

Quantum-chemical study of the properties of the excited states of organic molecules

IV. Photodissociation of nitrogen oxide

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Dedicated to Academician V. Kellö, in honour of his 65th birthday

Photodissociation of N_2O into N_2 and O using an HF operator of Nesbet's type with limited configuration interaction has been studied. Calculations have been done in semiempirical MINDO/2 and INDO parametrizations. The realistic course of dissociation curves was obtained by combining excitation energies computed in INDO parametrization with the ground state energy calculated by the MINDO/2 method. The course of photolytic reaction from different excited states is discussed on the basis of an analysis of orbital and state correlation diagrams and calculated dissociation curves.

Была изучена фотодиссоциация молекулы N_2O на N_2 и O используя HF оператор типа Несбета и метод конфигурационного взаимодействия. Расчеты выполнены в рамках полуэмпирических MINDO/2 и INDO параметризаций. Реалистический ход диссоциационных кривых возбужденных состояний был получен в случае, когда к энергии основного состояния рассчитанной в MINDO/2 параметризации были прибавлены энергии возбуждения рассчитанные в INDO параметризации. Обсуждается механизм фотолитических реакций из разных возбужденных состояний на основании орбитальных корреляционных диаграмм и корреляционных диаграмм состояний и также на основании рассчитанных диссоциационных кривых.

Nitrogen oxide is important in atmospheric reactions as an intermediate of collision processes of atomic oxide and molecule nitrogen and as a source of unstable photolysis products, of which were identified [1]: $N(^2D)$, $O(^1S)$, $O(^1D)$, $N_2(^3\Sigma^+)$, $N_2(^3\Pi)$. Absorption spectrum of N_2O in the near ultraviolet region consists of three bands of continuous absorption starting at 306.5 nm with shallow maxima at 290 nm, 273 nm, and 182 nm [2].

Spomer *et al.* [3] and Zelikoff *et al.* [4] investigated the N_2O spectrum and discussed correlation of individual absorption bands with various dissociation

products. The excited ${}^3\Pi$ and ${}^3\Sigma$ states are assigned to the long-wave absorption starting at 306.5 nm, which is supposed to be responsible for photochemical dissociation into $\text{N}_2({}^1\Sigma)$ and $\text{O}({}^3P)$. Thermochemical data show that dissociation of N_2O into the mentioned products requires 1.71 eV [4] (1.68 eV according to [2]); i.e. it might theoretically take place even at 720 nm. Dissociation into $\text{N}_2({}^1\Sigma^+)$ and $\text{O}({}^1D)$ requires 3.68 eV [4] and is spin- and orbital-allowed from ${}^1\Sigma^+$, ${}^1\Pi$, ${}^1\Delta$ states of an N_2O molecule. The $\text{N}_2({}^1\Sigma^+)$ and $\text{O}({}^1S)$ products require 5.9 eV and are adiabatically attainable from the ${}^1\Sigma^+$ state of N_2O . *Zelikoff et al.* [4] used experimental data for outlining dissociation curves for possible photochemical dissociations of N_2O . *Chutjian et al.* [5] calculated energies for the excited states of N_2O in INDO approximation. They computed wavefunctions at the SCF level; since the used formalism cannot be applied to linear molecules (with respect to degeneration of most states), the authors calculated energies at bent geometries and the energy of a linear molecule they obtained by extrapolation. By putting the results and experimental data on dissociation limits together, they delineated qualitatively dissociation curves for dissociations of $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$ and $\text{N}_2\text{O} \rightarrow \text{NO} + \text{N}$.

Diffusion character of the N_2O spectrum leads to difficulties in the classification of absorption bands; therefore assignment of the theoretical results to experimental data is not unambiguous. Extensive nonempirical CI computations of *Peyerimhoff et al.* [6] and *Winter* [7] differ in assigning some transitions.

Transition energies for N_2O calculated by the CI method in MINDO/2, INDO, and CNDO/S parametrizations have been given in Part III of this series [8].

Calculations

The HF operator of Nesbet's type was employed for SCF calculations within semiempirical MINDO/2 and INDO approximations. For π configuration arising from $\pi \rightarrow \sigma^*$ excitation of N_2O , the HF operator was

$$\hat{F} = \hat{h} + \sum_i (2\hat{J}_i - \hat{K}_i) - \frac{1}{2}(\hat{J}_\mu + \hat{J}_\nu - \frac{1}{2}\hat{K}_\mu - \frac{1}{2}\hat{K}_\nu) + (\hat{J}_b - \frac{1}{2}\hat{K}_b) \quad (1)$$

where the index i passes through completely occupied orbitals in the ground state, indices μ and ν correspond to π_x and π_y MO's and b belongs to σ^* MO. Using the operator (1) the orbitals π_x and π_y remain degenerated also in uncompletely occupied π shells. The wavefunctions being eigenfunctions of \hat{L}_z operator and representing respective states (Σ , Π , Δ ...) of linear molecule could be constructed from these MO's. The 20 lowest singly excited configurations, 4 paired biexcited, and a ground state configuration were included into CI.

