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VIRTUAL NITROGEN DIOXIDE MOLECULE DISSOCIATION IN EXTERNAL ELECTROMAGNETIC FIELDS

A.V. Alforova²⁾, B.V. Borts¹⁾, V.I. Tkachenko^{1),2)}

¹⁾ National Science Center "Kharkov Institute of Physics and Technology"

1, Akademicheskaya St., 61108, Kharkov, Ukraine

E-mail: tkachenko@kipt.kharkov.ua

²⁾ V.N. Karazin Kharkiv National University

4, Svobody Sq, 61022, Kharkiv, Ukraine

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The model is proposed for describing a real nitrogen dioxide molecule by its two-dimensional analog, namely, the virtual molecule (VM). The proposed VM model provides the condition of coincidence between the fundamental eigenfrequencies of the real molecule and its virtual analog. The other VM parameters (bond length and atomic mass) are renormalized so that the molecule should steadily exist for a long time interval. Linear dynamics of VM atoms in the field of a monochromatic electromagnetic wave has been investigated. It is shown that under the action of an external electromagnetic field on the molecule at a resonance frequency, secular modes of vibrations are observed. The last ones are characterized by a time-linear growth of atomic oscillation amplitudes. The influence of the turn on of an external force at the time of stabilization of eigenfrequencies of the VM on the stability of VM atomic oscillations were made. It is shown that in some cases breaking of one of the VM bonds inevitably leads to the VM dissociation as a whole. As a result of numerical simulation, it has been established that the bond breaking has a threshold character, i.e., dissociation is not observed at the external force, which is below a certain value. In the region of forces exceeding the threshold values, the variation in the external electromagnetic field frequency is insensitive to the resonance effects that are due to the presence of dedicated frequencies of the VM. It is demonstrated that in the region, where the $N - O$ bond breaking always takes place, there exist the $O - O$ bond stability islands. Optimum parameters of VM dissociation have been determined.

KEY WORDS: virtual nitrogen dioxide molecule, eigenfrequencies, bond length, atomic mass, external force, dissociation.

ДИСОЦІАЦІЯ ВІРТУАЛЬНОЇ МОЛЕКУЛИ ДВООКИСУ АЗОТУ У ЗОВНІШНІХ ЕЛЕКТРОМАГНІТНИХ ПОЛЯХ

О.В. Алфьорова²⁾, Б.В. Борц¹⁾, В.І. Ткаченко^{1),2)}

¹⁾ Національний Науковий Центр "Харківський фізико-технічний інститут"

61108, Харків, Академічна, 1

²⁾ Харківський національний університет імені В.Н. Каразіна

61022, Харків, пл. Свободи, 4

У роботі запропонована модель опису реальної молекули двоокису азоту її двовимірним аналогом - віртуальною молекулою (ВМ). У запропонованій моделі ВМ забезпечена умова збігу основних власних частот молекули і її аналога. Інші параметри ВМ (довжина зв'язків і маси атомів) перенормовані таким чином, щоб молекула стійко існувала тривалий інтервал часу. Досліджено лінійну динаміку атомів ВМ у полі монохроматичної електромагнітної хвилі. Показано, що при впливі зовнішнього електромагнітного поля на молекулу на резонансній частоті спостерігаються секулярні режими коливань, які характеризуються лінійним у часі ростом амплітуд коливань атомів. Досліджено вплив включення зовнішньої сили в момент установлення власних коливань ВМ на стійкість коливань її атомів. Показано, що в деяких випадках розрив однієї зі зв'язків ВМ неминуче призводить до її розпаду в цілому. У результаті чисельного моделювання встановлено, що розрив зв'язків має граничний характер, тобто дисоціація не спостерігається при зовнішній силі, меншій певного значення. В області сил, що перевищують граничні, варіювання частоти зовнішнього електромагнітного поля не відчутно до резонансних ефектів, обумовлених наявністю виділених частот у ВМ. Показано, що в області, де завжди відбувається розрив зв'язку, існують острівці стабільності. Визначено оптимальні параметри дисоціації ВМ.

КЛЮЧОВІ СЛОВА: віртуальна молекула двоокису азоту, власні частоти, довжина зв'язку, атомна маса, зовнішня сила, дисоціація.

ДИССОЦИАЦИЯ ВИРТУАЛЬНОЙ МОЛЕКУЛЫ ДВООКИСИ АЗОТА ВО ВНЕШНИХ ЭЛЕКТРОМАГНИТНЫХ ПОЛЯХ

А.В. Алфёрова²⁾, Б.В. Борц¹⁾, В.И. Ткаченко^{1),2)}

¹⁾ Национальный Научный Центр «Харьковский физико-технический институт»

61108, Харьков, Академическая, 1

²⁾ Харьковский национальный университет имени В.Н. Каразина

61022, Харьков, пл. Свободы, 4

В работе предложена модель описания реальной молекулы двуокиси азота ее двумерным аналогом - виртуальной молекулой (ВМ). В предложенной модели ВМ обеспечено условие совпадения основных собственных частот молекулы и ее аналога. Остальные параметры ВМ (длина связей и массы атомов) перенормированы таким образом, чтобы молекула устойчиво существовала длительный интервал времени. Исследована линейная динамика атомов ВМ в поле монохроматической электромагнитной волны. Показано, что при воздействии внешнего электромагнитного поля на молекулу на резонансной частоте наблюдаются секулярные режимы колебаний, которые характеризуются линейным во

времени ростом амплитуд колебаний атомов. Исследовано влияние включения внешней силы в момент установления собственных колебаний ВМ на устойчивость колебаний ее атомов. Показано, что в некоторых случаях разрыв одной из связей ВМ неизбежно приводит к ее распаду в целом. В результате численного моделирования установлено, что разрыв связей имеет пороговый характер, т.е. диссоциация не наблюдается при внешней силе, меньшей определенного значения. В области сил, превышающих пороговые, варьирование частоты внешнего электромагнитного поля не чувствительно к резонансным эффектам, обусловленным наличием выделенных частот у ВМ. Показано, что в области, где всегда происходит разрыв связи $N - O$, существуют островки стабильности связи $O - O$. Определены оптимальные параметры диссоциации ВМ.

