectively. \( d_q \) are related to the Cartesian components of the transition dipole by

\[
d_0 = d_z, \quad d_{\pm 1} = \mp \frac{1}{\sqrt{2}} (d_x \mp id_y).
\]

Substituting Eq. (12) into Eq. (11) and employing the following Clebsch–Gordan series\(^{17,18}\)

\[
D_{0,m}^{1}(\omega)D_{\pm K,M}^{J_p}(\omega) = \sum_{J = J_{-1}}^{J+1} C_{1,m; J, M}^{J_p,m+M}C_{1,\pm K, J, \pm K}^{J_p} \ D_{\mp K,m+M}^{J_p}(\omega),
\]

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where $C^{J',m+M}_{1,m;J,M}$ and $C^{J',m+K}_{1,m;J,K}$ are Clebsch–Gordan coefficients,\textsuperscript{17,18} we obtain the body-fixed form of the initial wave function as

$$
\phi^{J',p}(R, r, \theta, \omega, t = 0) = \sum_{J'=J-1}^{J+1} C^{J',m+M}_{1,m;J,M} \times \sum_{K=\lambda} \sum_{j=K}^{J} \phi_{K}^J(r) \phi_{j,K,M}(\theta, \omega),
$$

(15)

where

$$
\phi_{J,K,M}^{J',p}(\theta, \omega) = \sqrt{\frac{2J+1}{8\pi^2}} \frac{\Theta_{J,K}(\theta)}{\sqrt{2(1 + \delta_{0,K})}} \{d_{-1}[D_{-1-K,m+M}(\omega)C^{J',-1-K}_{1,-1;J,K}]
$$

$$
+ (-1)^{J+K+p} D_{-1-K,m+M}(\omega)C^{J',-1-K}_{1,-1;J,K} + d_{0}[D_{0,K,m+M}(\omega)C^{J',K}_{1,0;J,K} + (-1)^{J+K+p}
$$

$$
\times D_{-1-K,m+M}(\omega)C^{J',-K}_{1,0;J,-K} + d_{1}[D_{1,K,m+M}(\omega)C^{J',1-K}_{1,1;J,K} + (-1)^{J+K+p} D_{1-K,m+M}(\omega)C^{J',1-K}_{1,1;J,-K}]\}. \quad (16)
$$

Equation (15) implies that the function $\phi^{J',p}$ contains the totally symmetric representation if either $J \geq 1$ and $J' = J$, $J \pm 1$, or, $J = 0$ and $J' = 1$. We thus obtain the general rotational selection rule for an electric dipole transition $\Delta J = 0, \pm 1$ where transition from $J = 0$ to $J' = 0$ is forbidden by symmetry and this rule is often attributed to the conservation of angular momentum, with a photon of light contributing one unit of angular momentum to the molecule. This later condition is clearly a very natural interpretation of the Clebsch–Gordan coefficients in Eq. (15). The coefficients vanishes unless it satisfies the triangle inequality $|1 - J| \leq J' \leq |1 + J|$.

The physical content of the function $\phi_{j,K,M}^{J',p}$ is that the function relies on the projection of the polarization vector of the light onto the plane of the molecule which lies in the body-fixed $xz$-plane for a parallel transition and onto the body-fixed $y$-axis for a perpendicular transition. For the parallel transition, the spherical basis in Eq. (13) becomes

$$
d_0 = d_z, \quad d_{+1} = \frac{1}{\sqrt{2}}d_x = -d_{-1},
$$

(17)

where $d_y = 0$. Using symmetry properties,\textsuperscript{17,18}

$$
C^{J',-K}_{1,0;J,-K} = (-1)^{1+J'+J} C^{J',K}_{1,0;J,K} \quad (18)
$$

and

$$
C^{J',-1-K}_{1,-1;J,-K} = (-1)^{1+J'+J} C^{J',1+K}_{1,1;J,K} \quad (19)
$$
and the spherical basis in Eq. (17), Eq. (16) can be simplified as

\[
\phi_{j,j,K,M}(\theta, \omega) = \sqrt{\frac{2J+1}{8\pi^2}} \frac{\Theta_{j,K}(\theta)}{\sqrt{2(1 + \delta_{0,K})}} \left\{ \frac{1}{\sqrt{2}} \right. \\
\left. d_x [D^J_{-1+K,m+M}(\omega)] C^{J,-1+K}_{1,1;J,K} \\
+ (-1)^{J+K+p} D^J_{-1-K,m+M}(\omega)(-1)^{1+J+J'} C^{J,1+K}_{1,1;J,K} \\
+ d_z [D^J_{K,m+M}(\omega)] C^{J,0;K}_{1,0;J,K} + (-1)^{J+K+p} \\
\times D^J_{1-K,m+M}(\omega)(-1)^{1+J+J'} C^{J,K}_{1,1;J,-K} \\
- \frac{1}{\sqrt{2}} d_z [D^J_{1+K,m+M}(\omega)] C^{J,1+K}_{1,1;J,K} + (-1)^{J+K+p} \\
\times D^J_{1-K,m+M}(\omega)] C^{J,-1-K}_{1,1;J,-K} \right\}.
\]

