Translational radiative transitions in atomic collisions

G. V. Shlyapnikov and I. P. Shmatov

I. V. Kurchatov Institute of Atomic Energy, Moscow

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A quantum-mechanical theory of translational radiative transitions in atomic collisions is developed. It is shown that in the case of light atoms the idea of nuclear motion along classical trajectories cannot be used to describe spectral characteristics of such processes. However, in the case of heavy atoms the quantum approach is essential only at relatively high photon energies. A method is suggested for the reconstruction of the potential curves of quasimolecules from the experimental absorption spectrum. Specific calculations are carried out for rare gas quasimolecules.

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1. Infrared optical properties of dense atomic gases are governed largely by translational radiative transitions which occur in collisions between atoms. This process represents radiative transitions in quasimolecules formed by colliding atoms and they are not accompanied by a change in the electron state. Such transitions alter only the kinetic energy of atoms. The transition cross section considered as a function of the frequency includes information on the form of the potential curve of the electron term. The most interesting feature, mainly in connection with the possibility of experimental observation, is the photoabsorption reaction in collisions between rare gas atoms.[1)]

The published experiments[1-6] have given extensive information on the translational absorption spectra of strongly compressed mixtures of rare gases. The integrated characteristics of such spectra were subjected to a detailed theoretical analysis by Poll and Van Kranendonk.[7] In most of the investigations of this subject[8-10] an empirical dipole moment of a transition and model potentials of the atomic interaction are used to calculate the form of the absorption spectrum. However, the nature of the spectrum is very sensitive to the form of the potential curve of a quasimolecule formed in collisions and calculations of this type are not reliable. On the other hand, precisely for this reason the inverse problem of reconstruction of the potential curve from spectroscopic experimental data can be solved with a high precision if reliable information is available on the dipole moment of a phototransition considered as a function of the distance between nuclei.

An asymptotic method for the calculation of the dipole moment of a transition is developed in the present paper: it is based on the existence of a small parameter in the form of the ratio of the characteristic atomic size to the internuclear distance. A quantum-mechanical treatment is given of the relationship between the form of the absorption spectrum and the parameters of the interatomic potential and dipole moment of a transition. A comparison of the results of the theory for an absorption spectrum of a mixture of argon and krypton with the experimental data is used to reconstruct the repulsive part of the potential curve of the $\mathrm{ArKr}(^1\Sigma^+)$ quasimolecule.

2. The absorption cross section of light for atomic collisions is governed by the familiar formula (see, for example, Refs. 11 and 12). The matrix element of the dipole moment operator of the quasimolecule, which occurs in this formula, can be reduced to the following form in the Born–Oppenheimer approximation:

$$\mathbf{D}_{ij}=\int \Psi^{*}_{i\,\mathrm{nu}}(\mathbf{R})\,\mathbf{d}(R)\,\Psi_{j\,\mathrm{nu}}(\mathbf{R})\,d\mathbf{R}. \tag{1}$$

Here, $\mathbf{R}$ is the vector representing the internuclear distance; $\Psi_{i\mathrm{nu}}$ and $\Psi_{j\mathrm{nu}}$ are the wave functions of the motion of nuclei in the initial and final states. In the case of translational transitions the R-dependent dipole moment of a phototransition is

$$\mathbf{d}(R)=\int |\Psi_{\mathrm{el}}(\mathbf{r}_k,\mathbf{R})|^2\mathbf{D}\,d\mathbf{r}_k, \tag{2}$$

where $\mathbf{D}$ is the operator of the dipole moment of the quasimolecule; $\Psi_{\mathrm{el}}(\mathbf{r}_k,\mathbf{R})$ is the electron wave function; $\mathbf{r}_k$ is the set of the electron coordinates.

Our first task will be to calculate $\mathbf{d}(R)$. The potential for the interaction of the atoms of rare gases (and many other atoms) is repulsive even at internuclear distances considerably greater than the characteristic atomic size. Therefore, the translational radiative transitions in collisions of such atoms occur only when the distances between the atoms are large. This makes it possible to represent the dipole moment $\mathbf{d}(R)$ of Eq. (2) as a sum of the short-range and exchange parts. Methods for the calculation of the long-range part of the dipole moment, associated with the multipole interaction of atoms, have been developed to a sufficiently high degree.[13] However, as shown below, the probability of a translational transition depends most strongly on the exchange part of the dipole moment $\mathbf{d}_{\mathrm{exch}}(R)$ which is due to the overlap of the electron shells of the atoms.

