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## METASTABLE QUASIMOLECULES IN EXCITED GASES

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UDC 538.9; 538.915; 517.957  
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Quasimolecules which consist of two differently excited atoms in a resonantly excited gas are considered. The energy of dissociation and typical sizes of such molecules are calculated in the first order of quantum-mechanical perturbation theory with the help of a dipole-dipole interaction operator. It is shown that there exist metastable quasimolecules, for which the dipole radiative transition to the ground state (two non-excited atoms) is forbidden. The lifetime of such molecules is estimated. Those quasimolecules can appreciably affect the transport processes in resonantly excited gases.

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### 1. Introduction

As is well known [1], the interaction energy between atoms which do not form stable molecules, can be calculated by means of quantum-mechanical perturbation theory using a dipole-dipole interaction operator. Particularly, the interaction between atoms in the ground state is described with the help of the van-der-Waals potential

$$U_{VW}(R) = -\frac{\text{const}}{R^6}, \quad R \gg a,$$

where  $R$  is a distance between the atoms, and  $a$  is a typical size of an atom. The potential  $U_{VW}(R)$  is obtained in the second order of perturbation theory and always corresponds to attraction. The above-mentioned forces are the so-called van-der-Waals forces which form a relatively shallow potential well (approximately  $10^{-3}$  eV for  $\text{He}_2$  [2] and  $2 \cdot 10^{-2}$  eV for  $\text{Kr}_2$  [3] that corresponds to temperatures of the order of 10 and 200 K, respectively), so that the formation of stable

molecules in such gases at room temperature does not happen.

The situation changes cardinally if one of the atoms is in an excited state, from which the dipole transition to the ground state is possible. In this case, the dipole-dipole interaction operator gives a non-zero contribution even in the first order of perturbation theory due to the fact that non-perturbed wave functions must take into account the exchange of excitations between the atoms. The transition of the excitation from one atom to another in this case replaces the exchange interaction which leads to the chemical valence. Such an interaction between the atoms is conventionally called a resonance interaction. It is described with the help of the potential

$$U_R(R) = \pm \frac{\text{const}}{R^3}$$

and can have a character of not only attraction, but also repulsion.

The dissociation energies of bound states, which can be formed at the expense of the resonance dipole-dipole interaction, appear to be of the order of 1 eV according to the below-presented estimations. This means that quasimolecules which consist of atoms in the ground and excited states can be formed at room temperature. It should be emphasized that a relatively large energy of the resonance interaction is related, as mentioned above, to the exchange of excitations between the identical atoms which is realized through the dipole-dipole interaction operator.

It is worth noting that, in the case of differently excited identical atoms, when the dipole transitions from excited states to the ground state are forbidden, the formation of quasimolecules (so-called excimers)

is also possible [4]. In contrast to resonantly excited quasimolecules, when the attractive part of the potential energy of the interaction as a function of  $R$  can be calculated analytically, the potential energy curves of the molecular states of excimer molecules, as known, can be calculated only with the help of numerical methods.

The presence of even relatively low concentrations of resonantly excited molecules can essentially affect the collective properties of excited gases and plasma. The thermodynamic functions of resonantly excited gases were firstly considered in [5]. Quasimolecules of two differently excited one-electron atoms in such gases were discussed in [6], and the role of quasimolecules in resonantly excited gases was considered in [7].

The purpose of the present paper is an analytical calculation of the long-range part of the potential energy curves of molecular states of the resonantly excited quasimolecules of identical atoms with the closed electron shells and atoms with one valence electron, which do not form stable molecules in the ground state at room temperature. We are also show that a radiative transition of resonantly excited quasimolecules to the ground state (two non-excited atoms) is forbidden in the dipole approximation. Therefore, the considered quasimolecule is metastable and its lifetime appears to be of the order of  $10^{-5}$  s.

## 2. Quasimolecule of Helium $\text{He}_2^*$

Consider an interaction of two helium atoms, one of which is in the ground state, while another is in the excited  $P$ -state. Let us denote the nuclei of these atoms as A and B and assume that the distance between them equals  $R$ . We will use two coordinate systems, which describe the electrons of the atoms, and match their origins with the corresponding nuclei (A and B). Next, we direct the  $z$  axes of these coordinate systems along the line, which connects these nuclei. Further, we denote the electrons which belong to the first atom (nucleus A) by means of indices 1, 2. The electrons which belong to the second atom (nucleus B) are denoted by indices 1', 2'.