(20)

Rearranging Eq. (20), using relations of \((-1)^{-J'} = (-1)^J\)

and

\[\]

\[C^{J,-1+K}_{1,1;J,K} = (-1)^{1+J+J'} C^{J,1-K}_{1,1;J,-K}\]

as in Refs. 17 and 18, we obtain

\[
\phi_{j,j,K,M}(\theta, \omega) = \sqrt{\frac{2J+1}{8\pi^2}} \frac{\Theta_{j,K}(\theta)}{\sqrt{2(1 + \delta_{0,K})}} \left\{ -d_x [C^{J,1+K}_{1,1;J,K} D^J_{1+K,m+M}(\omega)] \\
+ (-1)^{J+(1+K)+p+1} D^J_{-(1+K),m+M}(\omega)) + (-1)^{J+J'} C^{J,1+K}_{1,1;J,-K} \\
\times (D^J_{K-1,m+M}(\omega) + (-1)^{J+(K-1)+p+1} D^J_{-(K-1),m+M}(\omega)) \\
+ d_z C^{J,K}_{1,0;J,K} \sqrt{2} (D^J_{K,m+M}(\omega) + (-1)^{J+K+p+1} D^J_{-K,m+M}(\omega)) \right\}.
\]

(22)

Using the parity-adapted body-fixed angular momentum wave function defined in Eq. (4), Eq. (22) may be simplified to

\[
\phi_{j,j,K,M}(\theta, \omega) = \sqrt{\frac{2J+1}{2J'+1}} \frac{\Theta_{j,K}(\theta)}{\sqrt{2(1 + \delta_{0,K})}} \left\{ -d_x [C^{J,1+K}_{1,1;J,K} F^J_{1+K,m+M}(\omega)] \\
+ (-1)^{J+J'} C^{J,1-K}_{1,1;J,-K} \sqrt{2} (1 + \delta_{0,K-1}) F^J_{K-1,m+M}(\omega)) \right\} \\
\times \{ -d_x [C^{J,1+K}_{1,1;J,K} F^J_{1+K,m+M}(\omega)] \\
+ (-1)^{J+J'} C^{J,1-K}_{1,1;J,-K} \sqrt{2} (1 + \delta_{0,K-1}) F^J_{K-1,m+M}(\omega)) \right\}.
\]

(23)

We can separate the \(K = 0\) term to obtain the following equation

\[
\phi_{j,j,K,M}(\theta, \omega) = \sqrt{\frac{2J+1}{2J'+1}} \frac{\Theta_{j,K}(\theta)}{\sqrt{2}} \left\{ -d_x [C^{J,1+K}_{1,1;J,K} F^J_{1+K,m+M}(\omega)(1 - \delta_{0,K}) \\
+ (-1)^{J+J'} C^{J,1-K}_{1,1;J,-K} \sqrt{2} (1 + \delta_{0,K-1}) F^J_{K-1,m+M}(\omega)) \right\}.
\]
transition as spherical basis in Eq. (28), we can write the function
\[
\phi_{j,0}(\omega) = \frac{\sqrt{2J + 1}}{2J + 1} \Theta_{j,K}(\theta) \left\{ \begin{array}{l}
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right] \\
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right]
\end{array} \right.
\]
Using the definition of \( \lambda \) in Eq. (6) namely
\[
(-1)^{J+p} = 1 \quad \text{if} \quad K = \lambda = 0
\]
and the symmetry relation of Wigner D-matrix
\[
D_{-1,m+m}^{J+1} = -D_{1,m+m}^{J+1}
\]
we obtain the final expression of the function \( \phi_{j,J,K}^{J+1} \) for the parallel transition as
\[
\phi_{j,K,M}^{J+1}(\theta, \omega) = \sqrt{2J + 1} \frac{\Theta_{j,K}(\theta)}{2J + 1} \left\{ \begin{array}{l}
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right] \\
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right]
\end{array} \right.
\]
If the transition dipole moment is perpendicular to the molecule plane, the spherical basis in Eq. (13) becomes
\[
d_0 = 0, \quad d_+ = \frac{1}{\sqrt{2}} i d_y = d_-
\]
where \( d_0 = d_+ = 0 \). Using the symmetry properties in Eqs. (18) and (19), and the spherical basis in Eq. (28), we can write the function \( \phi_{j,K}^{J,0} \) for the perpendicular transition as
\[
\phi_{j,K}^{J,0}(\theta, \omega) = \sqrt{2J + 1} \frac{\Theta_{j,K}(\theta)}{2J + 1} \left\{ \begin{array}{l}
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right] \\
+ \frac{1}{\sqrt{2}} \left[ d_z C_{1,1,J,0}^J F_{2J + 1,0,0}^{J+1}(\omega)(1 - \delta_{0,K}) \right]
\end{array} \right.
\]
Rearranging Eq. (29), we obtain