TABLE I.

	d_1	d_2	δ	γ		d_1	d_2	δ	γ
H–Ar	0.071	0.027	2.075	4.379	Kr–Xe	0.762	0.326	1.96	4.577
H–Kr	0.018	0.007	2.015	4.474	Ar–Xe	1.131	0.586	2.02	4.482
H–Xe	0.082	0.026	1.945	4.602	Xe–Ne	0.11	0.069	2.603	3.692
Kr–Ar	0.416	0.261	2.09	4.352					

Note. In actual calculations we used the asymptotic coefficients A and B found in Ref. 18.

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We shall find $\mathbf{d}_{\mathrm{exch}}(R)$ using the electron wave function of a quasimolecule $\Psi_{\mathrm{el}}(\mathbf{r}_k,\mathbf{R})$ obtained employing the Racah genealogical scheme,[14] i.e., expressed in the form of a linear combination of the products of the wave functions of the atomic cores and two-electron wave functions of specific valence electrons (one from each atom)[15]:

$$\Psi_{\mathrm{el}\,IM_I}(\mathbf{r}_k,\mathbf{R})=(2N_aN_b)^{-1/2}$$
$$\times\sum_n^{N_a}\sum_j^{N_b}\sum_{\substack{ls,l's',M_s'M_s'\\ m_lm_l',m_sm_s',\sigma\sigma'}}(-1)^{n+j-N_a-N_b}G_{ls}{}^{LS}G_{l's'}^{L'S'}\begin{bmatrix}S' & S & I\\ M_S' & M_S & M_I\end{bmatrix}\begin{bmatrix}l & l_e & L\\ m_l & m & M_L\end{bmatrix}$$
$$\times\begin{bmatrix}l' & l_e' & L'\\ m_l' & m' & M_L'\end{bmatrix}\begin{bmatrix}s & 1/2 & S\\ m_s & \sigma & M_S\end{bmatrix}\begin{bmatrix}s' & 1/2 & S'\\ m_s' & \sigma' & M_S'\end{bmatrix}$$
$$\times\Phi^{(a)}_{lsm_lm_s}(1,\dots,n-1,n+1,\dots,N_a)\,\Phi^{(b)}_{l's'm_l'm_s'}(1,\dots,j-1,j+1,\dots,N_b)$$
$$\times[\varphi_{\mathrm{el}}(na,jb)-\varphi_{\mathrm{el}}(ja,nb)]. \qquad (3)$$

Here, I is the total electron spin of a quasimolecule; M_I is the projection of this spin onto an axis which is fixed in space; $l_e^{1/2}m\sigma$, lsm_lm_s, and LSM_LM_S are the quantum numbers representing the states of a valence electron, the atomic core, and the whole atom, respectively; G_{ls}^{LS} are the genealogical coefficients; N_a and N_b are the numbers of valence electrons in the atoms;

$$\Phi^{(a)}_{lsm_lm_s}(1,\dots,n-1,\dots,n+1,\dots N_a)$$

is the wave function of the atomic core; $\varphi_{\mathrm{el}}(na,jb)$ is the two-electron wave function of n-th and j-th specific electrons, corresponding to the situation when the n-th electron is localized mainly near the atomic core a, whereas the j-th electron is close the atomic core b.

Then, the required dipole moment is identical, apart from a constant factor, with the quantity

$$\mathbf{d}^{(0)}_{\mathrm{exch}}(R)=\int\varphi_{\mathrm{el}}(1a,2b)\mathbf{D}\varphi_{\mathrm{el}}(1b,2a)\,d^3r_1\,d^3r_2. \qquad (4)$$

In the presence of a small parameter[2)] $|\alpha-\beta|R\ll 1$, where $\alpha^2/2$ and $\beta^2/2$ are the binding energies of electrons in atoms, the main contribution to $\mathbf{d}^{(0)}_{\mathrm{exch}}(R)$ of Eq. (4) is due to the electron density localized near the internuclear axis. Therefore, in the case of the two-electron wave functions φ_{el} we can use the Gor'kov–Pitaevskiĭ representation[16,17]

$$\varphi_{\mathrm{el}}(1a,2b)=\varphi(1a)\varphi(2b)\chi_{\mathrm{I}},$$
$$\varphi_{\mathrm{el}}(1b,2a)=\varphi(1b)\varphi(2a)\chi_{\mathrm{II}}. \qquad (5)$$