Calculations were done for the reaction



The reaction pathway was modelled by changing the distance of oxygen from N₂ in the direction of the bond. The experimental geometry of N₂O, $R_{NN} = 1.128 \times 10^{-10}$ m, $R_{NO} = 1.184 \times 10^{-10}$ m, $\angle NNO = 180^\circ$ [2], was used, the distance N—N being constant.

Results and discussion

Fig. 1 shows an orbital correlation diagram for the above reaction. Orbital energies were calculated for the $1^3\Pi$ state using an HF operator (1) in MINDO/2 parametrization. Let us follow the correlation between MO's of reactants and those of products. Oxygen 2s orbital correlates with 2 σ orbital of N₂O, p_x and p_z on oxygen with 2 π orbitals of N₂O, and p_x with 5 σ^* orbital of N₂O. 1 σ , 3 σ , and 4 σ orbitals of N₂O correlate with 1 σ_g , 1 σ_u , and 2 σ_g orbitals of N₂ and 1 π orbitals of N₂O correlate with π_u of N₂. The observed difference in values of orbital energies for oxygen p_x , p_y , and p_z orbitals is due to different "effective" occupation of the mentioned orbitals by employing the HF operator (1): for p_y and p_z three electrons and one electron for p_x .

Construction of the state correlation diagram for linear dissociation of N₂O in Fig. 2 is based on MINDO/2 energies for individual states of reactants and products connected according to the Wigner—Witmer rules [2], i.e. so that

$$\lambda = |M(L_1) + M(L_2)| \quad (2)$$

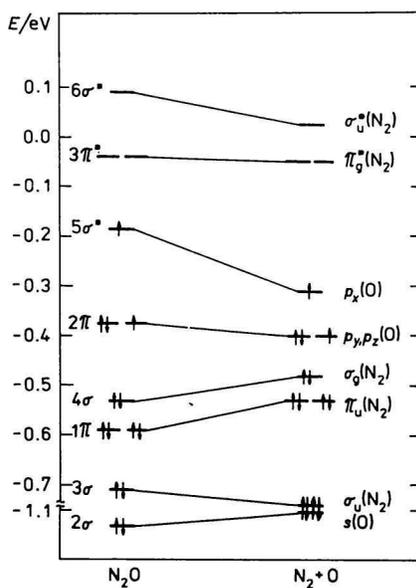


Fig. 1. Orbital correlation diagram for dissociation
N₂O → N₂ + O (MINDO/2).

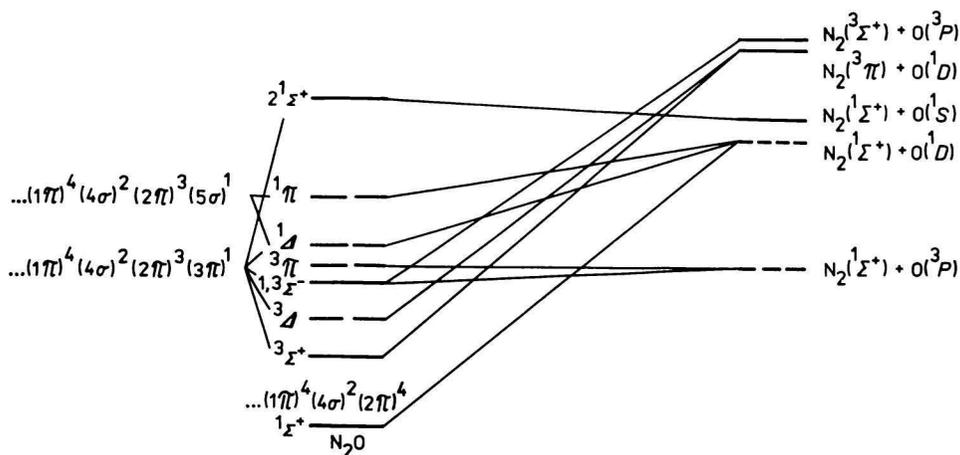


Fig. 2. State correlation diagram for dissociation of N_2O (MINDO/2).

where λ is the z component of the total orbital momentum belonging to a certain state of N_2O molecule, $M(L_1)$ and $M(L_2)$ are the corresponding values of z components for N_2 and O in the respective states ($M(L_1) = \pm \lambda(\text{N}_2)$; $M(L_2) = L, L - 1, -L(\text{O})$).