\[
\phi_{j,K,M}^{J,p} (\theta, \omega) = \sqrt{\frac{2J+1}{2^{J+1}}} \frac{i \Theta_{j,K}(\theta)}{\sqrt{2}} dy \{ C_{1,1,J,K}^{J,p} (D_{1,K,m+M}^J (\omega) \\
+ (-1)^{J+K+1} D_{-1,K,m+M}^J (\omega)) + (-1)^{J+1} C_{1,1,J,K}^{J,p} \\
\times (D_{K-1,m+M}^J (\omega) + (-1)^{J+1+K} D_{-1,K-1,m+M}^J (\omega)) \}. \\
\]

(30)

Using the same way of manipulation as for the parallel transition, we finally obtain the expression of the \( \phi_{j,K,M}^{J,p} \) function for the perpendicular transition as

\[
\phi_{j,K,M}^{J,p} (\theta, \omega) = \sqrt{\frac{2J+1}{2^{J}+1}} \frac{i \Theta_{j,K}(\theta)}{\sqrt{2}} dy \{ C_{1,1,J,K}^{J,p} F_{1,K,m+M}^J (\omega) (1 - \delta_{0,K}) \\
+ \sqrt{(1 + \delta_{0,-1+K})} (-1)^{J+1+K} C_{1,1,J,-K}^{J,p} F_{1,K-1,m+M}^J (\omega) (1 - \delta_{0,K}) \\
+ i \sqrt{\frac{2J+1}{2^{J}+1}} \Theta_{j,0}(\theta) dy C_{1,1,J,0}^{J,p} F_{1,0,m+M}^J (\omega) \delta_{0,K}. \\
\]

(31)

Using the orthonormal property of normalized associated Legendre polynomials, we rewrite Eq. (15) in a more compact form as

\[
\phi_{j,K,m}^{J,p} (R, r, \theta, \omega, t = 0) = \sum_{J=J-1}^{J+1} C_{1,1,m,J,M}^{J,p} \phi_{j,K,m}^J (R, r, \theta, \omega, t = 0), \\
\]

(32)

where

\[
\phi_{j,K,m}^J (R, r, \theta, \omega, t = 0) = \sum_{K=K-L}^{J} \sum_{J=J-k}^{J_k} \varphi_{K}^{J,p} (R, r) \delta_{j,J,K} \phi_{j,K,m}^{J,p} (\theta) F_{K,m+M}^{J,p} (\omega). \\
\]

(33)

In our current two-dimensional model, \( \varphi_{j} \) is kept constant. Rearranging Eq. (9), the time-dependent coefficient for the parallel transition located in the asymptotic region of the potential can be derived as

\[
C_{j,K}^{J,p}(R, r, t) = \int_0^\pi \Theta_{j,K}(\theta) \varphi(r) \left\{ \sum_{K=K-L}^{J} \sum_{J=J-k}^{J_k} \varphi_{K}^{J,p} (R, r) \phi_{j,J,K}^{J,p} (\theta) \right\} \sin \theta d\theta \\
= \sqrt{\frac{2J+1}{2^{J}+1}} \varphi(r) \sum_{K=K-L}^{J} \sum_{J=J-k}^{J_k} \varphi_{K}^{J,p} (R, r) \delta_{j,J,K} \delta_{J,p+1} \\
\times \left\{ -d_x [C_{1,1,J,K}^{J,p+1} \delta_{K,K+1} (1 - \delta_{0,K})] + (-1)^{J+1} \sqrt{(1 + \delta_{0,-1+K})} \\
\times C_{1,1,J,-K}^{J,p} \delta_{K,K-1} (1 - \delta_{0,K}) - C_{1,1,J,K}^{J,p} \delta_{K,0} (1 - \delta_{0,K}) \right\} \\
+ \sqrt{\frac{2J+1}{2^{J}+1}} \varphi(r) \delta_{J,J,K} \delta_{J,p+1} \delta_{K,0} \\
+ C_{1,1,J,0}^{J,p} \delta_{J,K,0} \delta_{J,p+1} (1 - \delta_{K,0}). \\
\]

(34)
Due to the parity conservation of the total wave function upon absorption of a photon, it is obvious from Eq. (34) that the parity of the nuclear wave function is changed from $p$ in the initial state to $p + 1$ in the final state.