Here,

$$\varphi(1a)=A\left(\frac{2l_e+1}{4\pi}\right)^{1/2}r_{1a}^{1/\alpha-1}\exp(-\alpha r_{1a}),$$
$$\varphi(2b)=B\left(\frac{2l_e+1}{4\pi}\right)^{1/2}r_{2b}^{1/\beta-1}\exp(-\beta r_{2b}) \qquad (6)$$

are the wave functions of electrons in isolated atoms for distances between the electron and the atomic core r_{1a} and r_{2b} much greater than the atomic size; A and B are the asymptotic coefficients. These wave functions correspond to zero projections of the orbital electron momenta of the internuclear axis. The expressions for the functions χ_{I} and χ_{II} are given in Ref. 17.

If we select the coordinate origin at the midpoint of the internuclear distance and carry out integration, we find that

$$\mathbf{d}^{(0)}_{\mathrm{exch}}(R)=\frac{\mathbf{R}}{R}\frac{A^2B^2}{2^{2/\alpha+2/\beta-2/(\alpha+\beta)+3}}(2l_e+1)(2l_e'+1)$$
$$\times\Gamma\left(1+\frac{1}{\alpha+\beta}\right)R^{2/\alpha+2/\beta-1/(\alpha+\beta)+1}\exp^{-(\alpha+\beta)R}(c(\alpha,\beta,R)-c(\beta,\alpha,R)), \qquad (7)$$

$$c(\alpha,\beta,R)=\iint 2^{2/\beta}\exp\left[\frac{t_1+t_2-2}{2\beta}-R\frac{(\alpha-\beta)(t_1+t_2)}{2}\right]$$
$$\times\left[\frac{(1+t_1)(1+t_2)}{(1-t_1)(1-t_2)}\right]^{1/\alpha-1/\beta}\frac{\{[(1-t_1)+(1-t_2)\alpha\beta^{-1}][(1-t_2)+(1-t_1)\alpha\beta^{-1}]\}^{1/\alpha-1/(\alpha+\beta)}}{\{[\alpha+\beta-t_1(\alpha-\beta)][\alpha+\beta-t_2(\alpha-\beta)]\}^{1+1/(\alpha+\beta)}} \qquad (8)$$
$$\times[\alpha(1-t_1)(1-t_2)(2+t_1+t_2)+\beta(1+t_1)(1+t_2)(2-t_1-t_2)]^{1/(\alpha+\beta)}(t_1+t_2)\,dt_1\,dt_2.$$

The integration domain in Eq. (8) is a triangle with the coordinates (–1,1), (1,1), and (1,–1). In the case of finite projections of the orbital electron momenta there is an additional small factor amounting to $(R^{|m|+|m'|})^{-1}$, where m and m' are the projections of the electron orbital momenta on the internuclear axis. Using then Eq. (3) for $\Psi_{\mathrm{el}}(\mathbf{r}_k,\mathbf{R})$ and averaging over the projection of the total spin M_I of the quasimolecule, we obtain

$$\mathbf{d}_{\mathrm{exch}}(R)=\mathbf{d}^{(0)}_{\mathrm{exch}}(R)N_aN_b(2S+1)(2S'+1)$$
$$\times\sum_{ls,l's'}\begin{Bmatrix}s & 1/2 & S\\ 1/2 & s' & S'\\ S & S' & I\end{Bmatrix}[G_{ls}^{LS}G_{l's'}^{L'S'}]^2\begin{bmatrix}l & l_e & L\\ M_L & 0 & M_L\end{bmatrix}^2\begin{bmatrix}l' & l_e' & L'\\ M_L' & 0 & M_L'\end{bmatrix}^2. \qquad (9)$$

Here,

$$\begin{Bmatrix}s & \frac{1}{2} & S\\ \frac{1}{2} & s' & S'\\ S & S' & I\end{Bmatrix}$$

is the 9j Wigner symbol.