The electron wave function of atom A (in the ground state) calculated with the help of the variational method looks like [8]

$$\Psi(1, 2) = \frac{\alpha^3}{\pi a^3} e^{-\alpha \frac{r_1+r_2}{a}}, \alpha = 27/16, \quad (1)$$

and represents the product of two hydrogen-like wave functions for each electron in the field of the nucleus

with an effective charge  $Z = \alpha$  :

$$\tilde{\psi}_0(r) \equiv |\tilde{0}\rangle = \frac{\alpha^{3/2}}{\sqrt{\pi} a^{3/2}} e^{-\alpha \frac{r}{a}}. \quad (2)$$

Here and further,  $a$  designates the Bohr's radius

$$a = \frac{\hbar^2}{m_e e^2} \simeq 0.529 \text{ \AA}. \quad (3)$$

We take the electron wave function of the excited  $P$ -state of a helium atom in the form of an antisymmetrized product of the hydrogen-like wave functions of an  $S$ -electron in the field of the nucleus with charge  $Z = 2$  and  $P$ -electron in the field of the atomic residue with charge  $Z = 1$  [8]:

$$\Psi(1', 2') = \frac{1}{\sqrt{2}} [\psi_0(1')\varphi_i(2') \pm \psi_0(2')\varphi_i(1')], \quad i = x, y, z, \quad (4)$$

where

$$\psi_0(r) \equiv |0\rangle = \frac{\beta^{3/2}}{\sqrt{\pi} a^{3/2}} e^{-\beta \frac{r}{a}}, \quad \beta = 2, \quad (5)$$

and

$$\begin{cases} \varphi_x(\mathbf{r}) \equiv |x\rangle = R_{n1}(r) \sqrt{\frac{3}{4\pi}} \sin \theta \cos \varphi, \\ \varphi_y(\mathbf{r}) \equiv |y\rangle = R_{n1}(r) \sqrt{\frac{3}{4\pi}} \sin \theta \sin \varphi, \\ \varphi_z(\mathbf{r}) \equiv |z\rangle = R_{n1}(r) \sqrt{\frac{3}{4\pi}} \cos \theta. \end{cases} \quad (6)$$

The degenerated wave functions (6) are chosen so that they are transformed as vector components at rotations of a coordinate system.

Henceforth, we restrict ourselves by the description of the interaction of atoms in the dipole-dipole approximation. As is well known [5], a resonance interaction (between atoms in the ground and excited states) is inversely proportional to  $R^3$  and can be shown to be the most intensive for low-excited states. Therefore, we will consider the lowest excited  $P$ -state with the principal quantum number  $n = 2$ , for which

$$R_{21}(r) = \frac{2}{\sqrt{3}} \frac{\gamma^{5/2}}{a^{3/2}} \frac{r}{a} e^{-\gamma \frac{r}{a}}, \quad \gamma = \frac{1}{2}. \quad (7)$$

A wave function in the zero-order approximation is a linear combination

$$\Psi(1, 2, 1', 2') = \sum_{i=1}^{12} C_i \psi_i(121'2') \quad (8)$$

of the following 12 wave functions:

$$|\tilde{0}\tilde{0}0x\rangle, |\tilde{0}\tilde{0}x0\rangle, |0x\tilde{0}\tilde{0}\rangle, |x0\tilde{0}\tilde{0}\rangle, \quad (9)$$

$$|\widetilde{000}y\rangle, |\widetilde{00}y0\rangle, |0y\widetilde{00}\rangle, |y0\widetilde{00}\rangle, \quad (10)$$

$$|\widetilde{000}z\rangle, |\widetilde{00}z0\rangle, |0z\widetilde{00}\rangle, |z0\widetilde{00}\rangle. \quad (11)$$

The wave functions (9)–(11) are products of the one-particle wave functions (2), (5), and (6) with the electron coordinates taken in the sequence 121'2'. For instance,  $\psi_6(121'2') = |\widetilde{00}y0\rangle = \widetilde{\psi}_0(r_1)\widetilde{\psi}_0(r_2)\varphi_y(\mathbf{r}_{1'})\psi_0(r_{2'})$ .

