The Formation of Molecules in Three Atom Collisions using the Eikonal Approximation

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A new approach to the calculation of a teratomic recombination rate constant $k(T)$ has been demonstrated. An expression for $k(T)$ has been obtained in the eikonal approximation. The numerical calculation has been carried out for the Rb*-Xe system. Good agreement in the order of magnitude between the present results and the experimental data of Carrington et al. has been obtained.

1. Introduction

The present work is devoted to the calculation of the quantum teratomic recombination rate constant for diatomic molecules in the framework of the eikonal approximation. If any two atoms are able to form a diatomic molecule at all, then both the energy and angular momentum of such a molecule are quantized. But two free atoms, approaching each other during a collision, have non quantized relative energy and angular momentum. Therefore, two colliding atoms can form a bound state only if some part of their total energy and angular momentum is taken away by a third particle in the course of the collision (see Born [1]). For these reasons, the role of teratomic collisions in the formation of gaseous diatomic molecules is quite evident.

All such recombination rate constants were calculated so far classically (cp. [2] and [3]). The basis of those calculations are the classical Hamilton equations of motion of the corresponding systems. In the case of three particles, by eliminating the center of mass motion of the system, the motion of the system is described classically in the 12-dimensional phase space of positions and momenta divided into reactant and product regions by an 11-dimensional surface. The division of the phase space into reactant and product regions is made on the basis of the internuclear distances such that for the reactants (three free atoms) each internuclear distance R is greater than a specified distance R_{m} (equilibrium distance of the molecule). On the other hand for the products (one molecule and one free atom) one of the R's is smaller than R_{m}. At complete chemical and thermal equilibrium, the density of points in phase space may be specified, and the flux of points across the dividing surface can be calculated to obtain the equilibrium reaction rate. Since multiple crossings of the surface may occur, it is necessary to examine individual trajectories to determine the true reaction rate. In contrast to this purely classical treatment, the present calculations are based on a quantum approach.

We begin our considerations by giving a brief description of the three-body scattering formalism (Section 2). Further, starting from the quantum expression for the recombination rate constant (Sect. 3) to transform it in the framework of the eikonal approximation to a form appropriate for numerical calculations (Sect. 4 and 5). The details of the calculations and the results are presented in Section 6.

2. Three-body Scattering Problem

In this section we shall give a brief review of the S-matrix formalism for the three-body scattering problem. Let the considered atomic system be composed of one Rb atom and two Xe atoms. Following Schmid and Ziegelmann [4] we denote the Rb atom by 1 and the two Xe atoms by 2 and 3. When neglecting three-particle potentials, the Hamiltonian for the considered system has the form

$$H' = \frac{p_1^2}{2\,m_1} + \frac{p_2^2}{2\,m_2} + \frac{p_3^2}{2\,m_3} + V_1 + V_2 + V_3\,, \qquad (1)$$

where the potentials V_i describe the two-particle interactions according to:

$$V_1 = V(2,3)\,, \quad V_2 = V(1,3)\,, \quad V_3 = V(1,2)\,. \qquad \mathbf{(2)}$$

To separate out the center-of-mass motion of the system it is useful to introduce Jacobi coordinates.

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The cartesian space coordinates are $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ and $\boldsymbol{r}_3$. The Jacobi coordinates for which particles 1 and 2 appear as a subsystem are denoted by $\boldsymbol{\xi}$, $\boldsymbol{\eta}$ and $\boldsymbol{R}$. The transformation reads

$$\begin{aligned} \boldsymbol{\xi} &= \boldsymbol{r}_2 - \boldsymbol{r}_1 , \\ \boldsymbol{\eta} &= \boldsymbol{r}_3 - \frac{m_1 \boldsymbol{r}_1 + m_2 \boldsymbol{r}_2}{m_1 + m_2} , \\ \boldsymbol{R} &= \frac{m_1 \boldsymbol{r}_1 + m_2 \boldsymbol{r}_2 + m_3 \boldsymbol{r}_3}{m_1 + m_2 + m_3} . \end{aligned} \tag{3}$$

The corresponding transformation for the momentum coordinates becomes

$$\begin{aligned} \boldsymbol{p} &= \frac{m_1 \boldsymbol{p}_2 - m_2 \boldsymbol{p}_1}{m_1 + m_2} , \\ \boldsymbol{q} &= \frac{(m_1 + m_2) \boldsymbol{p}_3 - m_3 (\boldsymbol{p}_1 + \boldsymbol{p}_2)}{m_1 + m_2 + m_3} \\ \boldsymbol{P} &= \boldsymbol{p}_1 + \boldsymbol{p}_2 + \boldsymbol{p}_3 . \end{aligned} \tag{3 a}$$

The coordinate $\boldsymbol{p}$, which is the canonical conjugate to $\boldsymbol{\xi}$, is the momentum of particle 2 in the center-of-mass system of particles 1 and 2, and $\boldsymbol{q}$, which is canonical conjugate to $\boldsymbol{\eta}$, is the momentum of particle 3 in the center-of-mass system of all three particles. The Hamiltonian (1) has in Jacobi coordinates the form

$$H' = \frac{P^2}{2\,(m_1 + m_2 + m_3)} + \frac{p^2}{2\,\mu_1} + \frac{q^2}{2\,\mu_2} + \sum_{\gamma=1}^{3} V_\gamma , \tag{4}$$

with the reduced masses

$$\mu_1 = \frac{m_1\, m_2}{m_1 + m_2} \quad \text{and} \quad \mu_2 = \frac{m_3\,(m_1 + m_2)}{m_1 + m_2 + m_3} .$$

On neglecting in (4) the term corresponding to the translational motion of the center-of-mass of the system we get

$$H = \frac{p^2}{2\,\mu_1} + \frac{q^2}{2\,\mu_2} + \sum_{\gamma=1}^{3} V_\gamma \equiv H_0 + \sum_{\gamma=1}^{3} V_\gamma . \tag{5}$$

In general the Hamiltonian H is denoted by

$$H = \frac{p_a{}^2}{2\,\mu_a} + \frac{q_a{}^2}{2\,M_a} + \sum_{\gamma=1}^{3} V_\gamma , \tag{6}$$

where the index a stands for the free particle of the system. In our case $a = 3$, $p_a = p$, $q_a = q$, $\mu_a = \mu_1$ and $M_a = \mu_2$. Usually one designates the breakup of a three-particle system (all particles free) with the index 0 and, according to the definition (2), $V_0 \equiv 0$.

Let us introduce so-called channel Hamiltonian h_a given by

$$h_a = \frac{p_a{}^2}{2\,\mu_a} + \frac{q_a{}^2}{2\,M_a} + V_a . \tag{7}$$

Then the full Hamiltonian H can be written

$$H = h_a + \overline{V}_a \tag{8}$$

with

$$\overline{V}_a = \sum_{\gamma=1}^{3} V_\gamma - V_a . \tag{9}$$

The scattering of a three-particle system is completely described by the time-dependent Schrödinger equation

$$H\, \Psi_{\alpha m}^{(+)}(t) = i \frac{\partial}{\partial t} \Psi_{\alpha m}^{(+)}(t) \tag{10}$$

with the proper boundary conditions. The superscript (+) indicates that the system is in an experimentally prepared state before scattering and is gradually scattered with increasing time. The index a denotes the definite channel and m stands for the m^{th} bound state of a two-particle subsystem. Analogically, as in the two-particle scattering problem, the time development of a three-particle wave packet is given by

$$\Psi_{\alpha m}^{(+)}(t) = e^{-iHt}\, \Psi_{\alpha m}^{(+)} , \tag{11}$$

while the reference wave packets develop according to

$$\Phi_{am}(t) = e^{-ih_a t}\, \Phi_{am} . \tag{12}$$

The wave packet Φ_{am} describes the free motion of particle a ($a = 1, 2, 3$) relative to the other two particles being in their m^{th} bound state. Starting from the well-known boundary condition

$$\lim_{t \to -\infty} \| e^{-iHt}\, \Psi_{\alpha m}^{(+)} - e^{-ih_a t}\, \Phi_{am} \| = 0 , \tag{13}$$

we arrive at

$$\Psi_{\alpha m}^{(\pm)} = s - \lim_{t \to \mp\infty} e^{iHt}\, e^{-ih_a t}\, \Phi_{am} \equiv \Omega_a{}^{(\pm)}\, \Phi_{am} , \tag{14}$$

where, according to the definition,

$$\Omega_a{}^{(\pm)} = s - \lim_{t \to \mp\infty} e^{iHt}\, e^{-ih_a t} . \tag{15}$$