With same manipulation, the time-dependent coefficient for the perpendicular transition located in the asymptotic region of the potential can be shown as

$$C_{j,K}(R_\infty, t) = \sqrt{\frac{2J + 1}{2J' + 1}} \varphi(r) \sum_{K=\lambda}^{J_{\max}} \sum_{J=K}^{J_{\max}} \varphi_K^{(J,p)}(R_\infty, r) \frac{i\delta_{J,j}\delta_{J',p}}{\sqrt{2}} dy \times \left\{ C_{1,1,J,K}^{(J,1+K)} \delta_{K,K+1}(1 - \delta_{0,K}) + \sqrt{1 + \delta_{0,-1+K}}(-1)^{J+J'+1} \right\} \times \varphi^{(J,p)}_0(R_\infty, r) \delta_{J',0}\delta_{p,0+p+1} C_{1,1,J,0}^{(J,-1)} \delta_{K',1}.$$  

Due to the parity conservation of the total wave function, it is obvious from Eq. (35) that the initial parity of the nuclear wave function, $p$, remains unchanged.

### 3. Computational Procedures

The lowest three electronic singlet potential energy surfaces consisting of the ground state $X^1A'$ and the lowest two excited states $2^1A'$ and $1^1A''$ of N$_2$O have been computed using MOLPRO suite of ab initio programs. The calculations were performed using aug-cc-pVQZ basis function in $Cs$ symmetry. Electron correlation effects were treated using highly correlated, internally contracted multireference configuration interaction (MRCI) wave functions preceded by state-averaged complete active space self-consistent field (CASSCF) wave functions. Figure 1 shows the N$_2$O molecule defined in the Jacobi coordinates system $(R, r, \theta)$ and its relation with the transition dipole moment vector in body-fixed Cartesian coordinates $(x, y, z)$. Figure 2 shows the cut through of the potential energy surfaces in linear and bent geometries. It is clear that the $2^1A'$ and $1^1A''$ states represent the first absorption band of N$_2$O. Figure 3 shows the cut through of the transition dipole moment vector.
moment surfaces in bent geometries. From the magnitude of the transition dipoles, it is clear that transition to $2^1A'$ dominates the overall photofragmentation process. Detail discussion of the potential and transition dipole moment surfaces can be found in Ref. 22.
A grid uniform based method\(^2\,^3\) has been used where the number of grid points in \(R\) was 384 and the number of angular \(\theta\) grid points and basis functions were 64. In the calculation of the expansion coefficients of \(\varphi^J_{K}^{p}\) (as described by Eq. (5)) on the grid points, this was performed by diagonalization of Hamiltonian matrices of order 384 and 64 variationally the time-independent Schrödinger equation based upon the ground state potential energy surface, \(X^1A'\). Direct use of the basis functions in Eq. (3) would lead to an unmanageably large basis set. Therefore, a further simplification arises from the use of parity-adapted eigenfunctions, described by Eq. (5).

In the present work, the N–N internuclear distance was fixed at its equilibrium geometry, \(2.13199\) bohr. The justification of using two-dimensional model is based on the fact that experiments have shown that the \(N_2\) products are produced vibrationally cold with the amount of \(v = 1\) less than 2\% of the \(v = 0\) products\(^1^2,^1^3\). Furthermore, the \(N_2\) bond distance contracts less than 3\% from 2.13199 Bohr in \(N_2O\) to 2.07416 Bohr in \(N_2\) following dissociation. Hence, we believe that a two-dimensional calculation on this system should be just enough for an accurate description of the dynamics involved.

In current case, notations of \(v_1\), \(v_2\) and \(v_3\) have been used thoroughly to denote vibrational quanta for the \(N_2O\) stretching and bending, and \(N-NO\) stretching, respectively. In addition to that the notation of \((v_1, v_2^[,], v_3^[,])\) was used for the degenerate states of \((v_1, v_2, v_3)\), distinguished by a vibrational angular momentum \(l\) that the allowed values of \(l\) are connected with the bending quantum numbers, \(v_2\), by \(l = -v_2, -v_2 + 2, \ldots, + v_2\). The allowed values of the total angular momentum quantum number \(J\) are connected with \(l\) by \(J = |l|, |l| + 1, \ldots\). Accordingly, to compute the rotational-vibrational energy and wave function for the state with odd bending quantum number, we considered \(J = 1\) with parity state either odd \((p = 1)\) or even \((p = 2)\). For an odd parity state, the allowed \(K\) values are 0 and 1, while for an even parity state the allowed \(K\) value is 0. For even bending quantum number, we considered \(J = 0\) with even parity in the calculations. \(J = 0\) with odd parity is forbidden by symmetry and in this case, the allowed \(K\) value is 0. Since \(J\) and parity are good quantum numbers, the calculations were performed separately for different values of \(J\) and parity. On the other hand, \(K\) is not a good quantum number and different values of \(K\) are coupled.