Expansion of the functions $c(\alpha,\beta,R)$ and $c(\beta,\alpha,R)$ in terms of the small parameter $R|\alpha-\beta|$ readily reduces Eq. (9) to

$$d_{\mathrm{exch}}(R)=(d_1+d_2R)R^{\gamma}e^{-\delta R}, \qquad (10)$$

where $\gamma=2/\alpha+2/\beta-1/(\alpha+\beta)+1$ and $\delta=\alpha+\beta$. The coefficients d_1 and d_2 are listed in Table I for some specific systems.

The quantity $d_{\mathrm{exch}}(R)$ calculated from Eq. (10) is compared in Fig. 1 with the results of numerical calculations[19] for the He–Ne and Ar–Kr systems, and also with the long-range dipole moment $d_{l.r}(R)$ (Ref. 13).

3. We shall now determine the frequency and temperature dependences of the absorption coefficient of a gas $K(\omega)$, associated with the translational transitions

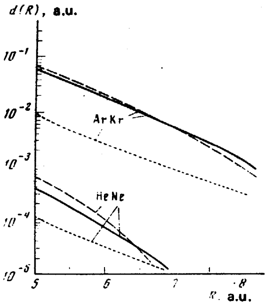

FIG. 1. Dependences $d(R)$ for HeNe and ArKr quasimolecules: the continuous curves represent $d_{\mathrm{exch}}(R)$ calculated from Eq. (10), whereas the dashed curves are the results of numerical calculation of $d_{\mathrm{exch}}(R)$ taken from Ref. 19; the dotted curves represent the long-range part of the dipole moment $d_{L.r}(R)$ (Ref. 13).

$$A+B+\hbar\omega \rightleftharpoons A+B+\Delta E \quad (11)$$

(ΔE is the increase in the kinetic energy of an atom because of the absorption of a photon). We shall do this employing two approaches. The first approach is based on the motion of nuclei along classical trajectories. The second approach (quantum-mechanical) allows for the wave nature of the nuclear motion. We shall employ initially a simple model: we shall assume that the interatomic interaction potential and the dipole moment of a transition decrease with distance R in accordance with the same $\exp(-\delta R)$ exponential law.[3)] In the case of this potential this is justified by the fact that the exchange interaction is affected most strongly by the internuclear distance and this interaction decreases exponentially on increase in R.

It follows from the calculations that the absorption coefficient of a gas associated with translational transitions is a smooth curve with a single maximum (Fig. 2). The position of the maximum is found from the condition that the distance between the phases of the nuclear wave functions of the initial and final states, which is accumulated in the region of transitions, is of the order of unity. Then,

$$\omega_{max} \propto \omega_M = \delta (T/\mu)^{1/2}, \quad (12)$$

where T is the gas temperature and μ is the reduced mass of the atoms.

The absorption coefficient obtained by both calculation variants is governed by two parameters:

$$\theta = \frac{\hbar\omega}{T}, \quad b = \frac{\pi}{\delta}\left(\frac{\mu T}{2}\right)^{1/2}.$$

The results of classical and quantum-mechanical approaches are identical in the limit $\theta \ll 1$. Since under real conditions we have $\omega_{max} \ll T$, the classical approximation is clearly adequate at low frequencies ($\omega \ll \omega_{max}$). In this range, we have

$$K(\omega) = \text{const}(\omega/\omega_{max})^2, \quad \omega \ll \omega_{max}. \quad (13)$$

Moreover, at high gas temperatures in the case of heavy atoms the classical approximation describes satisfactorily the region of the maximum even at room temperature because $\omega_{max} \ll T$.

The dependences of the absorption coefficient on the parameter θ for three values of the coefficient b is shown in Fig. 2. Curves 1, 2, and 3 correspond approximately to collisions of helium, neon, and argon atoms with heavier partners at room temperature. We can easily see that in the case of helium and neon a correct description in the region of the maximum (and also in the range where $\omega > \omega_{max}$) is provided only by a quantum-mechanical approach. In the case of heavier atoms this approach is essential only at frequencies $\omega \gg \omega_{max}$.