КЛЮЧЕВЫЕ СЛОВА: виртуальная молекула двуокиси азота, собственные частоты, длина связи, атомная масса, внешняя сила, диссоциация.

Triatomic molecules (H_2O , CO_2 , NO_2 , SO_2 , H_2S , etc.) are characterized by the presence of a fine structure of their absorption spectra. A full and exact information on the parameters of these spectra is of basic importance for solving many applied and fundamental problems such as the development of theory and practice of femtochemistry [1]; analysis of the impact of volcanic outbursts, “greenhouse” effect, ozone layer on the ecology and climate variations of the Earth [2]; creation of alternative energy sources based on the controlled molecule dissociation in external electromagnetic fields [3, 4].

One of the methods to control the internal dynamics of triatomic molecules is to act upon them through an electromagnetic field, which is oscillating at frequencies close to the frequencies of atomic oscillations in molecules [3,4]. Since the frequencies of atomic oscillations in molecules lie in the infrared spectrum [5], the resonance action on the internal dynamics of the molecule is entirely feasible with the use of lasers that generate electromagnetic radiation of corresponding wave lengths [1].

The other method of water molecule dissociation, different from laser technologies, has been described by Meyer in his patent [6]. Here, to achieve the objective, a sequence of special-shape unipolar voltage pulses was used, with the voltage-time step function for the leading and trailing edges of the pulse and the exponentially increasing function for the pulse peak.

Since the above-described methods of triatomic molecule dissociation by external electromagnetic fields are far from creating of adequate model [3,4] or are based on empirical facts [6], it appears of importance and necessity to continue the research in this direction.

The present paper deals with the modeling of the interaction between the real triatomic molecule (NO_2 as an example) and the external electromagnetic fields of the virtual molecule (VM).

THE MODEL OF NITROGEN DIOXIDE MOLECULE

The nitrogen dioxide molecule presents a triatomic molecule NO_2 that consists of one nitrogen atom and two oxygen atoms. Its schematic view is shown in Fig. 1.

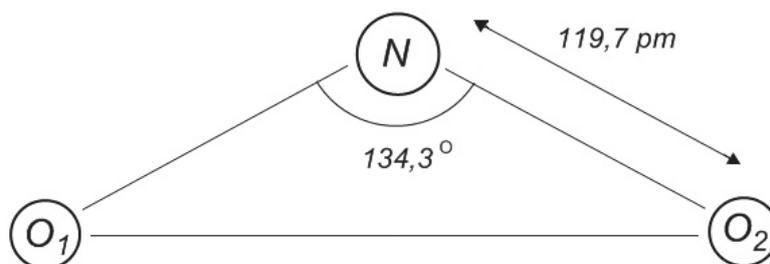


Fig. 1. Scheme of nitrogen dioxide molecule

The oxygen atoms are linked with the nitrogen atom by covalent chemical bonds, each bond involving two electrons (in the figure, the bonds are shown by lines). The equilibrium length of the $N - O$ bond makes 1.197 \AA . The valence angle (angle between valence bonds) is equal to 134.3° [4]. The $N - O$ bond energy is determined to be 112 kcal/mole [7]. This energy is also called the dissociation energy, because its excess leads to bond breaking, and that corresponds to the molecule dissociation.

DETERMINATION OF FICTITIOUS $O - O$ BOND COEFFICIENT AND VM PARAMETERS

Similarly to ref. [4], we consider a planar (two-dimensional) model of nitrogen dioxide molecule. We shall represent the atoms by point masses, denoting the nitrogen atomic mass by m_N , and the oxygen atomic mass by m_O . In the equilibrium state, the oxygen atoms are situated at the ends of the base of the isosceles triangle, and the nitrogen atom is found at the vertex of the angle formed by its lateral sides. We introduce the notation a_{NO} and a_{OO} , which correspond to the equilibrium distance between the nitrogen atom and the oxygen atom, and between oxygen atoms, respectively.

In the centre-of-mass system (C.M.S.) the equations of motion for the molecule atoms being in the external electromagnetic field are written as

$$\begin{cases} m_O \frac{d^2 \vec{R}_{O_1}}{dt^2} = \vec{F}_{O_1} + \vec{F}_{O_1 N} + \vec{F}_{O_1 O_2}, \\ m_N \frac{d^2 \vec{R}_N}{dt^2} = \vec{F}_N + \vec{F}_{NO_1} + \vec{F}_{NO_2}, \\ m_O \frac{d^2 \vec{R}_{O_2}}{dt^2} = \vec{F}_{O_2} + \vec{F}_{O_2 N} + \vec{F}_{O_2 O_1}. \end{cases} \quad (1)$$

Here $\vec{R}_N = \{X_N, Y_N\}$, $\vec{R}_{O_1} = \{X_{O_1}, Y_{O_1}\}$ and $\vec{R}_{O_2} = \{X_{O_2}, Y_{O_2}\}$ are the radii-vectors of nitrogen and oxygen atoms, drawn from the centre of mass; $\vec{F}_N, \vec{F}_{O_1}, \vec{F}_{O_2}$ are the vectorial forces of electromagnetic field action on nitrogen and oxygen atoms; $\vec{F}_{O_1 N}, \vec{F}_{NO_1}, \vec{F}_{O_2 N}, \vec{F}_{NO_2}, \vec{F}_{O_1 O_2}, \vec{F}_{O_2 O_1}$ are the vectorial action forces of atoms indicated by the first on the atoms indicated by the second.