The $\pi \rightarrow \sigma^*$ excitation leads to ${}^{1,3}\Pi$ states with electron configuration $\dots(1\pi)^4(4\sigma)^2(2\pi)^3(5\sigma)^1$, and at unchanged occupation of orbitals we obtain correct configurations of the products (${}^1\Sigma^+$) N_2 ($(\pi_u)^4(\sigma_g)^2$) and (${}^1D, {}^3P$) O s^2p^4 .

The $\pi \rightarrow \pi^*$ type excitation in N_2O gives rise to six states: ${}^{1,3}\Sigma^-$, ${}^{1,3}\Delta$, and ${}^{1,3}\Sigma^+$. The respective electron configuration A $(1\pi)^4(4\sigma)^2(2\pi)^3(3\pi^*)^1$ (Scheme 1) leads, at unchanged occupation of orbitals, to ionic products of N_2^- ($(\pi_u)^4(\sigma_g)^2(\pi_g)^1$) and O^+ s^2p^3 . The biexcited electron configuration B $(1\pi)^4(4\sigma)^2(2\pi)^2(5\sigma)^2$ (Scheme 1) of N_2O molecules correlates with the s^2p^4 configuration of oxygen atom and $\dots(\pi_u)^4(\sigma_g)^2$ configuration of nitrogen molecule. Excited states of ${}^1\Delta$, ${}^3\Sigma^+$, and ${}^1\Sigma^+$ of N_2O with higher energies are assigned to the above configuration. Three of the six states corresponding to the configuration A interact with the corresponding states formed from the configuration B and using the mechanism of avoided crossing the products are described in their lowest energetic states.



Scheme 1

A large energy barrier can be expected for the given three states $^1\Delta$, $^3\Sigma^-$, $^1\Sigma^+$ and therefore they should be forbidden for dissociation. That is why only $^{1,3}\Pi$ states from among disturbed excited states ought to have dissociative characteristics.

The starting configuration for which we constructed an HF operator was the π configuration $\dots(1\pi)^4(4\sigma)^2(2\pi)^3(5\sigma^*)^1$. But for the starting state, i.e. for N_2O at experimental geometry of the ground state, the SCF calculation of this monoexcited configuration did not converge as a result of changes in the order of MO 1π and 2π and the corresponding oscillations in SCF computations. We thus selected the $\dots(1\pi)^4(4\sigma)^1(2\pi)^4(3\pi)^1$ as starting configuration also corresponding to the Π state.

We took spin-adapted double-determinant functions for paired biexcited configurations into configuration interaction. However, for linear molecules these the so-called configuration functions do not represent eigenfunctions of \hat{L}_z operator. Linear combinations of these functions with the functions formed from them by cyclic permutation of π_y and π_z orbitals in not fully occupied π -electron shells represent more completely the respective states since they are also eigenfunctions of \hat{L}_z . Therefore coefficients at such pairs of configuration functions are of the same absolute values (Table 1a). Coefficients in Table 1b correspond to coefficients before functions which are correct with respect to the \hat{L}_z operator.

Table 1

1a. CI expansion coefficients for the first $^1\Delta$ state of N_2O at dissociation

Configurations	$\Delta R_{\text{No}}/10^{-10} \text{ m}$			
	0.0	0.3	0.5	1.0
I $(1\pi)^4(4\sigma)^2(2\pi_y)^2(5\sigma)^2$	-0.0050	-0.0671	-0.6776	-0.7071
$(1\pi)^4(4\sigma)^2(2\pi_z)^2(5\sigma)^2$	0.0050	0.0671	0.6776	0.7071
II $(1\pi)^4(4\sigma)^2(2\pi_z)^2(2\pi_y)^1(3\pi_y)^1$	0.6865	0.6585	0.1883	0.0017
$(1\pi)^4(4\sigma)^2(2\pi_y)^2(2\pi_z)^1(3\pi_z)^1$	-0.6865	-0.6585	-0.1883	-0.0017
III $(1\pi_y)^2(1\pi_z)^1(4\sigma)^2(2\pi)^4(3\pi_z)^1$	0.1696	0.2486	0.0621	—
$(1\pi_z)^2(1\pi_y)^1(4\sigma)^2(2\pi)^4(3\pi_y)^1$	-0.1696	-0.2486	-0.0621	—