According to Eq. (7), to construct the partial cross-section, the selection rule on \(J\) has to be applied as required by Eq. (15) (or (32)). Since the odd bending quantum number is forbidden by symmetry for \(J = 0\), we considered only \(J = 1\) for the calculations of its cross-section. On the other hand, for the initial vibrational state with even bending quantum number, we chose \(J = 0\). For the \(X^1A' \rightarrow 2^1A'\) parallel transition, this leads to the specific rotational rules,

\[
J = 0, \quad K = 0, \quad p = 2 \rightarrow J' = 1, \quad K = 0,1, \quad p = 1 \\
J = 1, \quad K = 0,1, \quad p = 1 \rightarrow J' = 0, \quad K = 0, \quad p = 2 \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \rightarrow J' = 1, \quad K = 1, \quad p = 2 \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \rightarrow J' = 2, \quad K = 0,1,2, \quad p = 2
\]
and for the $X^1A' \rightarrow 1^1A''$ perpendicular transition, this leads to

\[
J = 0, \quad K = 0, \quad p = 2 \rightarrow J' = 1, \quad K = 1, \quad p = 2
\]

\[
J = 1, \quad K = 1, \quad p = 1 \rightarrow J' = 1, \quad K = 0, 1, \quad p = 1
\]

\[
\rightarrow J' = 2, \quad K = 1, 2, \quad p = 1,
\]

while, transition from $J = 1$ to $J' = 0$ was not considered because state with odd parity for $J' = 0$ is symmetry forbidden.

The initial wave packet $\phi^{J,p}(t = 0)$ for the parallel transition is constructed from a real function $\phi^{J,J',p}_{j,K,M}$ as described by Eq. (27). Nonetheless, for the perpendicular transition, it is constructed from an imaginary function $\phi^{J,J',p}_{j,K,M}$ as described by Eq. (31). For the parallel transition, Figs. 4(a) and 4(b) provide examples of the real part of the initial wave packets, associated with two possible values of $K$ quantum number, 0 and 1, at a fixed $J' = 1$. For the perpendicular transition, Fig. (5) shows an imaginary part of the initial wave packet, associated with $K = 1$ and $J' = 1$. In order to propagate the wave packet $\phi^{J,p}$ in time, we employed the time evolution

\[
\begin{align*}
\text{Fig. 4.} & \quad \text{(a) Re} \phi^{J,J',p}_{j,K,M}(t = 0) \quad \text{(b) Re} \phi^{J,J',p}_{j,K,M}(t = 0), \quad \text{evolving on the } 2^1A' \text{ potential. The } \text{N}_2\text{O molecule is initially in the } (0,0^0,0) \text{ vibrational state.}
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 5.} & \quad \text{Im} \phi^{J,J',p}_{j,K,M}(t = 0), \quad \text{evolving on the } 1^1A'' \text{ potential. The } \text{N}_2\text{O molecule is initially in the } (0,0^0,0) \text{ vibrational state.}
\end{align*}
\]
operator based on the complex Chebyshev polynomial expansion\(^{23}\) given by

\[
\exp\left(\frac{-i\hat{H}}{\hbar}\right) = \exp\left(\frac{-i}{\hbar} \left(\frac{\Delta E}{2} + V_{\text{min}}\right) t\right) \sum_{n=0}^{N} \left(2 - \delta_{n,0}\right) J_n\left(\frac{\Delta E t}{2 \hbar}\right) C_n\left(-i\hat{H}_{\text{norm}}\right),
\]

(36)

where \(J_n\) are the Bessel functions of the first kind of order \(n\) and \(C_n\) are the complex Chebyshev polynomials satisfying the recurrence relation \(C_{n+1} = -2i\hat{H}_{\text{norm}}C_n + C_{n-1}\).\(^{24}\) \(\hat{H}_{\text{norm}}\) is a normalized Hamiltonian defined by \(\hat{H}_{\text{norm}} = \{\hat{H} - i(\Delta E/2 + V_{\text{min}})\}/(\Delta E/2)\). It is normalized in such a way that the range of the Hamiltonian operator lies between \(E_{\text{max}}\) and \(E_{\text{min}}\), where \(\Delta E = E_{\text{max}} - E_{\text{min}}\). When the propagation was performed, the repeated operation of the normalized Hamiltonian operator on the function \(\phi^{J_p}\) was required, on an equally spaced grid that ranges from 1 Bohr to 14 Bohr with a step size of 0.03385 Bohr. The number of terms \(n\) used in the Chebyshev expansion was 27. Figures 6 and 7 display the snapshot of the time-dependent wave packets, \(\phi^{J_p}\), on the \(2^1A'\) and \(1^1A''\) surfaces propagating towards the exit channel.