We suppose that the electromagnetic field can be described by a monochromatic wave propagating in the assigned direction, and take into consideration only the electric field strength. Since the treatment is carried out in the C.M.S., and the molecule is immobile, then the total action of the electric field strength on the molecule equals zero. In this case, the following equalities may be considered as fulfilled for the moduli of external forces:

$$|\vec{F}_{O_1}| = |\vec{F}_{O_2}| = -\frac{1}{2} |\vec{F}_N| \equiv |F|. \quad (2)$$

The external force direction \vec{F} is given by the unit vector \vec{e} : $\vec{F} = |\vec{F}| \cdot \vec{e}$, and the force value is given by the relation: $|\vec{F}| \approx d' \cdot E(t)$, where d' is the derivative of the dipole $N-O$ bond moment with respect to the interatomic distance, $E(t)$ is the electric field strength amplitude prescribed externally.

For intramolecular forces the relationship $\vec{F}_{AB} = -\vec{F}_{BA}$ is valid.

We now determine the intramolecular force values proceeding from the assumption that the forces are paired and central. The assumption corresponds to the Morse potential representation of the interaction force field [8]

$$\Pi_{AB}(\vec{r}) = D_{AB} \left(\exp(-2\alpha_{AB}(r - a_{AB})) - 2\exp(-\alpha_{AB}(r - a_{AB})) \right), \quad (3)$$

where $D_{AB} = D_{BA}$ is the binding energy between the atoms A and B , $a_{AB} = a_{BA}$ is the equilibrium distance between them, $\alpha_{AB} = \alpha_{BA}$ is the parameter describing the width of potential well.

Using eq. (3) we can determine the value and direction of force between the atoms A and B :

$$\vec{F}_{AB} = -\frac{d}{dr} \Pi_{AB}(\vec{R}_A - \vec{R}_B) \frac{\vec{R}_A - \vec{R}_B}{|\vec{R}_A - \vec{R}_B|}. \quad (4)$$

The analysis of a linearized set of equations (1) in the absence of the external electromagnetic field and with due regard for eq. (4) leads to the following equations for the eigenfrequencies [4]:

$$(2m_N a_{ON}^2 + m_O a_{OO}^2) C_{ON} - 2m_N m_O a_{ON}^2 \omega^2 = 0 \quad (5)$$

$$\begin{aligned} 2a_{ON}^2 m_N m_O^2 \omega^4 + (m_O^2 a_{OO}^2 C_{ON} - 4m_O^2 a_{ON}^2 C_{ON} - 4m_N m_O a_{ON}^2 C_{OO} - \\ - 2m_N m_O a_{ON}^2 C_{ON}) \omega^2 + 4m_N a_{ON}^2 C_{ON} C_{OO} + 8m_O a_{ON}^2 C_{ON} C_{OO} - \\ - m_N a_{OO}^2 C_{ON} C_{OO} - 2m_O a_{OO}^2 C_{ON} C_{OO} = 0, \end{aligned} \quad (6)$$

where $C_{AB} = 2\alpha_{AB}^2 D_{AB}$ are the stiffness factors of molecule bonds.

If in eqs. (5), (6) all the parameters were prescribed, then it would be possible to determine from them the eigenfrequencies of antisymmetric ω (eq. (5)) and symmetric $\omega_s^{(1)}$, $\omega_s^{(2)}$ (eq. (6)) molecular oscillations.

However, in our case we have only the experimentally measured eigenfrequencies, molecular dimensions a_{NO} , a_{OO} and the bond energy D_{NO} . Their values are listed in Table 1 [5, 7, 9].

Table 1.

Equilibrium parameters of the nitrogen dioxide molecule			
Parameter	Notation	Values	
		SI units	Hartree units
Nitrogen atomic mass	m_N	$2.325 \cdot 10^{-26}$ kg	25529
Oxygen atomic mass	m_O	$2.657 \cdot 10^{-26}$ kg	29176
N-O bond dissociation energy	D_{ON}	$7.781 \cdot 10^{-19}$ J	0.179
N-O bond equilibrium distance	a_{ON}	$1.190 \cdot 10^{-10}$ m	2.249
O-O bond equilibrium distance	a_{OO}	$2.190 \cdot 10^{-10}$ m	4.138
Antisymmetric vibration frequency	$\omega_0 \equiv \omega_a$	1618 cm^{-1}	$7.37 \cdot 10^{-3}$
Symmetric vibration frequency	$\omega_1 \equiv \omega_s^{(1)}$	1318 cm^{-1}	$6.00 \cdot 10^{-3}$
	$\omega_2 \equiv \omega_s^{(2)}$	750 cm^{-1}	$3.42 \cdot 10^{-3}$

Provided that the parameters $C_{ON} \cdot m_O^{-1}$, $C_{OO} \cdot m_O^{-1}$ are prescribed, the set of equations (5), (6) unambiguously determines the eigenfrequencies as $\omega = \omega_i$, where $i = 0; 1; 2$. If, however, the eigenfrequencies are measured experimentally, then, as it may seem at first glance, their substitution into the initial set would permit the calculation of the lacking values of the parameters $C_{ON} \cdot m_O^{-1}$, $C_{OO} \cdot m_O^{-1}$. Precisely these calculations have been made in [4]. However, this has resulted in the negative value of the stiffness coefficient C_{OO} . That obtained result is unphysical, and any changes in the model (transition from the linear spring to the angular) call for the change of the model as a whole.