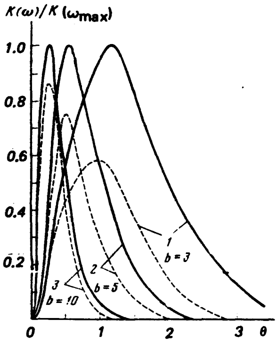

FIG. 2. Classical and quantum absorption coefficients in the model problem [$d(R) \propto U(R) \propto \exp(-\delta R)$]. The continuous curves represent $K_{qu}(\omega)/K(\omega_{max})$, whereas the dashed curves give $K_{cl}(\omega)/K(\omega_{max})$.

It is important to note also that the calculated absorption coefficient of a gas depends strongly on the parameters of the interatomic interaction potential and on the dipole moment $d(R)$. Therefore, in real cases one can solve much more accurately the inverse problem of reconstruction of the repulsive part of the potential energy curve from the known dipole moment and the known frequency dependence of the absorption coefficient.

On the basis of the above analysis, we shall tackle this problem by a quantum-mechanical approach. The effective potential energy will be represented by

$$U_{eff}(R) = \varepsilon e^{-\lambda R} - U_0 + J(J+1)/2\mu R^2, \quad (14)$$

where J is the rotational momentum of a quasimolecule; ε, λ, and U_0 are characteristic constants. This representation is justified for two reasons. Firstly, it follows from the condition $R \gg a_0 \sim 1/\alpha \approx 1/\beta$ that the potential energy $U(R)$ in the region of the investigated transitions is a sum of the exchange and long-range parts, and the exchange interaction—which decreases exponentially on increase in the distance R—is the one that depends most strongly on the internuclear distance. On the other hand, the exponential nature of the dependence $d(R)$ means that the range of radiative transitions corresponds indeed to the repulsive part of the potential curve $U(R)$ and the presence of a shallow well in this curve can be allowed for by adding a constant term U_0 to Eq. (14).

Application of the familiar formulas for the cross sections of radiative transitions[14] and an allowance for the simultaneous induced absorption and induced emission, together with the representation of the distribution of particles by the Maxwellian law, yields

$$K(\omega) = n_1 n_2 \frac{\mu\omega}{\sigma c}(1-e^{-\omega/T})\left(\frac{2\pi}{\mu T}\right)^{3/2} \int_0^\infty \sum_{J=0}^{\infty} (J+1)(S^2_{J,J+1}+S^2_{J+1,J}) \frac{e^{-E/T}dE}{[E(E+\omega)]^{1/2}}. \quad (15)$$

Here, ω is the photon frequency; n_1 and n_2 are the densities of the colliding atoms; E is the collision energy;

$$S_{J,J'} = \int \chi_{k_i,J}(R) d(R) \chi_{k_f,J'}(R) dR, \quad (16)$$

where $\chi_{kJ}(R)$ is the wave function for the radial motion of nuclei normalized on the $k/2\pi$ scale; $k=(2\mu E)^{1/2}$ is the momentum of the relative motion of the nuclei.

If the wave functions $\chi_{kJ}(R)$ are solutions of the Schrödinger equation with the potential energy given by Eq. (14), if $R=R_{tJ}$ applies in the centrifugal energy, where R_{tJ} is the classical turning point, and if the dipole moment is represented in the form

$$d(R) = d_0 e^{-\delta R}, \quad d_0 = (d_1 + d_2 R_{tJ}) R_{tJ}^{\gamma}, \quad (17)$$

it is found from Eq. (15) that

$$K(\omega)=n_1n_2\frac{4\pi}{3c}\frac{\omega(1-e^{-\omega/T})\mu}{\lambda^2(2\pi\mu T)^{3/2}\Gamma^2(2\delta/\lambda)}\left(\frac{\lambda^2}{2\mu\varepsilon}\right)^{2\delta/\lambda}$$

$$\times\int_0^\infty\sum_{J=0}^\infty\frac{d_0^2(R_{tJ})e^{-E/T}\,dE}{[E(E+\omega)]^{1/2}}\{(J+1)|\Omega_1|^2+J|\Omega_2|^2\};\qquad(18)$$

$$\Omega_1=\left|\Gamma\left(\frac{\delta}{\lambda}+i\frac{q+q'}{2}\right)\Gamma\left(\frac{\delta}{\lambda}+i\frac{q-q'}{2}\right)\right|^2(qq'\operatorname{sh}\pi q\operatorname{sh}\pi q')^{1/2},$$