In order to calculate the partial cross-section \(\sigma_j\) given by Eq. (7), the analysis plane was performed located at a \(\text{N}_2\)-O separation of 11.34 Bohr corresponding to the radial grid point at 311 out of 384 points. This plane was defined to lie perpendicularly across the asymptotic region. At each time step, a cut was taken through the wave packet along this plane and the resulting two-dimensional wave function was analyzed into its fragment state contribution by evaluating the time-dependent coefficients \(C'_{JpK}\) in Eqs. (34) and (35). The exchange symmetry of the two \(\text{N}\) nuclei was used. This means that 64 Gauss–Legendre angular quadrature points

![Image](image.png)

Fig. 6. Snapshot of the time-dependent wave packets, \(|\phi^{0,1}(t)|^2\), evolving on the \(2^1A'\) potential energy surface with the \(\text{N}_2\text{O}\) molecule starting from the \((0,0,0)\) vibrational state. The time evolving wavepackets are: (a) 0 fs; (b) 200 fs; (c) 600 fs.
allows us to represent N\textsubscript{2} rotational wave functions with rotational quantum number \( j \) up to 127. The propagation was continued until all the wave packet has completely left the interaction region, by which the time-dependent coefficients had decreased to zero. The total propagation time required for the wave packet to leave the interaction region was 10240 a.u., with a time step used for the propagation being 10 a.u.

Figure 8 shows the selected low \( j \) partial cross-section for the X\textsuperscript{1}A\textsuperscript{0} \rightarrow 2\textsuperscript{1}A\textsuperscript{0} transition with \( J = 0 \) and \( J' = 1 \). We can see that the \( j = 0 \) is significantly populated in this transition. Figure 9 shows the partial cross-section for transition to the 2\textsuperscript{1}A\textsuperscript{0} state with \( J = 1 \), where the \( j = 0 \) rotational state absent in Fig. 9(b). This is due to

![Fig. 7. Snapshot of the time-dependent wave packets, \(|\psi(t)|^2\), evolving on the 1\textsuperscript{1}A\textsuperscript{0} potential energy surface with the N\textsubscript{2}O molecule starting from the (0,0,0) ground vibrational state. The time evolving wavepackets are: (a) 0 fs; (b) 200 fs; (c) 600 fs.](image)

![Fig. 8. Partial absorption cross-sections for the X\textsuperscript{1}A\textsuperscript{0} \rightarrow 2\textsuperscript{1}A\textsuperscript{0} transition with the N\textsubscript{2}O molecule initially in its (0,0,0) vibrational state and \( J = 0 \), even parity (\( p = 2 \)). The final total angular momentum in the excited state is \( J' = 1 \), odd parity (\( p = 1 \)).](image)
Fig. 9. Partial absorption cross-sections for the $X^1A' \rightarrow 2^1A'$ transition with the N$_2$O molecule initially in its $(0,1^1,0)$ vibrational state and $J = 1$, odd parity ($p = 1$). The parity of the molecule in the excited state is even ($p = 2$) and the final total angular momentum: (a) $J' = 0$; (b) $J' = 1$; (c) $J' = 2$. 
the fact that \( K = 0 \) is forbidden for the transition from \( J = 0 \) with odd parity to the \( J' = 1 \) with even parity state, so we can expect the \( j = 0 \) rotational state is forbidden. For \( j = 0 \) to \( j = 9 \), the partial cross-section increases monotonically with increasing the rotational state. Similar feature also can be found for the perpendicular transition from the initial \( J = 0 \) to the final \( J' = 1 \), both in the even parity states, and for transition from \( J = 1 \) to the \( J' = 2 \) as well, both in the odd parity states. The partial cross-sections for the \( \chi A^0 \rightarrow \chi A^\prime \) transition are extremely small, so the corresponding figures are not illustrated here. We should note that it has been found experimentally that the \( \mathrm{N}_2 \) photofragment products are produced in high rotational states which can stretch up from \( j = 64 \) to \( j = 96 \) around the excitation wavelength 182 nm and the absolute magnitude of the cross-section is of the order of \( 10^{-21} \text{cm}^2 \). These aspects will be discussed in the following sections. Figures 8 and 9 illustrate the partial cross-sections with relatively very small magnitudes of order \( 10^{-26} \text{cm}^2 \) and \( 10^{-24} \text{cm}^2 \). They lie in the left shoulder of the absorption spectrum of \( \mathrm{N}_2\mathrm{O} \). It is also noticed that the cross-sections show some peak structures and the number of peaks increase with increasing \( j \). The number of peaks are also increased by increasing \( J' \).