To eliminate this discrepancy, we use the following approach [10].

Since the eigenfrequencies have been observed and measured for the real molecule, for the transition from its three-dimensional model to the planar one some parameters must be renormalized, i.e., they should be changed so that eqs. (5), (6) should become jointly. As a result of these manipulations, the parameters of the two-dimensional VM would be determined, with the use of which the processes in the real molecule could be modeled.

For this purpose we assume the eigenfrequencies ω_i in eqs. (5), (6) be prescribed, and the parameters that have to

be determined (i.e., their new values should be found (renormalized)), will be put to be $x = \frac{m_O}{m_N}$; $y = \frac{1}{2} \left(\frac{a_{OO}}{a_{NO}} \right)^2$. In

this case, the stiffness factors $C_{OO} \cdot m_O^{-1}$ and $C_{ON} \cdot m_O^{-1}$ are expressed in terms of the eigenfrequencies x, y in the following way:

$$G_{ON} \equiv C_{ON} \cdot m_O^{-1} = \frac{\omega_0^2}{1 + xy}, \quad (7)$$

$$G_{OO} \equiv C_{OO} \cdot m_O^{-1} = \frac{1}{2} (\omega_0^2 + \omega_1^2 + \omega_2^2) - \frac{1+x}{1+xy} \omega_0^2. \quad (8)$$

Transforming eq.(6) with regard for eqs. (7), (8), it is not difficult to derive the required equation, which relates the renormalized parameters x and y :

$$Z^2(x, y) - Z(x, y)(1+x)(1+y) + 1 + x(2-y) - \left(\frac{1+xy}{2} \right)^2 \left(\left(\frac{\omega_1}{\omega_0} \right)^2 - \left(\frac{\omega_2}{\omega_0} \right)^2 \right)^2 = 0, \quad (9)$$

$$\text{where } Z(x, y) = \frac{1+xy}{2} \left(1 + \left(\frac{\omega_1}{\omega_0} \right)^2 + \left(\frac{\omega_2}{\omega_0} \right)^2 \right) - x - 1.$$

Figure 2 shows the graphs of y and stiffness factors (7), (8) versus x , obtained with the help of eq. (9).

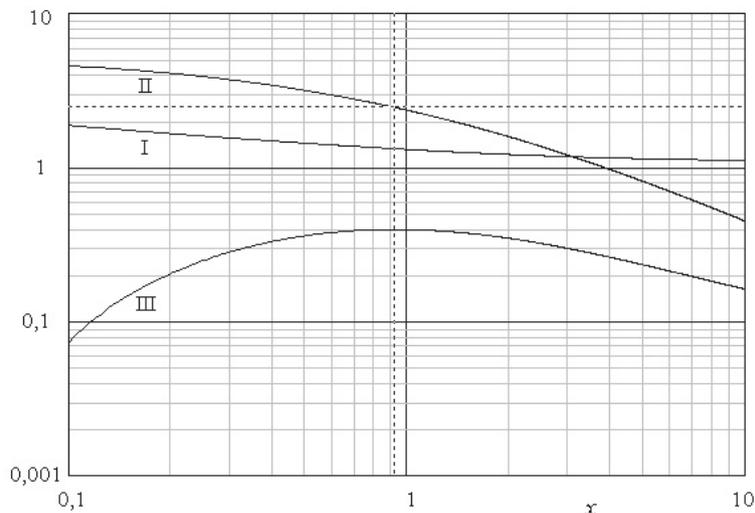


Fig. 2. Solution of eq. (9) for y versus x , curve I. Curves II and III show the molecule stiffness factors ($G_{ON} \cdot 10^5$ and $G_{OO} \cdot 10^5$, respectively) as functions of the parameter x .

It follows from the calculations that the $O-O$ bond stiffness has its maximum $C_{OO} = 0.115$ at $x = 0.92$. Therefore, in further estimations we shall use the VM parameters, which correspond to the peak value of the $O-O$ bond stiffness factor.

For unambiguous determination of the nitrogen dioxide VM parameters we consider the parameters m_O and a_{OO} as being prescribed. In this case the VM parameter values can be summarized in the table (Table 2). The table also gives the width values of potential wells $\alpha_{AB} = \sqrt{C_{AB} (2D_{AB})^{-1}}$ in the Morse representation. Note that to calculate the unknown width of the $O-O$ bond potential well, we assume the relation $D_{OO} \approx 0.2 \cdot D_{ON}$ to be true [4].

Table 2.