1b. CI extension coefficients for $^3\Pi$ state of N_2O at dissociation

Configurations	$\Delta R_{\text{No}}/10^{-10} \text{ m}$			
	0.0	0.3	0.5	1.0
IV $(1\pi)^4(4\sigma)^2(2\pi)^3(5\sigma)^1$	0.9492	0.9799	0.9943	0.9986
V $(1\pi)^3(5\sigma)^2(2\pi)^4(5\sigma)^1$	0.2290	0.1185	0.0085	0.0378
VI $(1\pi)^4(4\sigma)^1(3\pi)^4(3\pi)^1$	0.0936	0.0461	0.0198	0.0023

The course of most dissociation curves supports assumptions obtained from the analysis of correlation diagrams. The $^1\Sigma^+$, $^1\Delta$, and $^1\Pi$ states of the considered molecule dissociate into the same states of products, *viz.* into $N_2(^1\Sigma^+)$ and $O(^1D)$. The $^1\Delta$ state goes at $\Delta R > 0.3 \times 10^{-10}$ m (Fig. 3a) above $^1\Pi$ state and is responsible for a barrier originating from avoided crossing of the states described by configuration functions I and II (Table 1a). At distances $\Delta R > 1 \times 10^{-10}$ m, this state is represented only by 1D state of oxygen atom and $^1\Sigma^+$ of N_2 .

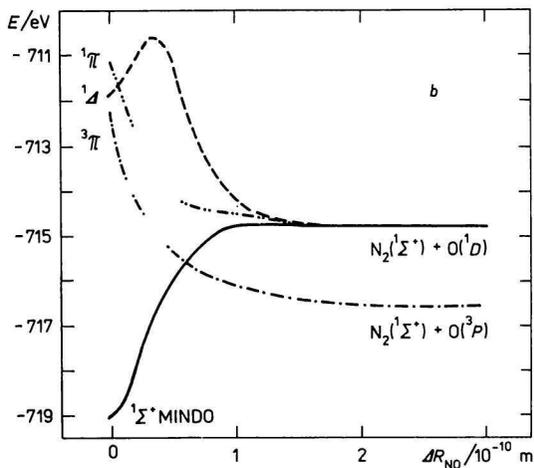
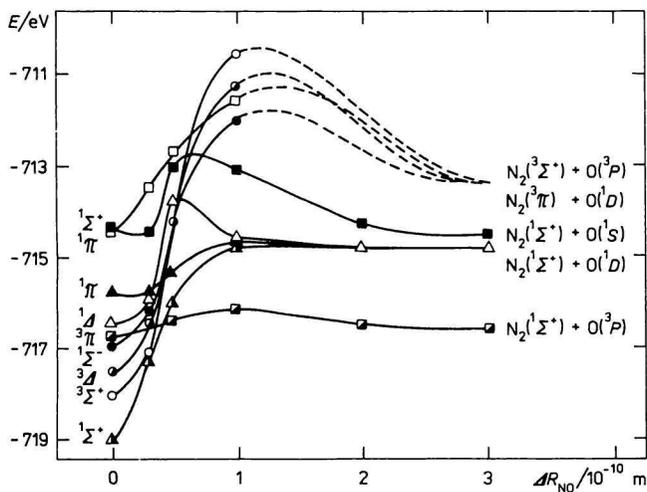


Fig. 3. Dissociation of $N_2O \rightarrow N_2 + O$.
a) MINDO/2; b) INDO (see the text).

The behaviour of the ${}^{1,3}\Sigma^-$ states is interesting. Our calculations show that singlet and triplet states have the same energies increasing rapidly with the increasing ΔR . Looking at the state correlation diagram, we might expect correlation of the ${}^3\Sigma^-$ state with $N_2({}^1\Sigma^+)$ and $O({}^3P)$ states and of the singlet ${}^1\Sigma^-$ state with $N_2({}^3\Sigma^+) + O({}^3P)$ states; we would also expect nonzero value for the singlet-triplet splitting.