$$\Omega_2=\left|\Gamma\left(\frac{\delta}{\lambda}+i\frac{q+q''}{2}\right)\Gamma\left(\frac{\delta}{\lambda}+i\frac{q-q''}{2}\right)\right|^2(qq''\operatorname{sh}\pi q\operatorname{sh}\pi q'')^{1/2};\qquad(19)$$

$$q^2=8\mu\varepsilon\lambda^{-2}\exp(-\lambda R_{tJ}),\qquad(20a)$$

$$q'^2=q^2+8\mu\omega/\lambda^2-8(J+1)/(\lambda R_{tJ})^2,\qquad(20b)$$

$$q''^2=q^2+8\mu\omega/\lambda^2+8J/(\lambda R_{tJ})^2.\qquad(20c)$$

In the case when J in Eq. (20b) is so large that q' assumes only imaginary values it is necessary to equate Ω_1 to zero.

A result of this type was obtained earlier by Tanimoto.[21] However, he used an empirical exponential relationship for the dipole moment and an exponential approximation for the interatomic interaction potential, which ignores the presence of a potential well.

If $\omega \ll \omega_{\max}$, it follows from Eqs. (18)–(20) that

$$K(\omega)=K_1(\omega/\omega_M)^2,\ \omega\ll\omega_{max},\qquad(13a)$$

where

$$K_1=n_1n_2\frac{R_T^2d^2(R_T)}{c^2(\mu T)^{1/2}}\frac{(2\pi)^{3/2}}{3}\frac{\Gamma^4(\delta/\lambda)2^{4\delta/\lambda+1}\delta^3}{\Gamma(2\delta/\lambda)(1+2\delta/\lambda)\lambda^3},$$

and R_T is found from the equation $U(R_T)=T$. In the frequency range $\omega \gg T$, we have

$$K(\omega)=K_2\left(\frac{\omega}{\omega_M}\right)^{4\delta/\lambda-1}\exp\left\{-\left(\frac{\omega}{\omega_M}\right)^{1/2}\left[\frac{8\pi^2\delta}{\lambda^2}(\mu T)^{1/2}\right]^{1/2}\right\},\quad\omega\gg T.\qquad(21)$$

Here,

$$K_2=n_1n_2\frac{R_T^2d^2(R_T)}{c^2(\mu T)^{1/2}}\frac{2^{3-2\delta/\lambda}\pi^5}{3\Gamma^2(2\delta/\lambda)}\left(\frac{\delta}{\lambda}\right)^{4\delta/\lambda-1}\exp\left(\frac{2\pi^2\mu T}{\lambda^2}\right).$$

A comparison of the absorption spectrum given by Eq. (18) with the experimental spectrum of a mixture of argon and krypton[3,6] shows that the best agreement between the theory and experiment is obtained for

$$\lambda=2.72,\ \varepsilon=4.23\cdot10^4,\ U_0=7.07\cdot10^{-4}.\qquad(22)$$

TABLE II.

Pair	$h\omega_{max}$, cm^{-1}		$K(\omega_{max})/n_1n_2$, × 10^{46} cm^5	
	theory	experiment	theory	experiment
ArKr	67	67 [6]	4.6	4.6 [6]
ArXe	70	57 [6]	21	28 [6]
HeNe	264 ~300 [25] ~206 [6]	–	$4.3\cdot10^{-2}$ $\sim6.1\cdot10^{-2}$ [25] $\sim25\cdot10^{-2}$ [6]	–

Figure 3 shows the repulsive part of the potential curve of the ArKr($^1\Sigma^+$) quasimolecule deduced from Eq. (14) using the parameters (22). This figure includes also the repulsive part of the curve deduced experimentally from the elastic scattering of atoms.[22] The difference between these two curves is slight.