The operators $\Omega_a{}^{(\pm)}$ are called Møller operators. A superscript (−) was introduced with respect to the further construction of the S-matrix. In the considered case the corresponding a-channel state reads

$$| \Phi_{3m} \rangle = | \boldsymbol{q}, \Psi_{3m} \rangle = | \boldsymbol{q} \rangle\, | \Psi_{3m} \rangle , \tag{16}$$

where

$$h_3\, | \Phi_{3m} \rangle = E_{3m}\, | \Phi_{3m} \rangle \tag{17}$$

with

$$E_{3m} = q^2 / 2\,\mu_2 + \varepsilon_m ,$$

and respectively for three free particles, neglecting their internal motion, the channel state is

$$|\Phi_0\rangle = |\mathbf{p}, \mathbf{q}\rangle = |\mathbf{p}\rangle\,|\mathbf{q}\rangle\,, \tag{18}$$

where
$$h_0\,|\Phi_0\rangle = \left(\frac{q^2}{2\,\mu_2} + \frac{p^2}{2\,\mu_1}\right)|\Phi_0\rangle\,. \tag{19}$$

If we now introduce the full resolvent

$$G(z) \equiv (z - H)^{-1} \tag{20}$$

and correspondingly the channel resolvent

$$g_\alpha(z) \equiv (z - h_\alpha)^{-1}\,, \tag{21}$$

then we get

$$|\Psi^{(\pm)}_{\alpha m}\rangle = \lim_{\varepsilon\to 0} \pm i\,\varepsilon\, G(E_{\alpha m} \pm i\,\varepsilon)\,|\Phi_{\alpha m}\rangle \tag{22}$$

or, making use of the equation

$$G(z) = g_\alpha(z) + g_\alpha(z)\,\overline{V}_\alpha\, G(z)\,,$$

we have

$$|\Psi^{(\pm)}_{\alpha m}\rangle = |\Phi_{\alpha m}\rangle + g_\alpha(E_{\alpha m} \pm i\,0)\,\overline{V}_\alpha\,|\Psi^{(\pm)}_{\alpha m}\rangle\,. \tag{23}$$

We now want to define the S-matrix for the problem considered. If we let a free state $e^{-ih_\alpha t}|\Phi_{\alpha m}\rangle$ develop into a scattering state $e^{-iHt}|\Psi^{(+)}_{\alpha m}\rangle$ and analyse the scattering state for free states $e^{-ih_\beta t}|\Phi_{\beta n}\rangle$ in the limit $t \to +\infty$, we get

$$S_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) = \lim_{t\to\infty} \langle e^{-ih_\beta t}\,\Phi_{\beta n}\,|\,e^{-iHt}\,\Psi^{(+)}_{\alpha m}\rangle\,, \tag{24}$$

where the index β denotes some other channel of the system and n stands for a bound state of the corresponding two particles. According to (15), the last expression goes over into

$$\begin{aligned} S_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) &= \lim_{t\to\infty} \langle e^{iHt}\,e^{-ih_\beta t}\,\Phi_{\beta n}\,|\,\Psi^{(+)}_{\alpha m}\rangle \\ &= \langle \Phi_{\beta n}\,|\,\Omega_\beta{}^{(-)\dagger}\,\Omega_\alpha{}^{(+)}\,|\,\Phi_{\alpha m}\rangle = \langle \Psi^{(-)}_{\beta n}\,|\,\Psi^{(+)}_{\alpha m}\rangle\,. \end{aligned} \tag{25}$$

It is seen that in the three-particle case the S-operator is a 4 times 4 matrix of operators, i. e.

$$S_{\beta\alpha} = \Omega_\beta{}^{(-)\dagger}\,\Omega_\alpha{}^{(+)}\,, \tag{26}$$

since in general $\alpha, \beta = 1, 2, 3, 0$. The matrix elements of this set of operators, taken with channel states $|\Phi_{\alpha m}\rangle$, form the S-matrix. Recall that the resolvent $G(z)$ satisfies the resolvent equation

$$G(z) = g_\beta(z) + G(z)\,\overline{V}_\beta\, g_\beta(z)\,. \tag{27}$$

If we now insert (27) into (22) and substitute there the index α for β we obtain

$$\begin{aligned} |\Psi^{(-)}_{\beta n}\rangle &= |\Phi_{\beta n}\rangle + G(E_{\beta n} - i\,0)\,\overline{V}_\beta\,|\Phi_{\beta n}\rangle \\ &= |\Psi^{(+)}_{\beta n}\rangle + [G(E_{\beta n} - i\,0) - G(E_{\beta n} + i\,0)]\,\overline{V}_\beta\,|\Phi_{\beta n}\rangle\,. \end{aligned} \tag{28}$$

Since

$$G(E_{\beta n} - i\,0) - G(E_{\beta n} + i\,0) = 2\,\pi\,i\,\delta(E_{\beta n} - H)$$

then, according to (25) and (28), we have

$$\begin{aligned} S_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) &= \langle \Psi^{(+)}_{\beta n}\,|\,\Psi^{(+)}_{\alpha m}\rangle \\ &\quad - 2\,\pi\,i\,\langle \Phi_{\beta n}\,|\,\overline{V}_\beta\,\delta\,(E_{\beta n} - H)\,|\,\Psi^{(+)}_{\alpha m}\rangle \\ &= \delta\,(\mathbf{q}_\beta{}' - \mathbf{q}_\alpha)\,\delta_{\beta\alpha}\,\delta_{mn} \\ &\quad - 2\,\pi\,i\,\delta(E_{\beta n} - E_{\alpha m})\,\langle \Phi_{\beta n}\,|\,\overline{V}_\beta\,|\,\Psi^{(+)}_{\alpha m}\rangle\,. \end{aligned} \tag{29}$$

The quantity

$$R^{(+)}_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) = \langle \Phi_{\beta n}\,|\,\overline{V}_\beta\,|\,\Psi^{(+)}_{\alpha m}\rangle \tag{30}$$

is usually called a transition matrix for a definite reaction. One can show that the transition matrix (30) is equivalent to

$$R^{(-)}_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) = \langle \Psi^{(-)}_{\beta n}\,|\,\overline{V}_\alpha\,|\,\Phi_{\alpha m}\rangle\,. \tag{31}$$

Substituting now (27) into (22) we can express the transition matrix (30) in terms of channel states

$$\begin{aligned} &R^{(+)}_{\beta n,\alpha m}(\mathbf{q}_\beta{}', \mathbf{q}_\alpha) \\ &\quad = \langle \Phi_{\beta n}\,|\,(\overline{V}_\beta + \overline{V}_\beta\, G(E_{\alpha m} + i\,0)\,\overline{V}_\alpha)\,|\,\Phi_{\alpha m}\rangle\,. \end{aligned} \tag{32}$$

The last expression gives us the transition matrix for the three-particle system which in the course of collision goes over from a (α, m)-state into a (β, n)-state. Such a transition connected with rearrangement or break up of the system is called a reaction. The indices α and β denote correspondingly the initial and final channels of the reaction.

3. Definition of the Teratomic Recombination Rate Constant

In this section we want to define the teratomic recombination rate constant for the Rb*-Xe system being in the gas phase. Let the considered system of volume V be composed of a mixture of N_{Rb^*} excited rubidium atoms and N_{Xe} xenon atoms so that $n_{\mathrm{Rb}^*} = N_{\mathrm{Rb}^*}/N$ and $n_{\mathrm{Xe}} = N_{\mathrm{Xe}}/V$ are the densities of Rb* and Xe, respectively. If the recombination of diatomic molecules proceeds via the teratomic reaction

$$\mathrm{Rb}^* + \mathrm{Xe} + \mathrm{Xe} \to \mathrm{RbXe}^* + \mathrm{Xe} \tag{33}$$

then we have the corresponding rate equation

$$-\frac{\mathrm{d}(n_{\mathrm{Rb}^*})}{\mathrm{d}t} = k(T)\,n_{\mathrm{Rb}^*}\,n^2_{\mathrm{Xe}} \tag{34}$$

(see Eliason [5] and Snider [6]).