VM parameters		
Nitrogen atomic mass (renormalized)	m_N^*	31713
Oxygen atomic mass	m_O	29176
$N-O$ bond stiffness factor	C_{NO}	0.715
$O-O$ bond stiffness factor	C_{OO}	0.115
Equilibrium length of the $N-O$ bond (renormalized)	a_{NO}^*	2.663
Equilibrium length of the $O-O$ bond	a_{OO}	4.138
Width of potential well for the $N-O$ bond	α_{ON}	1.413
Width of potential well for the $O-O$ bond	α_{OO}	1.267
Valence angle	ψ	108.808°

LINEAR DYNAMICS OF VM ATOMS IN THE FIELD OF MONOCHROMATIC ELECTROMAGNETIC WAVE

We write down the external force created by the electromagnetic wave field, which exerts action on the molecule atoms, as

$$\vec{F} = d' \cdot E(t) \cdot \vec{e} \equiv d' \cdot E_0 e^{-i(\omega t + \theta)} \cdot \vec{e}, \quad (10)$$

where E_0, ω, θ are, respectively, the amplitude, frequency and control phase of the electric field strength of the wave.

Let us investigate the linear response of the molecule to the action of the external electromagnetic field. To this end, we derive the equation describing the temporal variation of the bond lengthening $X_{O_1N} \equiv \delta \vec{R}_{O_1} \cdot \vec{e}_{O_1N}$, which characterizes small deviations of the oxygen atom O_1 (see Fig. 1) from the equilibrium position along the $N-O_1$ bond. In this case it is necessary to use the VM parameters presented in Table 2.

Since in the proposed model the atoms of nitrogen dioxide molecule are described by the triangle with the corresponding stiffness coefficients, to estimate the dynamic strength of this structure, it will suffice to have information about the lengthening of one of the bonds, e.g., $N-O_1$.

After linearization of the initial set of equations (1), assuming the peak value of force $F_d(t) \equiv d' \cdot E_0(t)$ to be the function weakly dependent on time ($\frac{dE_0}{dt} \ll \omega E_0$), we obtain the equation that describes the temporal variation of the bond lengthening X_{O_1N} under the action of the external field with the frequency ω_0 :

$$\frac{d}{dt} X_{O_1N} = -\frac{F_d}{2} \frac{C_{ON} \left(1 + 2 \frac{m_0}{m_N^*}\right)}{m_0^2 \omega_0^3} \cos \varphi_0 \cos \varphi, \quad (11)$$

where $\varphi_0 \approx 35.596^\circ$ is the renormalized angle at the base of the molecule, φ is the angle between the external force direction and the O_1-O_2 direction, t is the time in Hartree units, $\theta = -\pi/2$.

It is not hard to show that the lengthening of oxygen bonds with other atoms of the molecule is determined through X_{O_1N} in the following way:

$$\begin{aligned} \delta \vec{R}_{O_1} \cdot \vec{e}_{O_2N} \gamma^{-1} &= \delta \vec{R}_{O_1} \cdot \vec{e}_{O_1O_2} \beta^{-1} = -\delta \vec{R}_{O_2} \cdot \vec{e}_{O_1N} \gamma^{-1} = -\delta \vec{R}_{O_2} \cdot \vec{e}_{O_2N} = \delta \vec{R}_{O_2} \cdot \vec{e}_{O_1O_2} \beta^{-1} = \\ &= \delta \vec{R}_{O_1} \cdot \vec{e}_{O_1N}, \end{aligned} \quad (12)$$

where $\beta = \frac{a_{OO}}{2a_{NO}^*} \approx 0.78$, $\gamma = 1 - \frac{1}{2} \left(\frac{a_{OO}}{a_{NO}^*} \right)^2 \approx -0.21$.

From eq. (11) it follows that the $N-O_1$ bond length increases linearly with time at the angles of action $\pi/2 < \varphi < 3\pi/2$. The length of other bonds also changes with time by the linear law in accord with relations (12).

Thus, the presence of secular regimes in eq. (11), which result from the action of the external electromagnetic field on the molecule at a resonance frequency, points to the adequacy of the proposed model to the physical processes, which are to take place in the real molecule.

Since the linear dynamics of the molecule displays its resonant properties, it appears of interest to retrace the VM behavior at great atomic displacement amplitudes, i.e., to investigate VM nonlinear oscillations up to the bond breaking.

NONLINEAR DYNAMICS AND DISSOCIATIVE MODES OF THE VM IN THE MONOCHROMATIC ELECTROMAGNETIC WAVE FIELD

Nonlinear dynamics of the VM

The investigation on the VM nonlinear dynamics in external fields must be started from the adjustment of nonlinear oscillations of a free molecule, i.e., from initial data fitting in the original equations (1) in the absence of external fields. As a result of this adjustment, the VM oscillation spectrum must comprise eigenfrequencies ω_i . In this case, the initial arrangement of VM atoms must be in accord with the linear theory.

The numerical calculation data on the temporal change of VM atom coordinates as well as their spectral resolution are presented in Figs. 3, 4. It follows from these figures that with time the molecular atoms fit into the parameters of the Morse potential, i.e., oxygen atoms oscillate relative to the points with the coordinates $X_{O_1, O_2} \approx \pm 2.12$; $Y_{O_1, O_2} \approx -0.5$, and the nitrogen atom oscillates relative to the point with the coordinates $X_N \approx 0.0$; $Y_N \approx 0.92$.

The VM oscillation spectrum intensity I_Ω was obtained by the use of a fast Fourier transform of atomic displacement projections in the x, y coordinates, calculation of their arithmetic mean and a subsequent moving average smoothing (see Fig. 4). For identification of peaks of the thus obtained spectrum we make use of the fact that the maximum resonance frequency Ω_0 should have the peak intensity (Very Strong), and the lowest frequency Ω_2

should have a lower intensity (Strong) [11].