The interaction operator in the dipole-dipole approximation has a form

$$V = \frac{(\mathbf{d}_1 + \mathbf{d}_2)(\mathbf{d}_{1'} + \mathbf{d}_{2'}) - 3(\mathbf{d}_1 + \mathbf{d}_2, \mathbf{n})(\mathbf{d}_{1'} + \mathbf{d}_{2'}, \mathbf{n})}{R^3}, \quad (12)$$

where  $\mathbf{n} = \mathbf{R}/R$ , and the dipole moments of electrons in “their own” coordinate systems are equal to

$$\mathbf{d}_{1,2} = -e\mathbf{r}_{1,2}, \quad \mathbf{d}_{1',2'} = -e\mathbf{r}_{1',2'}. \quad (13)$$

In the first order of the stationary perturbation theory, the secular equation

$$\det|V_{ij} - \Delta E \delta_{ij}| = 0 \quad (14)$$

(the 12-th order determinant) constructed of matrix elements of the interaction operator on functions (9)–(11) breaks into 3 blocks for each of the sets of functions (9)–(11). Namely, for sets (9)–(10), we have

$$\begin{vmatrix} -\Delta E & 0 & A & A \\ 0 & -\Delta E & A & A \\ A & A & -\Delta E & 0 \\ A & A & 0 & -\Delta E \end{vmatrix} = 0, \quad (15)$$

and, for set (11), we have a similar equation with  $-2A$  in the place of  $A$ .

Here, constant  $A$  corresponds to 24 non-zero matrix elements of the dipole-dipole interaction operator on wave functions (9)–(11). Particularly, this value can be calculated as

$$\begin{aligned} A &= \langle \widetilde{00}x0 | V | x0\widetilde{00} \rangle = \frac{1}{R^3} \langle 0 | \widetilde{0} \rangle^2 \langle x | d_x | \widetilde{0} \rangle^2 = \\ &= \frac{e^2}{R^3} \left[ \int dV \frac{(\alpha\beta)^{3/2} e^{-(\alpha+\beta)\frac{r}{a}}}{\pi a^3} \right]^2 \times \\ &\times \left[ \int dV \frac{\alpha^{3/2} e^{-\alpha\frac{r}{a}}}{\sqrt{\pi} a^{3/2}} \varphi_x(r, \theta, \varphi) r \sin \theta \cos \varphi \right]^2 = \\ &= \frac{e^2 a^2}{R^3} \frac{2^{16} \alpha^6 \beta^3 \gamma^5}{(\alpha + \beta)^6 (\alpha + \gamma)^{10}}. \end{aligned} \quad (16)$$

The substitution of the constants  $\alpha = 27/16$ ,  $\beta = 2$ , and  $\gamma = 1/2$  gives

$$A \simeq 0.06 \frac{e^2 a^2}{R^3}. \quad (17)$$

From the secular equation which is reduced to 3 equations of the 4-th order, namely to  $\Delta E^4 - 4A^2 \Delta E^2 = 0$  for  $x, y$ -functions (9), (10) and  $\Delta E^4 - 16A^2 \Delta E^2 = 0$  for  $z$ -functions (11), we obtain the energy of states, into which the 12-fold degenerated energy level of the system of two non-interaction atoms is split:

$$\Delta E = \pm 2A, 0, 0 \quad (18)$$

for  $x, y$ -functions and

$$\Delta E = \pm 4A, 0, 0 \quad (19)$$

for  $z$ -functions.

The 6-fold degenerated level with zero energy and the levels with positive energies ( $+2A$ ,  $+4A$ ) are “dissociable” levels and do not form any bound states. We are interested in the levels with negative energies: the doubly degenerated (in  $x$  and  $y$ ) level with the energy  $-2A$  and the wave function (a linear combination, whose coefficients are eigenvectors of the correspondent secular equation)

$$\Psi_{-2A}^{(x)} = \frac{1}{2} \left( |\widetilde{000}x\rangle + |\widetilde{00}x0\rangle - |0x\widetilde{00}\rangle - |x0\widetilde{00}\rangle \right), \quad (20)$$

$$\Psi_{-2A}^{(y)} = \frac{1}{2} \left( |\widetilde{000}y\rangle + |\widetilde{00}y0\rangle - |0y\widetilde{00}\rangle - |y0\widetilde{00}\rangle \right), \quad (21)$$

and the non-degenerated level with the energy  $-4A$  and the wave function

$$\Psi_{-4A}^{(z)} = \frac{1}{2} \left( |\widetilde{000}z\rangle + |\widetilde{00}z0\rangle + |0z\widetilde{00}\rangle + |z0\widetilde{00}\rangle \right). \quad (22)$$

The eigenvalues (energies) are taken as indices in the wave functions (20)–(22).