The proportionality factor $k(T)$ is called the teratomic recombination rate constant and depends in general on the temperature T of the system. The calculation of $k(T)$ may be done quantum mechanically or classically. For chemical reactions, a quantum treatment will usually be preferable or perhaps necessary, but the classical approach may be useful in some cases. The quantum approach consists in finding a solution of the corresponding Schrödinger equation for the internal degrees of freedom of the individual atoms and the relative motion of the proper pairs. The number of collisions in unit volume and unit time which lead to the formation of diatomic molecules is given, in our notation, by

$$\mathcal{N} = n_{\mathrm{Rb}^*} n_{\mathrm{Xe}}^2 \langle P_{3,0}(\boldsymbol{p}, \boldsymbol{q}) \rangle_{\boldsymbol{p},\boldsymbol{q}} , \tag{35}$$

where $P_{3,0}(\boldsymbol{p}, \boldsymbol{q})$ denotes the $0-3$ channels reaction probability per unit time with the initial momenta $\boldsymbol{p}$ and $\boldsymbol{q}$. The parenthesis stands for the average over the initial momenta $\boldsymbol{p}$ and $\boldsymbol{q}$. For many chemically reacting systems it is a very good approximation to assume a Maxwell-Boltzmann distribution for the translational motion of the reacting atoms. In the quantum approach the recombination rate constant $k(T)$ takes, according to (34), (35) and (32), the following form

$$\begin{aligned} k(T) = \frac{2\pi}{\hbar} V^2 \sum_{vJ} \Big\langle \frac{V}{(2\pi\hbar)^3} \int \mathrm{d}^3\boldsymbol{q}' \big| \langle (^2\pi_{1/2}\, v\, J, 0) ; \boldsymbol{q}' \big| \\ \cdot \Big(\overline{V}_3 + \overline{V}_3 \frac{1}{E_0 - H + i\,0} \overline{V}_0\Big) \big| (\tfrac{1}{2}\,0\,0) ; \boldsymbol{p}, \boldsymbol{q} \rangle \big|^2 \\ \cdot \delta(E_0 - E_{3vJ}) \Big\rangle_{\boldsymbol{p},\boldsymbol{q}} , \end{aligned} \tag{36}$$

where $(\tfrac{1}{2}\,0\,0)$ denotes commonly the $5^2\mathrm{P}_{1/2}$ state of Rb and the ground state of both Xe atoms, but $(^2\pi_{1/2}\, v\, J, 0)$ stands for the $A^2\pi_{1/2}$ state of the quasimolecule RbXe* (life-time of the order 3×10^{-8} sec) and the ground state of one of the xenon atoms. The eigenfunctions of a free motion are given by

$$|\boldsymbol{p}\rangle = \frac{1}{\sqrt{V}} e^{i \boldsymbol{k}_1 \xi}, \quad |\boldsymbol{q}\rangle = \frac{1}{\sqrt{V}} e^{i \boldsymbol{k}_2 \eta}, \tag{37}$$
$$|\boldsymbol{q}'\rangle = \frac{1}{\sqrt{V}} e^{i \boldsymbol{k}_2' \eta} ,$$

where prime means that the corresponding momentum refers to the final state and $\boldsymbol{p} = \hbar \boldsymbol{k}_1$, $\boldsymbol{q} = \hbar \boldsymbol{k}_2$ and $\boldsymbol{q}' = \hbar \boldsymbol{k}_2'$. The energies E_0 and E_{3vJ} are given by

$$\begin{aligned} E_0 &= p^2/2\mu_1 + q^2/2\mu_2 + \varepsilon_{1/2,0,0} , \\ E_{3vJ} &= q'^2/2\mu_2 + \varepsilon_{1/2\,vJ,0} . \end{aligned} \tag{38}$$

The energy $\varepsilon_{1/2,0,0}$ and $\varepsilon_{1/2\,vJ,0}$ refer to the internal degrees of freedom of the particles; $\varepsilon_{1/2,0,0}$ is the sum of the energies of an excited Rb atom being in the $5\,^2\mathrm{P}_{1/2}$ state and two ground state Xe atoms and $\varepsilon_{1/2\,vJ,0}$ is the sum of the energies of the RbXe* molecule in a $(v\,J)$ vibrational-rotational state and a free Xe atom in the ground state. The interaction operators V_3 and V_0 are given by

$$\begin{aligned} \overline{V}_0 &= V(1,2) + V(1,3) + V(2,3) , \\ \overline{V}_3 &= V(1,3) + V(2,3) . \end{aligned}$$

Since, according to (38)

$$\begin{aligned} \int \mathrm{d}^3\boldsymbol{q}' &= \int \mathrm{d}\Omega \int_0^\infty q'^2\, \mathrm{d}q' \\ &= \int \mathrm{d}\Omega\, \mu_2 \sqrt{2\mu_2 (E_{3vJ} - \varepsilon_{1/2,vJ,0})}\, \mathrm{d}E_{3vJ} , \end{aligned}$$

the integration over moduli of the momentum $\boldsymbol{q}'$ in (36) can be easily performed and we get

$$\begin{aligned} k(T) = \frac{2\pi}{\hbar} V^2 \sum_{vJ} \Big\langle \frac{V \mu_2 \hbar k_{vJ}}{(2\pi\hbar)^3} \int \mathrm{d}\Omega \big| \langle (^2\pi_{1/2}\, v\, J, 0) ; \boldsymbol{q}' \big| \\ \cdot \Big(\overline{V}_3 + \overline{V}_3 \frac{1}{E_0 - H + i\,0} \overline{V}_0\Big) \big| (\tfrac{1}{2}\,0\,0) ; \boldsymbol{p}, \boldsymbol{q} \rangle \big|^2 \Big\rangle_{\boldsymbol{p},\boldsymbol{q}} \end{aligned} \tag{39}$$

with

$$q' = \hbar k_{vJ} = \sqrt{2\mu_2 (p^2/2\mu_1 + q^2/2\mu_2 + I_{vJ})}$$

and $I_{vJ} = \varepsilon_{1/2,0,0} - \varepsilon_{1/2\,vJ,0}$ the dissociation energy of the RbXe* molecule from the $|v, J\rangle$ state.

4. Recombination Rate Constant in the Eikonal Approximation

We want now to express the matrix element

$$\begin{aligned} \mathcal{M} = V \langle (^2\pi_{1/2}\, v\, J, 0) ; \quad \boldsymbol{q}' \big| \\ \cdot \Big(\overline{V}_3 + \overline{V}_3 \frac{1}{E_0 - H + i\,0} \overline{V}_0\Big) \big| (\tfrac{1}{2}\,0\,0) ; \boldsymbol{p}, \boldsymbol{q} \rangle \end{aligned} \tag{40}$$

in the eikonal approximation. In a first approximation we assume that the electronic wave function of the molecule considered is a product of the corresponding wave functions of the isolated atoms *. As will be seen in Sect. 6 our assumption seems to be well justified, since in the present calculation the long-range forces between the interacting atoms prove to play the decisive role. In the following we

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* Usually, to calculate the interaction energy between an alkali atom and one of the nobel gas atoms one takes a linear combination of some of atomic states of the alkali atom with different quantum numbers l. This is done so since only the projection of the orbital momentum of a molecule on the interatomic axis is well defined (see Baylis [7]).

assume the interaction between two atoms to be of the dipole-dipole type, i. e.

$$V[\boldsymbol{R}] = \frac{1}{R^3}\left[\mu_1\,\mu_2 - 3\,\frac{(\mu_1\,\boldsymbol{R})\,(\mu_2\,\boldsymbol{R})}{R^2}\right]. \quad (41)$$

Since the average value of that operator in each of the electronic states of the system is equal to zero, the matrix element (40) goes over into

$$\mathcal{M} = V\,\langle\,({}^2\pi_{1/2}\,v\,J\,0)\,;\quad \boldsymbol{q}'\,| \quad (42)$$
$$\cdot\,\overline{V}_3\,\frac{1}{E_0 - H_0 - \overline{V}_0 + i\,0}\,\overline{V}_0\,|\,(\tfrac{1}{2}\,0\,0)\,;\boldsymbol{p},\boldsymbol{q}\rangle\,,$$

where

$$H_0 = h_{0p} + h_{0q} + h_1 + h_2 + h_3 = h_0 + h\,. \quad (43)$$

Here h_0 is the Hamiltonian of the free motion of the system and h refers to the internal degrees of freedom of the Rb atom and the two Xe atoms. Putting now the resolvent in (42) in the integral form we obtain

$$\mathcal{M} = -\,i\,V\int_0^\infty \langle\,({}^2\pi_{1/2}\,v\,J,0)\,;\boldsymbol{q}'\,|\,\overline{V}_3 \quad (44)$$
$$\cdot\,e^{i(E_0 - H_0 - \overline{V}_0 + i0)t}\,\overline{V}_0\,|\,(\tfrac{1}{2}\,0\,0)\,;\boldsymbol{p},\boldsymbol{q}\rangle\,\mathrm{d}t\,.$$