Therefore, it is clear that rotation of the parent \( \mathrm{N}_2\mathrm{O} \) molecule and the final \( \mathrm{N}_2 \) product contribute to the increase of the fragmentation channels.

The portions of the dissociating wave packet will eventually reach the edge of the numerical grid. If no special precautions are taken, the parts of the wave packet that reach the edge of the grid will be unphysically reflected back onto the grid, invalidating the results of the calculations. In order to avoid such a reflection, a negative imaginary absorbing potential with a cubic form was employed at the edge of the \( R \) grid.

\[
V_{\text{damp}}(R) = \begin{cases} 
0.0; & R < R_{\text{damp}} \\
-iA_{\text{damp}} \left( \frac{R - R_{\text{damp}}}{R_{\text{max}} - R_{\text{damp}}} \right)^3; & R_{\text{damp}} \leq R \leq R_{\text{max}}
\end{cases}
\]  

(37)

With this scheme, the damping was switched on at \( R_{\text{damp}} = 356 \), while the dimensionless parameter \( A_{\text{damp}} \) has been previously optimized by Balint–Kurti and Vibók to be set 0.1014, giving the strength of the damping.

4. Results and Discussion

4.1. \( \mathrm{N}_2 \) partial cross-sections

Figure 10 displays the three-dimensional plot of the partial cross-sections for the \( \chi A' \rightarrow \chi A' \) transition with initial \( J = 0 \), covering the wavelength \( \lambda = 155 - 240 \text{ nm} \) and the \( \mathrm{N}_2 \) rotational states \( j = 60 - 100 \). Figure 11 shows the partial cross-sections for the \( \chi A' \rightarrow \chi A'' \) transition, covering the same wavelength range with \( j = 50 - 100 \). It clearly shows that the same tendency prevails for most of the cross-sections peaking around \( j = 60 - 100 \). Some degree of similarity between two kinds of transitions, with all the cross-sections display a smooth absorption line shape
without superimposed resonance structure on them. A couple of similarities are not surprising due to the resemblance in many aspects of the topography between the two surfaces (Figs. 6 and 7). Most importantly, the \( N_2 \) photofragmentation in the first absorption band has been dominated by transition to the \( ^2 \Pi_0 \) state.

It is not difficult to surmise that the \( ^1 \Pi \) cross-section is more structured than that of the \( ^2 \Pi \) one. The structure is reflected from the shape of the \( X^1 \Pi \rightarrow ^1 \Pi \) transition dipole moment \( d_y \) in the vicinity of Franck–Condon region. Detailed analysis reveals a sharp dip of the transition dipole moment crossing zero near the equilibrium collinear geometry, \( \theta = 1^\circ \) and \( R = 3.35 \) Bohr, resulting in the formation

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**Fig. 10.** Partial absorption cross-sections for the \( X^1 \Pi \rightarrow ^2 \Pi \) transition with the \( N_2O \) molecule starting from different initial vibrational states: (a) \((0,0^0,0)\); (b) \((0,2^0,0)\); (c) \((0,4^0,0)\); (d) \((1,0^0,0)\); (e) \((2,0^0,0)\); (f) \((1,2^0,0)\). The initial total angular momentum is \( J = 0 \), even parity \((p = 2)\).
of a node in the initial wave packet, as depicted by Fig. 7(a). This effect substantially increases the number of node in the cross-section. On the other hand, the manner in which the two components of the \( \text{X} \text{A} \rightarrow \text{1A} \) transition dipole moment (\( d_x \) and \( d_z \)) cross zero at different coordinates, produce a smooth change of the transition dipole moment function and the resulting initial wave packet in the Franck-Condon region.\(^{22}\) In general, the figures display that the pure bending excitation from the ground electronic state substantially increases the intensity of the cross-sections. Likewise for the excitation from pure stretching and coupled bending-stretching states.
Similar calculations of the partial cross-section can also be performed for \( J = 1 \). However, it requires a preparation of initial wave function in the ground electronic state with odd bending quantum number. We note that the most important feature of the method discussed here is that the partial cross-sections shown in each figure all have been obtained from one single solution of the Schrödinger equation. For instance, the energy in the present work covers 11,204 values, and the cross-sections at these values were all extracted from a single propagation of the time-dependent wave packet followed by a single (discrete) Fourier transformation of the time-dependent coefficients arising from its analysis in the asymptotic region. Therefore, for any given initial state, we can finally construct the product quantum state distribution over a wide range of selected energies.