According to the classification of the electron levels of diatomic molecules (see, for example, [1]), the considered excited  $P$ -states of a quasimolecule with the energies  $-2A$  and  $-4A$  belong to  ${}^1\Pi_u$  and  ${}^1\Sigma_g$  states, respectively.

Let us now turn our attention to the question of determination of the equilibrium distance  $R$  between the nuclei. By accounting only the long-range dipole-dipole attractive forces, it is impossible to find it. Therefore, one should consider repulsion forces, which are acting at small distances between the atoms. We calculate the

equilibrium distance starting from the following simple model: we accept that the electron shells of two atoms are not deformed by the interaction, and the equilibrium distance is attained when the maxima of their electronic probability densities are in contact with one another (notice that even this configuration corresponds to an essential overlapping of wave functions).

The maximum of the electron probability density of a helium atom in the ground state can be found from the equation

$$\frac{d}{dr} \left( r^2 \tilde{\psi}_0^2(r) \right) = \frac{d}{dr} \left( \frac{\alpha^3}{\pi a^3} r^2 e^{-2\alpha \frac{r}{a}} \right) = 0, \quad (23)$$

wherefrom

$$r_{\max} = a/\alpha = 16/27 a \simeq 0.6 a. \quad (24)$$

Similarly, we find the maximum of the electron probability density of a helium atom in the excited  $P$ -state. In this case, the most probable value of  $r$  equals

$$r^* = 4 a, \quad (25)$$

but the wave function also depends on the angle coordinates  $\theta$ ,  $\varphi$ . Taking this into account, we find the distribution for the probability density maximum for the  $x, y$ -wave functions  $|\varphi_{\perp}|^2 = |\varphi_x|^2 + |\varphi_y|^2$  as

$$r_{\max} = r^* \sin^2 \theta = 4 a \sin^2 \theta. \quad (26)$$

From the condition of contact of surfaces (24) and (26), we find the unknown equilibrium distance as

$$R_0^{(x,y)} \simeq 1.203 a, \quad (\theta \simeq 28.4^\circ). \quad (27)$$

Similarly, for  $z$ -functions, we have

$$r_{\max} = r^* \cos^2 \theta = 4 a \cos^2 \theta, \quad (28)$$

wherefrom we get

$$R_0^{(z)} \simeq 4.6 a, \quad (\theta = 0). \quad (29)$$

At last, knowing the equilibrium distances between the nuclei, we can calculate the corresponding binding energies (dissociation energies with an opposite sign)

$$\Delta E^{(x,y)} = -1.875 \text{ eV}, \quad (30)$$

$$\Delta E^{(z)} = -0.067 \text{ eV}. \quad (31)$$

We must emphasize that the total energy of a quasimolecule relative to the energy of non-interacting

helium atoms in the ground state is larger than the calculated dissociation energy by the value [9] (experimental data)

$$\begin{aligned} E(1s2p) - E(1s^2) &\simeq -57.787 \text{ eV} + 79.005 \text{ eV} \simeq \\ &\simeq 21.22 \text{ eV}. \end{aligned} \quad (32)$$

Just this energy must be used in considerations of the radiation energy of quasimolecules (see the next section).

### 3. Lifetime of $\text{He}_2^*$ Quasimolecules

Let us discuss a question about the lifetime of quasimolecules. For such a study, we have to use the radiation theory of molecular systems. The total probability of radiation is written in the form of a perturbation theory series, each member of which represents a multipole radiation of a certain type (electric or magnetic) and order (dipole, quadrupole, etc.). Moreover, it is well known that the increasing of the order of multipolarity by 1 decreases the radiation probability by  $\sim (ka_0)^2$  times, where  $a_0$  is a characteristic size of the radiative system and  $k = 2\pi/\lambda = \omega/c$  is a wave number of the radiated light [10].