Let

$$e^{-i(H_0 + \overline{V}_0)t} = S(t,0)\,e^{-iH_0 t}\,. \quad (45)$$

Differentiating the last equation with respect to time, we get

$$i\,\partial S(t,0)/\partial t = S(t,0)\,V(t)\,, \quad (46)$$

where

$$V(t) = e^{-iH_0 t}\,\overline{V}_0\,e^{iH_0 t} \quad (47)$$

and

$$S(t,0) = \mathbf{P}\exp\{-i\int_0^t V(t')\,\mathrm{d}t'\} \quad (48)$$

with the initial condition $S(0,0)=1$ and $\mathbf{P}$ denoting an antichronological operator. Substituting now (45) into (44) and making use of the equation

$$e^{iE_0 t}\,|\,(\tfrac{1}{2}\,0\,0)\,;\boldsymbol{p},\boldsymbol{q}\rangle = e^{iH_0 t}\,|\,(\tfrac{1}{2}\,0\,0)\,;\boldsymbol{p},\boldsymbol{q}\rangle\,,$$

we can transform $\mathcal{M}$ to the form

$$\mathcal{M} = -\,i\,V\int_0^\infty \langle\,({}^2\pi_{1/2}\,v\,J)\,;\boldsymbol{q}'\,| \quad (49)$$
$$\cdot\,\overline{V}_3\,S(t,0)\,e^{-iH_0 t}\,\overline{V}_0\,e^{iH_0 t}\,|\,(\tfrac{1}{2}\,0\,0)\,;\boldsymbol{p},\boldsymbol{q}\rangle\,\mathrm{d}t\,.$$

Expanding now $S(t,0)$ in a series

$$S(t,0) = 1 - i\int_0^t e^{-iH_0 t'}\,\overline{V}_0\,e^{iH_0 t'}\,\mathrm{d}t'$$
$$+\,(-i)^2\int_0^t\int_0^{t'} e^{-iH_0 t''}\,\overline{V}_0\,e^{iH_0 t''}\,\mathrm{d}t'' \quad (50)$$
$$\cdot\,e^{-iH_0 t'}\,\overline{V}_0\,e^{iH_0 t'}\,\mathrm{d}t' + \ldots$$

we get a corresponding expansion of $\mathcal{M}$. If we insert unity in the form

$$e^{i\boldsymbol{k}_1\xi}\,e^{i\boldsymbol{k}_2\eta}\,e^{-i\boldsymbol{k}_1\xi}\,e^{-i\boldsymbol{k}_2\eta}$$

between every two interaction operators in each of the expansion term we shall be able to transform each two-particle interaction operator $V(\boldsymbol{R})$ into $V(\boldsymbol{R} - \boldsymbol{v}\,t) = V(t)$, where $\boldsymbol{v}$ is the corresponding relative velocity of two atoms. That transformation corresponds in quantum mechanics to the classical path approximation or to the eikonal approximation. Thus the matrix element $\mathcal{M}$ transform to the form

$$\mathcal{M} = -\,\frac{i}{V^{\frac{1}{2}}}\,\langle 0, v\,J\,|\,e^{-i\boldsymbol{k}_{vJ}\eta}\,e^{i\boldsymbol{k}_1\xi}\,e^{i\boldsymbol{k}_2\eta} \quad (51)$$
$$\cdot\int_0^\infty \langle\tfrac{1}{2}\,0\,0\,|\,\overline{V}_3\,S(t,0)\,e^{-iht}\,\overline{V}_0(t)\,e^{iht}\,|\tfrac{1}{2}\,0\,0\rangle\,|\,0\rangle\,\mathrm{d}t\,,$$

where $|\,0\,v\,J\rangle$ denotes commonly the eigenstate of the momentum operator of the system with the eigenvalue zero and the corresponding vibrational-rotational state of the molecule. Inserting further the unit operator $\sum_{n_1 n_2 n_3} |\,n_1\,n_2\,n_3\rangle\,\langle n_1\,n_2\,n_3\,|$, (the quantum numbers n_1, n_2 and n_3 refer respectively to internal states of the rubidium and two xenon atoms), between every two interaction operators in each of the terms of the $\mathcal{M}$ expansion and performing there the time integration according to the appendix we arrive at the following expression for $\mathcal{M}$

$$\mathcal{M} = \frac{1}{V^{\frac{1}{2}}}\,\langle 0, v\,J\,|\,e^{-i\boldsymbol{k}_{vJ}\eta}\,e^{i\boldsymbol{k}_1\xi}\,e^{i\boldsymbol{k}_2\eta}\,[V_{13}(0) + V_{23}(0)$$
$$-\,i\int_0^\infty (V_{13}(0) + V_{23}(0))\,S^{\mathrm{cl}}(t,0)$$
$$\cdot\,(V_{12}(t) + V_{13}(t) + V_{23}(t))\,\mathrm{d}t]\,|\,0\rangle\,, \quad (52)$$

where V_{ik} denotes now the van der Waals potential acting between particles i and k and

$$S^{\mathrm{cl}}(t,0) = \exp\{-i\int_0^t [V_{12}(t')$$
$$+\,V_{13}(t') + V_{23}(t')]\,\mathrm{d}t'\} \quad (53)$$

is a classical function satisfying the equation

$$i\,\partial S^{\mathrm{cl}}(t,0)/\partial t = [V_{12}(t) + V_{13}(t) + V_{23}(t)]\,S^{\mathrm{cl}}(t,0)\,. \quad (54)$$

In deriving (52) we neglected some terms of the interaction energy which add to the corresponding London forces and which describe so-called non-additive forces acting in a three-particle system (see Acilrod and Teller [8]). Those forces contribute to the interaction energy only when all three particles are in close proximity of each other. Since in the present calculation the long-range forces appears to be decisive, neglecting those nonadditive energy terms seems to be sufficiently justified. Making use of Eq. (54) we can transform $\mathcal{M}$ to the form

$$\mathcal{M} = V^{-\frac{1}{2}} \langle 0, v\, J \,|\, e^{-i \boldsymbol{k}_{vJ} \eta}\, e^{i \boldsymbol{k}_1 \xi}\, e^{i \boldsymbol{k}_2 \eta} \cdot [V_{13}(0) + V_{23}(0)]\, S^{\mathrm{cl}}(\infty, 0) \,|\, 0 \rangle \,. \tag{55}$$

Note that the function $e^{i \boldsymbol{k}_1 \xi}\, e^{i \boldsymbol{k}_2 \eta}\, S^{\mathrm{cl}}(\infty, 0)$ is an approximate scattering wave function of three colliding particles obtained in the eikonal approximation (see Goldberger et al.[9], p. 620). Finally, we arrive at the more explicit form of the recombination rate constant

$$\begin{aligned} k(T) = \frac{2\pi}{\hbar} \sum_{vJ} \frac{\mu_2 \hbar\, k_{vJ}}{(2\pi\hbar)^3} \int \mathrm{d}\Omega \\ \cdot \langle \Big| \int \mathrm{d}^3\boldsymbol{\eta} \int \mathrm{d}^3\boldsymbol{\xi}\, e^{-i(\boldsymbol{k}_{vJ} - \boldsymbol{k}_2)\eta} \cdot e^{i \boldsymbol{k}_1 \xi} \langle v\, J \,| \\ \cdot [V_{13}(\boldsymbol{\xi}, \boldsymbol{\eta}) + V_{23}(\boldsymbol{\xi}, \boldsymbol{\eta})]\, S^{\mathrm{cl}}(\infty, 0) \Big|^2 \rangle_{\boldsymbol{p},\boldsymbol{q}} \,. \end{aligned} \tag{56}$$

The numerical calculation of that expression is the subject of the next two sections.