In view of the above, the spectrum analysis permits us to separate the following resonance frequencies of VM oscillations: $\Omega_0 \approx 0.2$, $\Omega_1 \approx 0.16$, $\Omega_2 \approx 0.09$, which, with an appropriate choice of a new oxygen atomic mass m'_0 , are equivalent to the eigenfrequencies ω_i (from the form of expressions (7)-(9) it follows that the new mass m'_0 must satisfy the relationship $\Omega_i^2 m'_0 = \omega_i^2 m_0$).

So, the data given in Fig. 4, show that the proposed model adequately describes nonlinear nitrogen dioxide molecular oscillations: the eigenfrequencies of VM oscillations correspond to the frequencies of symmetrical and antisymmetrical oscillations of real nitrogen dioxide.

VM dissociative modes in the field of a monochromatic electromagnetic wave

Let us investigate the dissociative modes of the VM in the fields of external electromagnetic radiations. For this purpose, it is necessary that at the moment of VM eigenfrequencies setting the external force should be switched on. The force value is determined by expression (10), where the control phase may equal zero, and the force direction is prescribed by the unit vector \vec{e} .

As it follows from the calculations, at the moment of external force switch on, the molecule atoms oscillate in the neighborhood of vertices of the isosceles triangle with the coordinates $X_{O1,02} \approx \pm 2.12$; $Y_{O1,02} \approx -0.5$; $X_N \approx 0.0$; $Y_N \approx 0.92$. This state of the VM will be characterized as equilibrium.

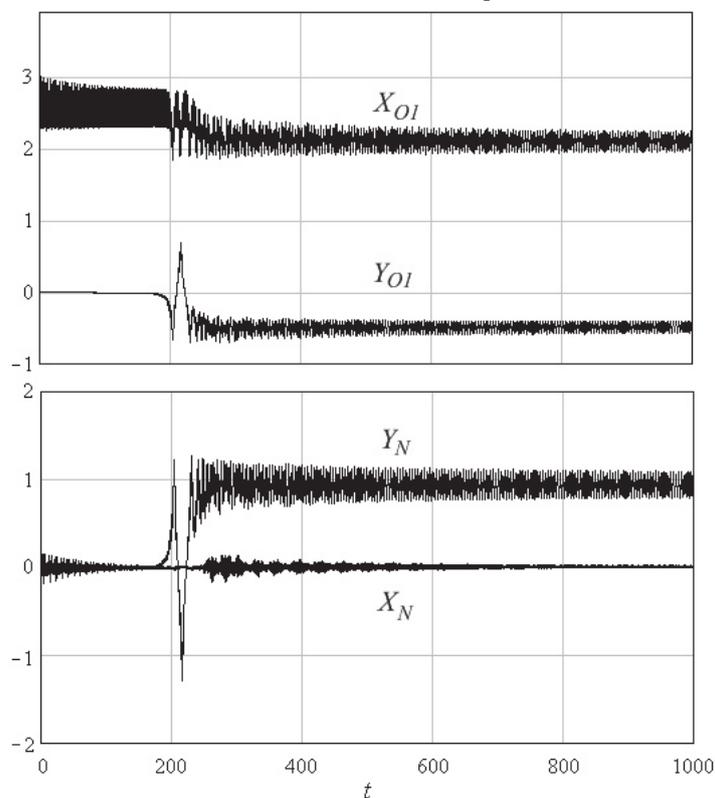


Fig. 3. Coordinates of oxygen and nitrogen atoms in the molecule versus time t .

In numerical calculations, the harmonic component of the external force is prescribed in the form of $\sim F \cdot \sin(\Omega t)$, where the amplitude F varies in the range $0 \leq F \leq 3$, and the angle of force action φ ranges within $0 \leq \varphi \leq 2\pi$. The real external force value in the Hartree units, F_X is related to the force F by $F_X = F \cdot 1.818 \cdot 10^{-6}$.

In calculations, we shall assume that an increase in the $O-O$ or $N-O$ bond length by more than two times leads to bond breaking. And if one takes into account that all the calculations are carried out in the C.M.S., then the breaking of one of the bonds gives such a reactive force to the other VM atoms, that it inevitably results in the VM dissociation as a whole. This conclusion is confirmed by numerical simulation, too.

The main question of numerical simulation of VM dynamics in the field of external forces consists only in what bond will be the first to break and at what conditions. The answer to this question is given by numerical simulation of atom dynamics of the triatomic VM in the field of the external electromagnetic wave.

Figures 5 to 8 show the numerical simulation results for VM bond dissociation versus the F amplitude and the

angle of action of the external force, φ , specified by both the electromagnetic wave (Figs. 5 to 7) and the stationary electric field (Fig. 8). In the figures, the bottom plane specifies the parameters of the $O-O$ bond breaking, and the top plane – $N-O$ bond breaking. The areas in the planes, marked by small squares with a side length of 0.1, correspond to these bond breakings. The angle $\varphi_0 \approx 0.188 \cdot \pi$ corresponds to the angle at the base of the equilibrium VM.

The data presented in Figs. 5 to 8 are characterized by the periodicity in the angle of external force action φ .

From Figs. 5 to 7 it follows that for all resonance frequencies the bond dissociation does not take place at the external force lower than a certain value $F \leq 0.5 \div 0.8$, the range of this value being dependent on the angle φ .