In our case of a quasimolecule in the state  $^1\Pi_u$ , the value of  $ka_0$  is of the order of  $10^{-2}$  ( $\hbar\omega \sim 20$  eV,  $a_0 \sim 1$  Å), which gives the decrease of the radiation probability by  $10^4$  times, when we proceed to the radiation with multipolarity by 1 order higher. For example, a characteristic time of the dipole radiation of an excited atom is of the order of  $10^{-9}$  s. In the case where a dipole transition is forbidden, the lifetime increases by 4 orders, i.e. up to  $10^{-5}$  s. Let us show that such a situation takes place in the case of helium quasimolecules  $\text{He}_2^*$  in the state  $^1\Pi_u$ .

A dipole matrix element for the transition of the quasimolecule in the ground state (two free atoms) is written in the form

$$\begin{aligned} \mathbf{d}_{\text{fi}} &\equiv \langle \Psi^{(x,y,z)} | \mathbf{d}_1 + \mathbf{d}_2 + \mathbf{d}_{1'} + \\ &+ \mathbf{d}_{2'} | \tilde{\psi}_0(1)\tilde{\psi}_0(2)\tilde{\psi}_0(1')\tilde{\psi}_0(2') \rangle, \end{aligned} \quad (33)$$

where  $\Psi^{(x,y,z)}$  are the correct wave functions of zero-order approximation (20)–(22).

It is easy to see that, after the interchange of electron pairs 1, 2 and 1', 2' that corresponds to physically identical states, wave functions (20) and (21) reverse

their signs as well as the whole integral (33). As a consequence, we get that this integral is equal to zero,

$$\langle \Psi^{(x,y)} | \mathbf{d}_1 + \mathbf{d}_2 + \mathbf{d}_{1'} + \mathbf{d}_{2'} | \tilde{\psi}_0(1) \tilde{\psi}_0(2) \tilde{\psi}_0(1') \tilde{\psi}_0(2') \rangle = 0, \quad (34)$$

and the dipole transition from the state  ${}^1\Pi_u$  to the ground state turns out to be forbidden.

However, for the  ${}^1\Sigma_g$  state [ $z$ -functions (22)], the symmetry does not forbid the dipole transition. In this case, only the matrix element of the  $z$ -component of the dipole moment is non-zero and turns to be

$$\begin{aligned} & \langle \Psi^{(z)} | (d_1 + d_2 + d_{1'} + d_{2'})_z | \tilde{\psi}_0(1) \tilde{\psi}_0(2) \tilde{\psi}_0(1') \tilde{\psi}_0(2') \rangle = \\ & = -\frac{2^9 \alpha^3 \beta^{3/2} \gamma^{5/2}}{(\alpha + \beta)^3 (\alpha + \gamma)^5} e a \simeq -0.49 ea. \end{aligned} \quad (35)$$

The probability of a dipole radiation of the excited system per unit time equals [10]

$$w = \frac{4\omega^3}{3\hbar c^3} |\mathbf{d}_{\text{fi}}|^2, \quad (36)$$

wherefrom one can calculate the lifetime of the  ${}^1\Sigma_g$  state:

$$\tau = \frac{1}{w} \simeq \frac{3\hbar^4 c^3}{4(\hbar\omega)^3} \frac{1}{(0.49 ea)^2} \simeq 0.18 \text{ ns}. \quad (37)$$

We see that the  ${}^1\Sigma_g$  state is short-lived and cannot be a pretender to a metastable state in contrast to the  ${}^1\Pi_u$  state, the dipole radiation for which is forbidden and therefore the quasimolecule in this state is metastable and lives at least  $10^{-5}$  s, that essentially greater than characteristic times of the dipole radiation,  $10^{-8} \div 10^{-9}$  s.

Let us notice that the given estimation (37) of the quasimolecule lifetime agrees in order with the experimental data for short-lived excited states of helium [11].

#### 4. Quasimolecules of Atoms with One Valence Electron

Let us consider a system, which consists of two identical atoms, where each atom has only one outer electron, while all the other electrons form entirely occupied electronic shells (chemical elements of the first group). We assume that one of the atoms is in the ground  $S$ -state (i.e. the valence electron has  $ns^1$ -configuration), but another is in the excited  $P$ -state ( $np^1$ -configuration).