5. Some Further Approximations

In the following we shall want to calculate the recombination rate constant for the quasimolecule RbXe* formed during a three-particle collision of one excited Rb atom with two ground state Xe atoms. Since the life-time of Rb* is of the order of 3×10^{-8} sec[11] and the duration of the collison is of the order of 10^{-13} sec one can, for an individual collision-act, treat the excited Rb atom as a stable one. In the present calculation we replace the van der Waals potentials in (56) by more realistic Lennard-Jones potentials of the form

$$V(R) = \varepsilon_{\mathrm{m}} \left[\frac{6}{n-6} \left(\frac{R_{\mathrm{m}}}{R} \right)^n - \frac{n}{n-6} \left(\frac{R_{\mathrm{m}}}{R} \right)^6 \right] \tag{57}$$

with the corresponding parameters ε_{m} and R_{m} (see Mahan et al.[10]). In particular, for the interaction between the Rb*-Xe atoms we utilize the Morse potential in the form

$$V[R] = \varepsilon_{\mathrm{m}} \{ [e^{-a(R - R_{\mathrm{m}})} - 1]^2 - 1 \} \tag{58}$$

with $\varepsilon_{\mathrm{m}} = 740\ \mathrm{cm}^{-1}$, $R_{\mathrm{m}} = 3.48$ Å and $a = 1.76$ Å^{-1} (see Carrington et al.[11]). For the xenon-xenon interaction we take $\varepsilon_{\mathrm{m}} = 159.155\ \mathrm{cm}^{-1}$ and $R_{\mathrm{m}} = 4.55$ Å (see Trantz et al.[12]). The three integrals occurring in $S(t, 0)$ [cp. (53)] can be easily calculated if we take all the potentials to be of the form (57). Putting for example $n = 8$, each of those integrals is given in a cylindrical coordinate system connected with any (i, k)-pair of particles, the z-axis pointing in the direction of the relative velocity of the particles, by the general expression

$$\begin{aligned} \frac{1}{\hbar} \int_0^\infty V_{ik}[R_{ik}(t)]\, \mathrm{d}t = \boldsymbol{\zeta}(T) \left\{ \frac{1}{2} \frac{1}{b^7} \frac{z/b}{[1 + (z/b)^2]^3} \right. \\ + \left(\frac{5}{8} \frac{1}{b^7} - \frac{1}{b^5} \right) \left(\frac{z/b}{[1 + (z/b)^2]^2} + \frac{3}{2} \frac{z/b}{1 + (z/b)^2} \right. \\ \left. \left. + \frac{3}{2} \arctan\left(\frac{z}{b} \right) + \frac{3\pi}{4} \right) \right\} \Big/ v \,, \end{aligned} \tag{59}$$

with $\qquad z = -\boldsymbol{R}_{ik} \cdot \boldsymbol{v}_{ik} / v_{ik} = \tau \cdot v_{ik}$,

and $b = \sqrt{R_{ik}^2 - z^2}$ a corresponding impact parameter. The relative velocity of the two (i, k)-particles is denoted by $\boldsymbol{v}_{ik}$. The other two parameters $\zeta(T)$ and v_{ik} are defined as follows

$$\boldsymbol{\zeta}(T) = \varepsilon_{\mathrm{m}}^{ik} R_{\mathrm{m}}^{ik} / \hbar\, \bar{v}_{ik}(T) \,,$$

$$v_{ik} = \sqrt{2\, k\, T / \mu_{ik}}\, v = \bar{v}_{ik}(T)\, v \,,$$

where $\bar{v}_{ik}(T)$ is the mean velocity and μ_{ik} denotes a reduced mass of the particles. According to Fig. 1 we get

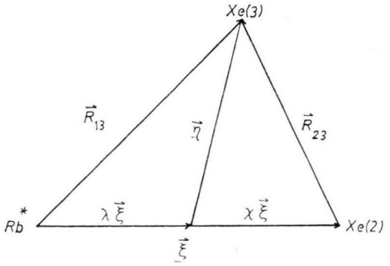

Fig. 1. The system of three interacting particles.

$$\boldsymbol{R}_{12} = \boldsymbol{\xi} \,, \quad \boldsymbol{R}_{13} = \boldsymbol{\eta} + \lambda\, \boldsymbol{\xi} \quad \text{and} \quad \boldsymbol{R}_{23} = \boldsymbol{\eta} - \chi\, \boldsymbol{\xi}$$

with $\lambda = m_2 / (m_1 + m_2)$ and $\chi = m_1 / (m_1 + m_2)$.

The average over all the possible initial positions of the interacting particles given by the position vectors $\boldsymbol{\xi}$, $\boldsymbol{R}_{13}$ and $\boldsymbol{R}_{23}$ i. e. the integration over $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ in (56) will be performed in a spherical coordinate system. The coordinate system is chosen in such a way that its z-axis is pointing along the direction of the initial momentum $\boldsymbol{p}$. In the coordinate system so chosen we put

$$\begin{aligned} \boldsymbol{\xi} &= (\xi, \varphi_1, \Theta_1) \,, \\ \boldsymbol{\eta} &= (\eta, \varphi_2, \Theta_2) \,, \\ \boldsymbol{q} &= (q, \varphi_3, \Theta_3) \,, \\ \boldsymbol{q}' &= (k_{vJ}, \varphi_3', \Theta_3') \,. \end{aligned} \tag{60}$$

For the present calculation we shall take the vibrational eigenfunctions of the RbXe* molecule which satisfy the Schrödinger equation for a diatomic molecule with the Morse potential (58) (see Norling[13]). Putting $\Psi_v(\xi) = (1/\xi) R_v(\xi)$, the function $R_v(\xi)$ is found to be

$$R_v(\xi) = N_v \exp\left\{-\frac{k}{2} e^{-a(\xi-\xi_{\mathrm{m}})}\right\} \cdot (k \cdot e^{-a(\xi-\xi_{\mathrm{m}})})^{\frac{1}{2}(k-2v-1)} L_{sv}(k \cdot e^{-a(\xi-\xi_{\mathrm{m}})}) , \tag{61}$$

where N_v is a normalizing factor

$$N_v = \left[\frac{a \cdot (k-2v-1)}{v!\,(k-v-1)\,\Gamma(k-v-1)}\right]^{\frac{1}{2}}$$

and L_{sv} are so-called generalized Laguerre polynomials given by

$$L_{sv}(x) = x^v - \frac{v}{1!}(s+v) x^{v-1} + \frac{v(v-1)}{2!} \cdot (s+v)(s+v-1) x^{v-2} + \ldots + (-1)^v (s+v)(s+v-1) \ldots (s+1)$$

with $s = k - 2v - 1$ and $k = 1/\mathrm{Xe}$ as a characteristic parameter of a molecule. Recall that the vibrational energy levels (expressed in cm^{-1}) of a diatomic molecule treated as an anharmonic oscillator are given by

$$G(v) = \omega_{\mathrm{e}}(v+\tfrac{1}{2}) - \omega_{\mathrm{e}}\,\mathrm{Xe}\,(v+\tfrac{1}{2})^2 + \ldots \tag{62}$$

(cf. e. g. Herzberg[14], p. 149), where the parameter $\omega_{\mathrm{e}} \cdot \mathrm{Xe}$ can be determined from the relation $\omega_{\mathrm{e}} \cdot \mathrm{Xe} = \omega_{\mathrm{e}}^2 / 4 \cdot De$, De being the energy of dissociation of the molecule. Having ω_{e} and $\omega_{\mathrm{e}} \cdot \mathrm{Xe}$ for the molecule we can readily find the parameter k. For the RbXe* molecular $\omega_{\mathrm{e}} = 40\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{e}} \cdot \mathrm{Xe} = 0.54$ and $k = 74$. In the expression (61) $\xi_{\mathrm{m}} = R_{\mathrm{m}}$ and all the other parameters have their usual meaning. On the other hand, the rotational wave functions for RbXe* will be taken to be those for a symmetric top given by so-called Jacoby (hypergeometric) polynomials (see also Herzberg[14], p. 118):

$$\langle \varphi_1, \Theta_1 | J M \Omega \rangle = \Phi^J_{M\Omega}(\varphi_1, \Theta_1, \psi) = \sqrt{\frac{2J+1}{8\pi^2}}\, e^{iM\varphi_1}\, d^J_{M\Omega}(\Theta_1)\, e^{i\Omega\psi} , \tag{63}$$

where ψ refers to the inner motion of a molecule (motion of electrons about the internuclear axis) and Ω is the quantum number of the resultant electronic angular momentum about the internuclear axis. In the considered case $\Omega = \frac{1}{2}$ and J takes the successive values.