The dominant configurations in the initial geometry for ${}^{1,3}\Sigma^-$ states are the $\pi \rightarrow \pi^*$ type configurations represented by configuration functions

$$\Psi({}^1\Sigma^-) = |2\pi_x\overline{3\pi_y}2\pi_y\overline{2\pi_x}| + |3\pi_y\overline{2\pi_x}2\pi_x\overline{2\pi_y}| - |2\pi_y\overline{3\pi_x}2\pi_x\overline{2\pi_x}| - |3\pi_x\overline{2\pi_y}2\pi_x\overline{2\pi_x}| \quad (3)$$

$$\Psi({}^3\Sigma^-) = |2\pi_x\overline{3\pi_y}2\pi_y\overline{2\pi_x}| - |3\pi_y\overline{2\pi_x}2\pi_x\overline{2\pi_y}| - |2\pi_y\overline{3\pi_x}2\pi_x\overline{2\pi_x}| + |3\pi_x\overline{2\pi_y}2\pi_x\overline{2\pi_x}| \quad (4)$$

Then the singlet-triplet splitting is

$$\Delta E = 2(\langle 2\pi_x 3\pi_y | 3\pi_y 2\pi_x \rangle - \langle 3\pi_y 2\pi_y | 2\pi_x 3\pi_x \rangle) \quad (5)$$

But we can easily show that both integrals on the right-hand side have the same value and thus the splitting is zero.

Correlation of the $N_2O({}^3\Sigma^-)$ state with the $N_2({}^1\Sigma^+)$ and $O({}^3P)$ states would require inclusion of the configuration $(1\pi)^4 (4\sigma)^2 (2\pi_x)^1 (2\pi_y)^1 (5\sigma)^2$ into CI, having also ${}^3\Sigma^-$ symmetry but representing unpaired biexcited configuration. Since we did not consider this type of configurations in CI, the mentioned expected state correlation was not obtained. Similarly to ${}^1\Sigma^-$, correct description of the behaviour of other states (dashed lines in Fig. 3a) during dissociation would require inclusion of configuration functions corresponding to unpaired biexcitations into CI computation. The ${}^1\Pi$ state (and similarly ${}^3\Pi$) is, along the reaction coordinate, represented by dominant configuration function IV. They are just the states that should be photochemically active from the point of view of their course. Nitrogen oxide (Fig. 3a) in the ${}^3\Pi$ state dissociates into products in the ground state with calculated dissociation limit of 2.46 eV (exp 1.68 eV) and in the ${}^1\Pi$ state it dissociates into $N_2({}^1\Sigma^+)$ and $O({}^1\Delta)$ products with the dissociation limit of 4.20 eV (exp 3.68 eV). But all curves near the reactant increase either directly or after passing through a little minimum, i.e. they correspond to curves of the bound states. This, however, disagrees with the experimentally found diffusion character of the spectrum of N_2O indicating presence of the repulsion dissociation states. The shape of the curves calculated is probably caused by too low values of computed energies for the excited states of a reactant in MINDO/2 approximations.*

* For details see Part III of this series.

On the other hand, INDO (CI) excitation energies for N₂O are a much better approximation to the experiment but dissociation energies from INDO calculation are more than three times higher than experimental values (e.g. for ¹Σ⁺, dissociation limit is 11.89 eV). This results from the known feature of INDO (also CNDO/2) parametrization — overestimation of bond energies.

If we take as a reference curve the ¹Σ⁺ state curve from MINDO/2 calculation and other curves will be constructed using INDO CI excitation energies, we obtain a much more realistic image of dissociation. The ^{1,3}Σ states become purely repulsion states and they represent two main photodissociation pathways (Fig. 3b).

The ³Π state also enables thermal dissociation of N₂O from the ground ¹Σ⁺ state by crossing this state. The activation energy of 2.6 eV [5] was found for such dissociation and is interpreted as the energy difference between interactions of ¹Σ⁺ and ³Π states and the ground state. It is interesting that this energy difference calculated by MINDO/2 method is 2.58 eV.

Other excited states in the long-wave region, ³Σ⁺, ³Δ, ³Σ⁻, and ¹Σ⁻ crossing repulsive ³Π state (Fig. 3a) may be transformed by predissociation to N₂(¹Σ⁺) and O(³P) products. The ¹Δ and upper ¹Σ⁺ states are not purely repulsive states as has been supposed by *Chutjian et al.* [5], but they pass through distinct barriers. Decomposition of the ¹Δ state probably proceeds through predissociation mechanism including repulsion ¹Π state to which it passes by internal conversion. ¹Δ and ¹Π states are probably sources of the N₂(¹Σ⁺) and O(¹D) products.

Conversion of the upper ¹Σ⁺ state to a lower lying state seems to be more probable than direct adiabatic dissociation along its “own” hypersurface.

The decomposition of the N₂O studied represents only one of the possible ways. But also the reaction



which has not been the subject of our study may proceed. Decomposition of this kind occurs, however, only from higher excited states. The lower excited states are bound in the direction of the N—N bond rupture [5].

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