A total electron wave function of each atom can be presented in the form of the product of the electron wave function of entirely occupied electronic shells  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  and the wave function of the outer electron  $\psi_{s,p}(\mathbf{r})$ :

$$\Psi = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \psi_{s,p}(\mathbf{r}), \quad (38)$$

where  $N = 2, 8, 10, 18, \dots$  is the number of electrons in the entirely occupied electronic shells.

The entirely occupied electronic shells have zero total spin and zero total angular momentum. Therefore, they do not take part in the chemical combinations and the chemical valence is conditioned only by outer electrons [1]. Hence, the wave function  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  appears invariantly in all the equations, where chemical combinations are considered and practically drops out from the calculations. Taking this fact into account, we will use only the wave functions of the valence electron  $\psi_{s,p}(\mathbf{r})$ , but keep in mind that the entirely occupied electronic shells must be considered for obtaining the equilibrium distances between the nuclei of atoms.

Thus, the problem reduces to the interaction of two hydrogen-like atoms, where one electron moves in the field of an atomic residue with effective charge  $Z(r)$ , which can be calculated when the wave function  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is known. But such a procedure can be realized only with help of numerical methods.

The angular part of the wave function of the outer electron is the spherical function  $Y_{lm}(\theta, \varphi)$ , but the radial one  $R_{nl}(r)$  is considered unknown. Wave functions of zero-order approximation of two non-interactive atoms with accounting the excitation exchange are constructed analogously to what has done in Section 2. Namely,

$$|0x\rangle, |x0\rangle, |0y\rangle, |y0\rangle, |0z\rangle, |z0\rangle, \quad (39)$$

where

$$\psi_s(r) \equiv |0\rangle = R_{n0}(r) \frac{1}{\sqrt{4\pi}}, \quad (40)$$

$$\psi_p(\mathbf{r}) = \begin{cases} |x\rangle = R_{n'1}(r) \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi, \\ |y\rangle = R_{n'1}(r) \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi, \\ |z\rangle = R_{n'1}(r) \sqrt{\frac{3}{4\pi}} \cos\theta. \end{cases} \quad n' \geq 2. \quad (41)$$

We emphasize that we neglect the exchange interaction of the outer electron with the inner ones.

A dipole-dipole interaction operator is written in the form

$$V = \frac{(\mathbf{d}_1 \mathbf{d}_{1'}) - 3(\mathbf{d}_1, \mathbf{n})(\mathbf{d}_{1'}, \mathbf{n})}{R^3}, \quad (42)$$

where indices 1, 1' correspond to electrons which belong to the different atoms with the distance between them equal to  $R$ .

After solving the secular equation constructed with the help of interaction operator (42) and the set of degenerate wave functions (39), we get

$$\Delta E^{(x,y)} = \pm A, \quad \Delta E^{(z)} = \pm 2A, \quad (43)$$

where  $A$  reads

$$A = \frac{e^2}{3R^3} \left( \int_0^\infty r^3 R_{n0}(r) R_{n'1}(r) dr \right)^2. \quad (44)$$

In the case of a hydrogen atom, the radial functions  $R_{nl}(r)$  are known. Particularly, at  $n = 1$  and  $n' = 2$ , we have

$$A \simeq 0.555 \frac{e^2 a^2}{R^3}. \quad (45)$$

With the help of the method described in Section 2., we estimate the equilibrium distance between the nuclei

$$R^{(x,y)} \approx 1.76 a \quad (\theta \approx 32.8^\circ), \quad R^{(z)} = 5 a \quad (\theta = 0),$$

and get the following binding energies of quasimolecules in the states  ${}^1\Pi_u$  and  ${}^1\Sigma_g$

$$E^{(x,y)} \simeq -2.77 \text{ eV}, \quad E^{(z)} \simeq -0.24 \text{ eV}, \quad (46)$$

respectively.

For other atoms, when the radial functions are unknown, we use the experimental atomic radii  $r_{\text{at}}$  [12] for estimations of the dissociation energies of quasimolecules and assume that  $A \approx \frac{e^2 a^2}{R^3}$ . The results of calculations (by the method of Section 2.) in the case where  $n = n'$  are listed in the table.