$$J = \Omega, \Omega+1, \Omega+2, \ldots$$

For $M = \frac{1}{2}$ and $J = \frac{1}{2}$, $\frac{3}{2}$ and $\frac{5}{2}$ we have respectively

$$\Phi^{\frac{1}{2}}_{\frac{1}{2}\frac{1}{2}}(\varphi_1, \Theta_1, \psi) = \frac{1}{\sqrt{2\pi}} e^{i\frac{1}{2}\varphi_1} \sqrt{\frac{1+x_1}{2}} \frac{1}{\sqrt{2\pi}} e^{i\frac{1}{2}\psi} ,$$

$$\Phi^{\frac{3}{2}}_{\frac{1}{2}\frac{1}{2}}(\varphi_1, \Theta_1, \psi) = \sqrt{\frac{1}{4\pi}} e^{i\frac{1}{2}\varphi_1} (3x_1 - 1) \sqrt{\frac{1+x_1}{2}} \cdot \frac{1}{\sqrt{2\pi}} e^{i\frac{1}{2}\psi} ,$$

$$\Phi^{\frac{5}{2}}_{\frac{1}{2}\frac{1}{2}}(\varphi_1, \Theta_1, \psi) = \sqrt{\frac{3}{8\pi}} e^{i\frac{1}{2}\varphi_1} (5x_1^2 - 2x_1 - 1) \cdot \sqrt{\frac{1+x_1}{2}} \frac{1}{\sqrt{2\pi}} e^{i\frac{1}{2}\psi} \tag{64}$$

with $x_1 = \cos\Theta_1$. The eigenenergy of the molecule being in a $|vJ\rangle$ state is given by

$$E_{vJ} = E_{\mathrm{el}} + E_v + E_J , \tag{65}$$

where E_{el} is the electronic energy of the molecule, E_v is given by (61) and

$$E_J = \frac{\hbar^2}{2I} [J(J+1) - \Omega^2] .$$

The quantity I is the moment of inertia of a molecule. For the RbXe* molecule I is found to be $1.04 \times 10^{-37}\ \mathrm{gcm}^2$.

Let us come back to the expression (56). In order to calculate $k(T)$ we replace, in a first approximation, the average over the momentum moduli p and q in (56) by taking $k(T)$ with the mean values $\bar{p}$ and $\bar{q}$. Thus we get

$$k(T) = \frac{2\pi}{\hbar} \sum_{vJ} \frac{\mu_2 \hbar k_{vJ}}{(2\pi\hbar)^3} \int \mathrm{d}\Omega \frac{1}{4\pi} \int \mathrm{d}\Omega_{\boldsymbol{k}_2} \Big| \int \mathrm{d}^3\boldsymbol{\eta} \int \mathrm{d}^3\boldsymbol{\xi} \cdot e^{-i\boldsymbol{\Delta k}\boldsymbol{\eta}} e^{i\boldsymbol{k}_1\boldsymbol{\xi}} \langle vJ | [V_{13}(\boldsymbol{\xi},\boldsymbol{\eta}) + V_{23}(\boldsymbol{\xi},\boldsymbol{\eta})] \cdot S^{\mathrm{cl}}(\infty, 0) \Big|^2 , \tag{66}$$

with $\boldsymbol{\Delta k} = \boldsymbol{k}_{vJ} - \bar{\boldsymbol{k}}_2$. Since the modulus of $\boldsymbol{\Delta k}$ takes rather large values we conclude that the dependence of the integrand in (66) on the direction of the vector $\boldsymbol{\eta}$ is mainly given through the first exponential factor. The remaining part of the integrand depends on the direction of $\boldsymbol{\eta}$ rather slightly, and as a result we can in the following replace it by its average value over all the directions of $\boldsymbol{\eta}$. Owing to that the integration over the directions of $\boldsymbol{\eta}$ in (66) can be carried out at once. The integrand in (66) except for the first exponential factor changes with η also slowly and decreases steeply for $\eta \to 0$ as well as for $\eta \to \infty$. Therefore, writing $\boldsymbol{\Delta k} \cdot \boldsymbol{\eta} = \Delta k\, \eta \cos\vartheta$, we infer that for any fixed direction of the vectors $\bar{\boldsymbol{k}}_2$ and $\boldsymbol{k}_{vJ}$ in integrating over $\cos\vartheta$ in (66) only those values of $\cos\vartheta$ contribute to (66) which satisfy the condition $\Delta k\cdot\eta_{\max}\cos\vartheta \leqq 1$. This enables us to integrate as goes

$$\int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} e^{-i\Delta k\eta\cos\vartheta}\sin\vartheta\,\mathrm{d}\vartheta = 2\pi\int_{-1}^{1} e^{-i\Delta k\eta x}\,\mathrm{d}x \approx 2\pi \int_{-1/\Delta k\eta_{\max}}^{1/\Delta k\eta_{\max}} e^{-i\Delta k\eta x}\,\mathrm{d}x = 4\pi\,\frac{\sin(\eta/\eta_{\max})}{\Delta k\,\eta}\,.$$

Thus the expression (66) takes the form

$$k(T) = \frac{2\pi}{\hbar}\sum_{vJ}\frac{\mu_2\hbar\,k_{vJ}}{(2\pi\hbar)^3}\int \mathrm{d}\Omega\,\frac{1}{4\pi}\int \mathrm{d}\Omega_{\boldsymbol{k}_2}\frac{1}{\Delta k^2}\Big|\int \mathrm{d}^3\boldsymbol{\eta}\int \mathrm{d}^3\boldsymbol{\xi}\,\frac{\sin(\eta/\eta_{\max})}{\eta}\,e^{i\boldsymbol{k}_1\boldsymbol{\xi}}$$
$$\cdot\langle v\,J|\,[V_{13}(\boldsymbol{\xi},\boldsymbol{\eta})+V_{23}(\boldsymbol{\xi},\boldsymbol{\eta})]\,S^{\mathrm{cl}}(\infty,0)\Big|^2, \tag{67}$$

with

$$\Delta k^2 = \bar{k}_2{}^2 - 2\,\bar{k}_2\,k_{vJ}\cos\Theta + k_{vJ}^2$$

and Θ being the polar angle between the vectors $\bar{\boldsymbol{k}}_2$ and $\boldsymbol{k}_{vJ}$. The integrand in (67) depends on the direction of the vector $\boldsymbol{k}_{vJ}$ through the modulus Δk only. This permits us to integrate (67) over the directions of $\boldsymbol{k}_{vJ}$ immediately. The result of the integration does not depend on the direction of $\bar{\boldsymbol{k}}_2$.

Since

$$\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\frac{\sin\Theta\,\mathrm{d}\Theta}{\bar{k}_2{}^2-2\,\bar{k}_2\,k_{vJ}\cos\Theta+k_{vJ}^2} = \frac{2\pi}{2\,\bar{k}_2\,k_{vJ}}\ln\left(\frac{\bar{k}_2{}^2+2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}{\bar{k}_2{}^2-2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}\right),$$

we obtain for $k(T)$ the expression

$$k(T) = \frac{2\pi}{\hbar}\sum_{vJ}\frac{\mu_2\hbar\,\pi}{(2\pi\hbar)^3\,\bar{k}_2}\ln\left(\frac{\bar{k}_2{}^2+2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}{\bar{k}_2{}^2-2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}\right)\frac{1}{4\pi}\int \mathrm{d}\Omega_{\boldsymbol{k}_2}\Big|\int \mathrm{d}^3\boldsymbol{\eta}\int \mathrm{d}^3\boldsymbol{\xi}\,\frac{\sin(\eta/\eta_{\max})}{\eta}\,e^{i\boldsymbol{k}_1\boldsymbol{\xi}}$$
$$\cdot\langle v\,J|\,[V_{13}(\boldsymbol{\xi},\boldsymbol{\eta})+V_{23}(\boldsymbol{\xi},\boldsymbol{\eta})]\,S^{\mathrm{cl}}(\infty,0)\Big|^2. \tag{68}$$

As is seen from (63) every rotational eigenfunction of the molecule contains the exponential factor $e^{iM\varphi_1}$ with M being a half-integer. The change of that factor with φ_1 is much stronger than that of the remaining part of the integrand in (68). If we then replace the latter by its average value over φ_1 we can perform the integration over φ_1 in (68) directly.