At $F > 0.8$, the change in the frequency of the external electromagnetic field gives no resonance effects specified by the presence of dedicated frequencies of the molecule. This may be due to a strong nonlinear link of atoms in the molecule, when linear connections cannot manifest themselves. The observed correlation of minimum forces F , leading to breaking of $O-O$ and $N-O$ bonds, can also be attributed to a strong nonlinear link of atoms in the molecule.

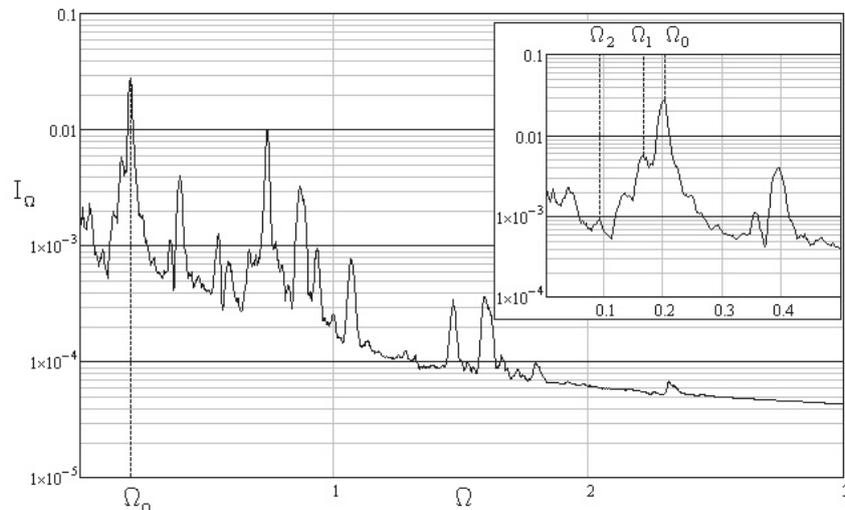


Fig. 4. Averaged and smoothed intensities I_{Ω} of the oscillation spectrum of nitrogen dioxide VM atoms. After appropriate transformations, the peaks, marked with dashed lines, coincide with resonant frequencies of the real nitrogen dioxide molecule ω_l .

From Figs. 5 to 7 it can be seen that at $F > 1.3$ the $N-O$ bond breaking always takes place, whereas the $O-O$ bond may exhibit the stability islands. This is particularly evident for the resonance frequency Ω_0 , which is characterized by the maximum amplitude of oscillations.

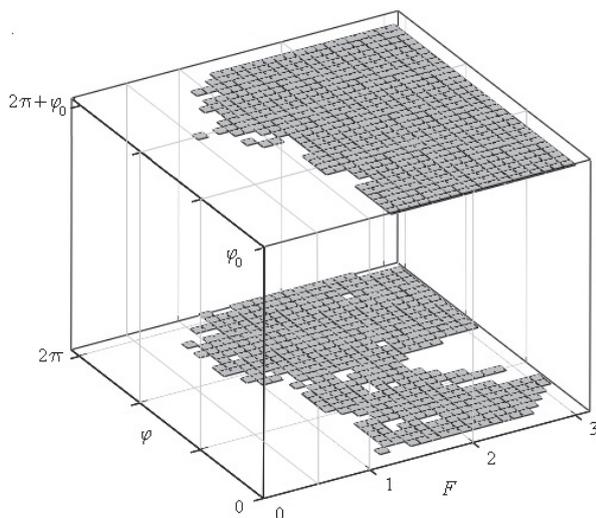


Fig. 5. Electromagnetic field frequency Ω_0 .

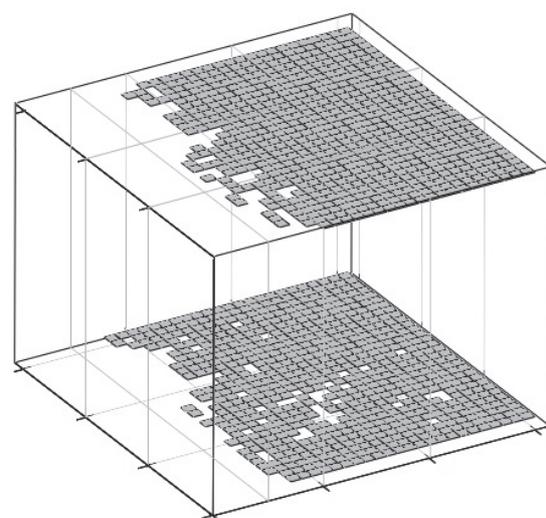


Fig. 6. Electromagnetic field frequency Ω_1 .

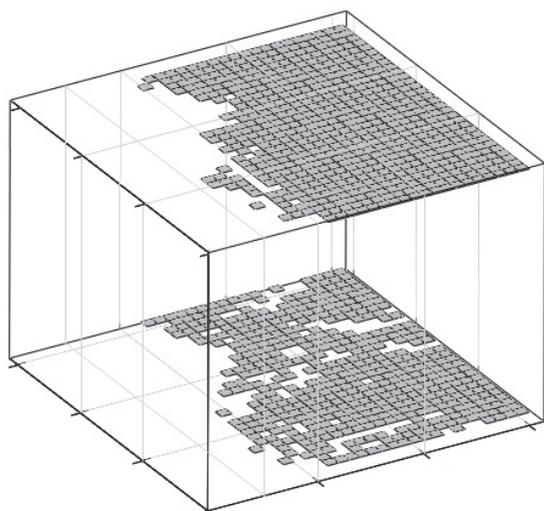
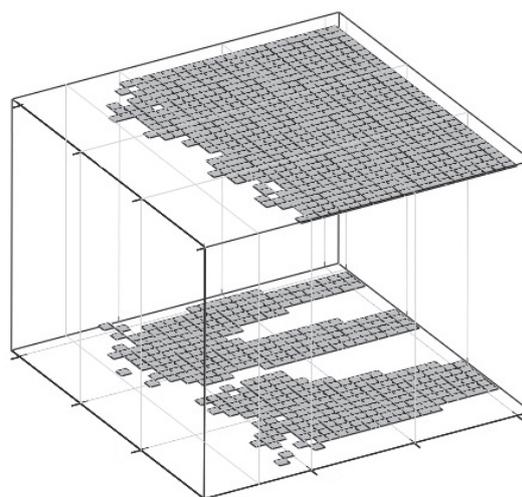
Fig. 7. Electromagnetic field frequency Ω_2 .