### 4.2. \( N_2 \) rotational state distributions

Figure 12 shows the sum of a Boltzmann averaged rotational state distribution at 203 nm over the \( X^1A' \rightarrow 2^1A' \) and \( X^1A' \rightarrow 1^1A'' \) transitions where the parent molecule is initially in the ground, one quantum and two quanta excited bending states. The distribution peaks at \( J = 74 \) is in excellent agreement with the experimentally observed distribution for photolysis at 203 nm.\(^{12,13}\) Detail analysis reveals that the large amount of rotationally hot \( N_2 \) comes exclusively from the ground and one bending excitation of the parent molecule. Moreover, the largest portion of the

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Fig. 12. \( N_2 \) rotational quantum state distributions at photolysis wavelengths of 203 nm. The distributions were calculated from contribution of two lowest excited states, \( 2^1A' \) and \( 1^1A'' \) obtained by Boltzmann averaging of three cross-sections with the \( N_2O \) molecule initially in its \( (0,0^0,0), (0,1^1,0) \) and \( (0,2^2,0) \) vibrational states at temperatures of 233 K, 238 K and 297 K.
rotationally hot $N_2$ originates primarily from transition to the $2^1A'$ state. The strongly repulsive nature of the $2^1A'$ potential energy surface along the $N_2$-O coordinate is consistent with the large positive anisotropy parameter observed by Neyer et al.\textsuperscript{13} We believe that their conclusion of a strong perpendicular contribution to the photofragmentation reflects the significant $x$ component of the transition dipole moment which is perpendicular to the $N_2$-O dissociation direction.

We also studied the rotational state distributions of $N_2$ for five rare isotopomers, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{15}N^{15}N^{16}O$, $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$, at photolysis wavelength of 203 nm which is the region of ultraviolet stratospheric window.\textsuperscript{26–28} Previous study showed that all the heavier isotopomers reveal strong isotopic enrichment at this photon energy. A single peak distribution predicted for the heavy isotopomers are quite similar to that obtained for $^{14}N^{14}N^{16}O$ at all temperatures studied ($T = 233$, 238 and 297). Figure 13 shows the distribution for oxygen substituted $N_2O$, $^{14}N^{14}N^{17}O$ and $^{14}N^{14}N^{18}O$, peaking at $j = 74$ which is identical with the $^{14}N^{14}N^{16}O$ isotopomer. Despite only a minor isotope effect is predicted, the intensity of the distribution decreases with increasing mass of oxygen.

Figure 14 shows the distributions for the nitrogen-substituted isotopomers, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{15}N^{15}N^{16}O$. In contrast to the case of the oxygen-substituted

![Graph](image-url)
Fig. 13. (Continued)

Fig. 14. \( \text{N}_2 \) rotational quantum state distributions at photolysis wavelength of 203 nm for the isotopically nitrogen substituted of \( \text{N}_2\text{O} \): (a) \(^{14}\text{N}^{15}\text{N}^{16}\text{O} \); (b) \(^{15}\text{N}^{14}\text{N}^{16}\text{O} \); (c) \(^{15}\text{N}^{15}\text{N}^{16}\text{O} \). The distributions were calculated from contribution of two lowest excited states, \(^2\text{A}'\) and \(^1\text{A}''\) obtained by Boltzmann averaging of three cross-sections with the \( \text{N}_2\text{O} \) molecule initially in its \((0,0^0,0),(0,1^1,0)\) and \((0,2^2,0)\) vibrational states at temperatures of 233, 238 and 297 K.
distributions, the distributions are shifted to higher rotational states. A simple classical explanation is that the larger moment of inertia of the $^{14}$N$^{15}$N and $^{15}$N$^{15}$N photofragments indirectly generate a strong torque around the center of mass of N$_2$O molecule. Consequently, the maximum peak of the $^{14}$N$^{15}$N$^{16}$O distribution is shifted to $j = 75$, of the $^{15}$N$^{14}$N$^{16}$O distribution is shifted to $j = 76$ and of $^{15}$N$^{15}$N$^{16}$O distribution is shifted to $j = 77$, relative to the parent $^{14}$N$^{14}$N$^{16}$O maximum peak. Interestingly, similar to its isotopic enrichment factors,$^{26}$–$^{28}$ the distributions of the asymmetric isotopomers $^{14}$N$^{15}$N$^{16}$O and $^{15}$N$^{14}$N$^{16}$O are found to be observably different. There is a difference in the intensities in that the $^{14}$N$^{14}$N$^{16}$O distribution is higher than that of the $^{14}$N$^{15}$N$^{16}$O and $^{15}$N$^{15}$N$^{16}$O isotopomers. Moreover, both $^{14}$N$^{14}$N$^{16}$O and $^{15}$N$^{14}$N$^{16}$O show almost the same intensity.

The influence of different temperatures, 233, 283 and 297 K, on the rotational quantum state distributions for six isotopomers are illustrated in Figs. 12–14. It is obvious that with increasing temperature, the intensity of the N$_2$ product distribution increases, most significantly at its maximum peak.

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References