We obtain

$$\int_0^{2\pi} e^{-iM\varphi_1}\,\mathrm{d}\varphi_1 = -i\,\frac{2}{M}$$

with $M=\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots$.

Thus

$$k(T) = \frac{2\pi}{\hbar}\sum_{vJ}\sum_{M=-J}^{J}\frac{4}{M^2}\,\frac{2J+1}{4\pi}\,\frac{\mu_2\hbar\,\pi}{(2\pi\hbar)^3\,\bar{k}_2}\ln\left(\frac{\bar{k}_2{}^2+2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}{\bar{k}_2{}^2-2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}\right)\frac{1}{4\pi}\int \mathrm{d}\Omega_{\boldsymbol{k}_2}\Big|\int \mathrm{d}^3\boldsymbol{\eta}\int \mathrm{d}^3\boldsymbol{\xi}\,\frac{\sin(\eta/\eta_{\max})}{\eta}$$
$$\cdot\,e^{i\boldsymbol{k}_1\boldsymbol{\xi}}\,d^J_{M\Omega}(\Theta_1)\,\Psi_v(\xi)\,[V_{13}(\boldsymbol{\xi},\boldsymbol{\eta})+V_{23}(\boldsymbol{\xi},\boldsymbol{\eta})]\,S^{\mathrm{cl}}(\infty,0)\Big|^2. \tag{69}$$

The other parameters needed for the present calculation have the values: $m_1=85.48$ g/mol, $m_2=m_3=131.30$ g/mol so that $\mu_1=51.77$ g/mol, $\mu_2=81.77$ g/mol as well as $\lambda=0.606$ and $\chi=0.394$. Introducing now the dimensionless variables ϱ and u, so that $\xi=R_{\mathrm{m}}\,\varrho$ and $\eta=R_{\mathrm{m}}\,u$, and putting $\cos\Theta_1=x_1$, $\cos\Theta_2=x_2$ and $\cos\Theta_3=x_3$ we can transform (69) as follows

$$k(T) = C(T)\cdot F(T)\,, \tag{70}$$

where

$$C(T) = \frac{\mu_2\,\varepsilon_{\mathrm{m}}{}^2\,R_{\mathrm{m}}{}^2}{4\pi^2\hbar^3\,\bar{k}_2(T)}\cdot R_{\mathrm{m}}{}^6\ [\mathrm{cm}^6/\mathrm{sec}]$$

with $\varepsilon_{\mathrm{m}}=740\ \mathrm{cm}^{-1}$ and $R_{\mathrm{m}}=3.48$ Å, and $F(T)$ is a dimensionless function of the recombination rate constant given by

$$F(T) = \sum_{vJ}\sum_{M=-J}^{J}\frac{2J+1}{M^2}\ln\left(\frac{\bar{k}_2{}^2+2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}{\bar{k}_2{}^2-2\,\bar{k}_2\,k_{vJ}+k_{vJ}^2}\right)\frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\varphi_3\int_{-1}^{1}\mathrm{d}x_3\Big|\int_{-1}^{1}dx_1\int_{\varrho_{\min}}^{\varrho_{\max}}\sigma\,\mathrm{d}\varrho\,e^{i\gamma(T,\varrho,x_1)}\,[G_r{}^v(T,\varrho,x_1)$$
$$-\,i\,G_i{}^v(T,\varrho,x_1)]\,d^J_{M\frac{1}{2}}(x_1)\,R_v(\varrho)\Big|^2, \tag{71}$$

where

$$G_r^v(T,\varrho,x_1)=\int_0^{2\pi}\mathrm{d}\varphi_1\int_0^{2\pi}\mathrm{d}\varphi_2\int_{-1}^{1}\mathrm{d}x_2\int_{u_{\min}}^{u_{\max}}u\sin(u/u_{\max})\,[V_{13}(R_{13})+V_{23}(R_{23})]\cos[\zeta(T)\,(\alpha_{13}+\alpha_{23})]\,,$$

$$G_i^v(T,\varrho,x_1)=\int_0^{2\pi}\mathrm{d}\varphi_1\int_0^{2\pi}\mathrm{d}\varphi_2\int_{-1}^{1}\mathrm{d}x_2\int_{u_{\min}}^{u_{\max}}u\sin(u/u_{\max})\,[V_{13}(R_{13})+V_{23}(R_{23})]\,\sin[\zeta(T)\,(\alpha_{13}+\alpha_{23})] \qquad (72)$$

and

$$\gamma(T,\varrho,x_1)=A(T)\,\varrho\,x_1-\zeta(T)\,\alpha_{12}(\varrho,x_1)$$

with $A(T)=(\sqrt{2\,k\,T\,\mu_2/\hbar})\,R_\mathrm{m}$. The functions $\alpha_{12}(\varrho,x_1)$,

$$\alpha_{13}=\alpha_{13}\,(T,\varrho,\varphi_1,x_1,\;u,\varphi_2,x_2,\varphi_3,x_3)\,,$$

and

$$\alpha_{23}=\alpha_{23}\,(T,\varrho,\varphi_1,x_1,\;u,\varphi_2,x_2,\varphi_3,x_3)\,,$$

are given according to (59) respectively for (1, 2)-, (1, 3)- and (2, 3)-pairs of the interacting Rb and Xe atoms. The potential $V_{13}(R_{13})$ is given by (58) and $V_{23}(R_{23})$ is taken according to (57) with $n=12$. The interatomic distances R_{13} and R_{23} are

$$R_{13}=[u^2+2\,\lambda\,\varrho\,u\,(\sqrt{(1-x_1{}^2)\,(1-x_2{}^2)}\cdot\cos(\varphi_2-\varphi_1)+x_1\,x_2)+\lambda^2\,\varrho^2]^{\frac{1}{2}},$$

$$R_{23}=[u^2-2\,\chi\,\varrho\,u\,(\sqrt{(1-x_1{}^2)\,(1-x_2{}^2)}\cdot\cos(\varphi_2-\varphi_1)+x_1\,x_2)+\chi^2\,\varrho^2]^{\frac{1}{2}}.$$

It turns out that in general the function $\gamma(T,\varrho,x_1)$ oscillates strongly in ϱ and x_1. But for x_1 in the range (0.74 – 0.94) γ changes slightly with ϱ for $\varrho>1.1$.

From those regions of ϱ and x_1 there comes the greatest contribution to the integral (69). Besides, the functions G_r^v and G_i^v change with ϱ slowly being nearly constant in the above mentioned x_1 region. This enables us to integrate (71) over ϱ and x_1 without taking into account the explicit dependence of G_r^v and G_i^v on these variables.

6. Details of the Calculation and Results

The recombination rate constant $k(T)$ has been calculated for the quasimolecule RbXe* for $T=300°$. For this temperature $C(T)$ is found to be $7.542\times10^{-30}\,\mathrm{cm}^6\,\mathrm{sec}^{-1}$. The function $F(T)$ has been calculated with the vibrational eigenfunctions of the molecule for $v=1$, 3, 6, 11, 14, 17, 20, 25, 30. For each of these vibrational states the rotational eigenfunctions were taken with $J=1/2$, 3/2 and 5/2 only. The results of the calculation showed that the respective J-components of $k(T)$ for a definite v-state differ from one another slightly in taken J values. This could indicate the independence of $k(T)$ from the rational quantum number J.

Neglecting the dependence of $k(T)$ on J we see that to get the total recombination rate constant $k(T)$ we need only to calculate its respective v-components for any J-state and to know the number of rotational states for each of the vibrational state. This facilitates the calculation of $k(T)$ considerably. The next step in our approximation procedure is to replace the average of $F(T)$ over directions of the vector $\overline{\boldsymbol{k}}_2$, which is expressed in (71) by the integration over φ_3 and x_3, by taking an arithmetical average of $k_v(T)$ calculated for 10 different values of φ_3 and x_3 chosen at random. Since the vibrational eigenstates of the molecule for large v are strongly oscillating our procedure was as follows: first the integrals G_r^v and G_i^v were calculated with the Monte Carlo method and second the corresponding integrals with a proper vibrational eigenfunction [as is seen in (71)] were calculated with the usual Gauss method. All the calculations were carried out on the CDC 6600 computer at the Computer Centre of the University Stuttgart. In calculating 4-fold integrals G_r^v and G_i^v there are points in the integration region for which the functions $\sin[\zeta(T)\cdot(\alpha_{13}+\alpha_{23})]$ and $\cos[\zeta(T)\cdot(\alpha_{13}+\alpha_{23})]$ oscillate rapidly and from which there comes the greatest error in the final results. Assuming that the total contribution from these points to the integrals equals zero, they could be removed from the integration range with some rejection method. The exact analysis of those points indicates that the main contribution to the integrals issues from the long-range forces acting among the interacting particles. The program for the integrals G_r^v and G_i^v was written in Fortran IV. It gave us both the calculated values of G_r^v and G_i^v and their statistical errors. At 50000 points chosen from the 4-dimensional (φ_1, u, φ_2, x_2) integration region at random the statistical error for each calculation was below 10% of the calculated values of G_r^v and G_i^v. The results of the present calculations are presented in Figure 2.