The typical sizes of quasimolecules can be roughly estimated with the formula  $R_M = 2R^{(z)}$ . Hence, the typical sizes of quasimolecules from Li to Cs are in the

Element	$n$	$r_{\text{at}}, \text{ \AA}$	$R^{(x,y)}, a$	$E^{(x,y)}, \text{ eV}$	$R^{(z)}, a$	$E^{(z)}, \text{ eV}$
Li	2	1.520	3.70	-0.54	5.75	-0.29
Na	3	1.858	4.53	-0.29	7.02	-0.16
K	4	2.272	5.54	-0.16	8.59	-0.09
Rb	5	2.475	6.03	-0.12	9.36	-0.07
Cs	6	2.655	6.47	-0.10	10.04	-0.05

interval from 6 to 10 Å. This means that the corresponding effective scattering cross-sections are approximately by one order larger than gas-kinetic ones.

As well as for helium quasimolecules, the dipole transition appears to be forbidden also in the case of the atoms with one valence electron due to the fact that the wave function symmetry remains the same (upon the exchange of nuclei). Thus, the quasimolecules are metastable only in the  $x, y$ -states.

## 5. Conclusions

Here, the analytic calculations of the molecular states of diatomic quasimolecules, which are formed of the atoms in the ground and excited states, are carried out. The calculations are made in the first order of perturbation theory with the use of a dipole-dipole interaction operator for atoms with entirely occupied electronic shells and atoms with one valence electron. The results well describe the molecular states at distances  $R$  greater than the typical sizes of atoms. At the distances  $R^{(x,y,z)}$  (phenomenological parameters of the theory) of the order of atom sizes, where the repulsion of atoms predominates, the potential energy is modelled by a solid wall. The dissociation energy of such molecules, by our estimates, appears to be of the order of 1 eV. In contrast to excimer molecules, whose typical lifetime varies from 0.1 to 10 ns [4], the quasimolecules are metastable systems. The estimates show that their radiation decay is forbidden relative to dipole transitions and is of the order of  $10^{-5}$  s.

The above-described quasimolecules exist in active media which are used for the generation of laser radiation [4, 9, 11]. It is worth noting that, even for the simplest excimer molecule  $\text{He}_2^*$ , there exist over 60 molecular potential curves [4], which complicates essentially the theoretical analysis of systems containing a noticeable quantity of excited atoms from the point of view of identification of the certain spectral levels.

The availability of excimers and quasimolecules in excited gases can essentially affect their collective properties. Particularly, one can affect the diffusion and thermal conductivity coefficients in excited gases with regard for the fact that quasimolecules have much greater effective cross sections than the gas-kinetic ones. In particular, the presence of quasimolecules will lead to a deceleration of the processes of diffusion and thermal conductivity.

The availability of diatomic quasimolecules can also assist a more active process of formation of clusters which consist of many atoms [13]. The formation of

quasimolecules with a finite lifetime  $\tau$  and their decay (dissociation) can be considered as a photo-stimulated chemical reaction. As is known [14], the anomalous sound absorption can be observed in this case at the expense of the mechanism of the second viscosity at frequencies  $\omega\tau \sim 1$ . Furthermore, a theory of non-equilibrium phase transitions in many-particle systems with finite lifetime is intensively developed [15]. The most essential conclusion of such theories is that there exist additional restrictions on a decay of systems into two coexistent phases (in our case — phases with different concentrations of excited atoms), which requires some improvements [16].

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Received 11.08.04

#### МЕТАСТАБІЛЬНІ КВАЗІМОЛЕКУЛИ У ЗБУДЖЕНИХ ГАЗАХ

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#### Резюме

Розглянуто квазімолекули, що складаються з двох різнозбуджених атомів у резонансно-збудженому газі. У першому порядку квантово-механічної теорії збурень за допомогою оператора диполь-дипольної взаємодії обчислено енергію дисоціації таких квазімолекул та їх типові розміри. Також показано, що існують метастабільні квазімолекули, для яких дипольний радіаційний перехід в основний стан (коли обидва атоми незбуджені) заборонено. Оцінено час життя такої молекули. Такі квазімолекули можуть суттєво впливати на процеси переносу в резонансно-збуджених газах.