Fig. 8. The electromagnetic field is constant.

Since the VM dissociation occurs at breaking of any bond, it is of interest to find the optimum parameters of dissociation, viz., the minimum force and the corresponding to it angle of action on the molecule.

The numerical simulation data on the optimum parameters of dissociation are presented in Table 3.

Table 3.

Optimum VM dissociation parameters

Electromagnetic wave field of the frequency Ω	Force F	Angle of action φ
Ω_0	0.6	$2\pi(2/3) \leq \varphi \leq 2\pi(21/30)$
Ω_1	0.7	$2\pi(7/30) \leq \varphi \leq 2\pi(3/10)$ $2\pi(11/30) \leq \varphi \leq 2\pi(2/5)$ $2\pi(13/30) \leq \varphi \leq \pi$
Ω_2	0.7	$2\pi(1/3) \leq \varphi \leq 2\pi(2/5)$
Constant field	0.6	$2\pi(23/30) \leq \varphi \leq 2\pi(4/5)$

CONCLUSIONS

Thus, we have proposed the model for description of the real nitrogen dioxide molecule by its two-dimensional analog, namely, the virtual molecule (VM). In the proposed VM model, the condition of coincidence between the eigenfrequencies of the molecule and its analog is provided. The other VM parameters (bond length and atomic mass) are renormalized so that the molecule should steadily exist for a long time interval.

Linear dynamics of VM atoms in the field of a monochromatic electromagnetic wave has been investigated. It has been shown that under the action of an external electromagnetic field on the molecule at a resonance frequency, secular regimes of oscillations are observed. The last ones are characterized by a time-linear growth of atomic oscillation amplitudes. The increase in the atomic oscillation amplitudes places the molecule in the nonlinear regime. Under these conditions, the dynamics of VM atoms in the field of the monochromatic electromagnetic wave causing the VM dissociation can be investigated only by the numerical simulation method. To this end, after the VM eigenfrequencies settled, the action of the external force on the molecule dissociation was investigated. It has been demonstrated that in some cases the breaking of one of VM bonds inevitably leads to the VM dissociation as a whole. As a result of numerical simulation, it has been established that the bond breaking has a threshold character, i.e., dissociation is not observed at the external force, which is lower than a certain value of $F \leq 0.5 \div 0.8$. The range of external force variations depends on the angle of external action φ . In the range of forces exceeding the threshold values, $F > 0.8$, the variation in the external electromagnetic field frequency is insensitive to the resonance effects that are due to the presence of dedicated frequencies of the VM. It has been demonstrated that at $F > 1.3$ the $N-O$ bond breaking always takes place, whereas the $O-O$ bond may exhibit stability islands. Optimum parameters of VM dissociation have been determined.

REFERENCES

1. Zewail A.H. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. Feature article //J. Phys. Chem. A 2000. – Vol. 104. - P. 5660-5694.
2. The Encyclopedia of Earth. <http://www.eoearth.org>.
3. Ivanova E.A., Krivtsov A.M. Polyatomic molecule energy control. In collected book: Control in physical-technical systems. - St. Petersburg: Nauka publ., 2004. - P. 197 – 212. (In Russian).
4. Volkovets I.B., Yefimov A.A., Krivtsov A.M., Tkachev P.V. //Trudy SPbGPU. - 2004. - № 489. – S. 152-161.
5. Melen F., Herman M. Vibrational Bands of $H_xN_yO_z$ Molecules //J. Phys. Chem. Ref. Data. - 1992. - Vol. 21, № 4. - P. 831 – 881.
6. United States Patent Number 4936961, Jun. 26, 1990.
7. Nekrasov B.V. Principles of general chemistry. - Vol. 1. – Moscow: Khimiya publ, 1973. - 656 p. (In Russian)
8. Morse P.M. Diatomic molecules according to the wave mechanics. II. Vibrational levels //Phys. Rev. – 1929. - Vol. 34. - P. 57-64.
9. Remy H. Inorganic Chemistry. - Vol. 1. – Moscow: Foreign Literature Publishing House, 1963. - 920 p. (Russian translation).
10. Borts B.V., Tkachenko V.I. Modeling of triatomic molecule dissociation in external radiation fields in terms of virtual molecule analog. //Proceedings of the XIX International Conference on Physics of Radiation Phenomena and Radiation Materials Science, 06-11 September, 2010, Alushta, Crimea, pp. 392-394. (In Russian).
11. Harris L., King G.W. The Infrared Absorption Spectra of Nitrogen Dioxide and Tetroxide //J. Chem. Phys. – 1934. - Vol. 2, №2. - P. 51 – 57.