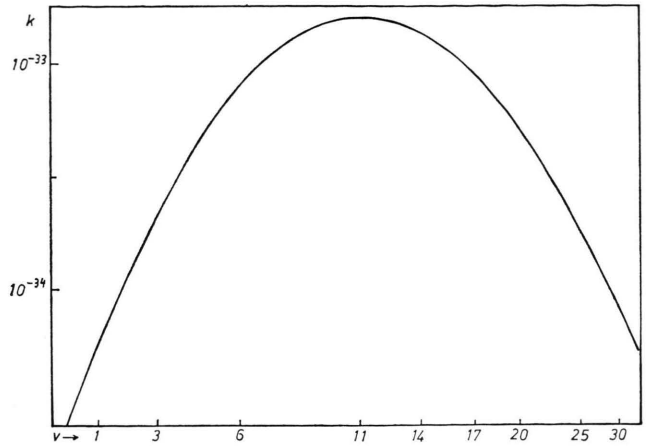

Fig. 2. The teratomic recombination rate constant k as a function of vibrational energy of the molecule. The dissociation limit is to the right and the potential minimum ($\varepsilon_m = -740$ cm^{-1}) to the left.

A rather pronounced dependence of $k(T)$ on the vibrational quantum number of the molecule is seen. Such a behaviour of $k(T)$ with v can readily be explained. As is seen from (71) every v-contribution of $k(T)$ consists of two factors: the first of them depends on the number of rotational states for a given v-state of the molecule, the other one depends on the value of the integral over ϱ with an appropriate v-eigenfunction. The number of rotational states for a given vibrational level decreases with increasing quantum number v. On the other hand the wave functions given by (61) are nearly symmetric for small v which implies rather small values of the corresponding integrals. But with increasing v the proper vibrational wave functions become more and more asymmetric especially at the right-hand side end from where there comes the greatest contribution to the integral. Those two factors tend in opposite directions in their growths. This leads to some maximum of $k(T)$ near the intermediate vibrational energies of the molecule. The total recombination rate constant $k(T)$ is found to be 2.4×10^{-32} cm^6 sec^{-1} with about 10% uncertainty. The value of k determined by Carrington et al.[11] is 8.2×10^{-32} cm^6 sec with about 20% uncertainty. The order of magnitude agreement of both the values $k(T)$ indicates that the present approach is correct and can successfully be used for other concrete calculations. From the explicit form of the rate constant $k(T)$ [cp. (70) and (71)] we can deduce its dependence on temperature. We see that $k(T)$ depends on T through the parameter $C(T)$ and the function $F(T)$. The parameter $C(T)$ decreases with increasing T as $T^{-\frac{1}{2}}$ whereas the function $F(T)$ should rather increase slightly with T. This is so since with increasing T the parameter $\zeta(T)$ diminishes, which implies less oscillations of the corresponding sin and cos functions occurring in G_i^v and G_r^v. Thus we conclude that $k(T)$ should depend on temperature about as $T^{-\frac{1}{2}}$.

7. Conclusion

In the present work a new approach to the calculation of a teratomic recombination rate constant k has been demonstrated. It has been shown that starting from the corresponding quantum expression one can obtain an expression for k in the eikonal approximation which is useful for further numerical calculations. Such calculations have been carried out for the RbXe* quasimolecule. The results of the present calculations were compared with those obtained by Carrington et al. from molecular spectrum measurements of the gaseous Rb*-Xe system. The good agreement of both results in the order of magnitude indicates that the present approach is correct and can successfully be used for other alkali-nobel gas systems. The investigation of the formation of quasimolecules from excited alkali atoms and ground state nobelgas atoms is of particular interest on account of the possibility of utilizing such systems to the realization of tunable gas lasers working with van der Waals diatomic molecules (see, e. g. Phelps[15]). It seems that the present approach can successfully be applied both to the recombination of gaseous molecules during teratomic collisions and to the recombination of ions and free electrons to give neutral atoms. The possibility to calculate k completely quantum-mechanically is interesting in principle. If, for example, we expanded the free wave-packets occurring in (40) in terms of the spherical Bessel functions $j_l(kr)$ then $k(T)$ could be expressed as a sum of probabilities of all the possible changes of the angular momenta of the colliding particles as a result of the interaction in the course of a collision. The quantum calculation of those probabilities seems to be possible.

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Appendix

Take the following expression

$$-i\sum_{n_1 n_2}\langle \tfrac{1}{2}\,0\,|\,V_{12}(\boldsymbol{\xi})\,|\,n_1 n_2\rangle \lim_{\eta\to 0}\int_0^\infty e^{-\eta t} \cdot \exp\{i(\omega_{1/2\,n_1}+\omega_{0\,n_2})t\}\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle\,\mathrm{d}t\,, \qquad (\mathrm{A}\,1)$$

where

$$\boldsymbol{\xi}(t)=\boldsymbol{\xi}-\boldsymbol{v}\,t \quad \text{with} \quad \boldsymbol{v}=\boldsymbol{p}/\mu_1\,.$$

In the following we consider the integral

$$I=\lim_{\eta\to 0}\int_0^\infty e^{-\eta t}\exp\{i(\omega_{1/2\,n_1}+\omega_{0\,n_2})t\} \cdot \langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle\,\mathrm{d}t\,. \qquad (\mathrm{A}\,2)$$

Integrating by parts we get

$$I=-\frac{\langle n_1 n_2\,|\,V_{12}(\boldsymbol{\xi})\,|\,\tfrac{1}{2}\,0\rangle}{i(\omega_{1/2\,n_1}+\omega_{0\,n_2})} -\lim_{\eta\to 0}\int_0^\infty \exp\{i(\omega_{1/2\,n_1}+\omega_{0\,n_2}+i\,\eta)t\} \cdot \frac{\dfrac{\mathrm{d}}{\mathrm{d}t}\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle\,\mathrm{d}t}{i(\omega_{1/2\,n_1}+\omega_{0\,n_2})}\,. \qquad (\mathrm{A}\,3)$$

According to (41), the matrix element occurring in the last integrand can be expressed in cylindrical coordinates by

$$\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle=\frac{\text{const}}{[b^2+v^2(\tau+t)^2]^{3/2}}\,, \qquad (\mathrm{A}\,4)$$

where the components x, y and z of the vector $\boldsymbol{\xi}$ are $x=b\cos\varphi$, $y=\mathrm{b}\sin\varphi$ and $z=-\boldsymbol{\xi}\,\boldsymbol{v}/v=\tau\,v$. Since

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle = -\,\text{const}\,\frac{3\,v^2\,(\tau-t)}{[b^2+v^2\,(\tau-t)^2]^{5/2}}\,,$$

we find that

$$\left|\frac{\dfrac{\mathrm{d}}{\mathrm{d}t}\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle}{\langle n_1 n_2\,|\,V_{12}[\boldsymbol{\xi}(t)]\,|\,\tfrac{1}{2}\,0\rangle}\right| = \frac{3\,(\tau-t)}{(b/v)^2+(\tau-t)^2}\approx\frac{1}{\tau_c}$$

because the time $\tau-t$ in the problem under consideration must be of the order of the collision time τ_c with $\tau_c=b/v$. For adiabatic collisions any transition frequency ω_{ik} must be much greater than the inverse of the collision time, i. e. the condition $\tau_c\cdot\omega_{ik}\gg 1$ must be fulfilled. Therefore, the integral I can be approximated by the first term in (A 3) and thus the expression (A 1) gives us the corresponding van der Waals potential.

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