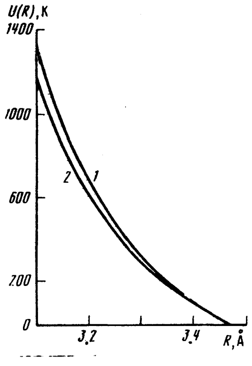

FIG. 3. Repulsive part of the potential energy of the ArKr($^1\Sigma^+$) quasimolecules; here, $U(R)$ is the potential energy; curve 1 is calculated on the basis of Eq. (11) with the coefficients (16), whereas curve 2 is based on the elastic scattering data.[22]

Table II gives the maximum values of the absorption coefficient deduced from Eq. (18) for room temperature, together with the frequencies $\omega_{\max}$ at which such maxima are observed. These values are calculated for the pairs ArKr, ArXe, and HeNe; in the case of ArKr it is assumed that the potential is given by Eq. (14) with the coefficient (22), whereas in the case of the pairs ArXe and HeNe the repulsive part of the potential energy curve is taken from the results on elastic scattering of atoms.[23,24] In the case of the HeNe system there are no reliable data on the absorption coefficient. Consequently, the results of calculations based on Eq. (18) with the potential of Ref. 24 are compared with estimates given in Ref. 6 and with an extrapolation of the numerical data.[25]

4. A theory of translational reactive transitions in atomic collisions given in the present paper makes it possible to deduce information on the interatomic interaction potential by a comparison of the experimental and theoretical absorption spectra. It follows from our analysis that in the case of collisions between light atoms the main part of the absorption spectrum has to be described by a quantum approach which allows for the wave nature of the nuclear motion. In the case of heavy atoms or very high temperatures this quantum approach is essential only at frequencies $\omega \gg \omega_{\max}$.

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1) We mean here collisions between atoms of different kinds because the translational radiative transitions are forbidden for collisions between two identical atoms on the basis of the selection rules governing the parity of the electron term.

2) Unless otherwise stated we shall always use atomic units.

3) In this case we in fact use a mathematical procedure known from the theory of vibrational relaxation (see, for example, Ref. 10).

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Contribution to the theory of heat exchange due to a fluctuating electromagnetic field

M. L. Levin, V. G. Polevoĭ, and S. M. Rytov

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The generalized Kirchhoff's law [M. L. Levin and S. M. Rytov, Theory of Equilibrium Thermal Fluctuations in Electrodynamics [in Russian], Nauka, 1967] is used to obtain general expressions for the spectral and total Poynting vector of a fluctuating electromagnetic field in a flat vacuum gap between two arbitrary semi-infinite media of different temperature (Sec. 2; to simplify the derivation, the medium is assumed to be isotropic and spatially local). Some general consequences and particular cases are discussed (Sec. 3), and the case of good conductors is investigated in detail in the impedence approximation both for the normal and for the anomalous skin effect (Sec. 4). The heat-flow formulas are generalized in Sec. 5 (using the concept of the generalized surface impedance) to include anisotropic media with spatial dispersion.

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1. INTRODUCTION

The question of "radiant" heat exchange was posed already in the classical theory of thermal radiation. An example of its solution is the Cristiansen integral formula (with respect to the frequency ω)[1] for the energy flux between "gray" bodies. Interest in this problem was again increased in the 60's, when, in connection with experiments at cryogenic temperatures, attention was called to the fact that consideration of only traveling waves (of radiation) is valid only if the gap thickness l between the bodies is large, i.e., when $l \gg \lambda_W$, where λ_W is the Wien wavelength corresponding to the temperature of the colder body. On the other hand in the case of thin gaps ($l \lesssim \lambda_W$) inhomogeneous waves (the near field) come into play and as a result the coefficient of heat transfer through the gap can depend on the gap width l.[2]

The presence (and even the role) of a near fluctuating field, of which sight was lost completely in the classical (i.e., geometrical-optics) theory of thermal radiation, was pointed out long ago.[3] This field is essential in all cases close enough to the surfaces of the body and by the same token for all sufficiently thin cavities or gaps.1) In particular, a general theory of thermal fluctuations of the electromagnetic field, developed by one of us,[3] was used by Lifshitz[5] to calculate the molecular adhesion forces between arbitrary bodies.

The solution of any problem dealing with average bilinear quantities was subsequently greatly facilitated when a simpler and general method was developed[6] for the calculation of correlators of a fluctuating electromagnetic field—the generalized Kirchhoff's law—and made it possible in many other applications to obtain an even shorter solution of the aforementioned adhesion-force problem (Ref. 6, Sec. 18). It is clear that also for heat exchange (average Poynting vector in a gap between two bodies) the near field should also play an essential role at small gap thicknesses l.

The heat flux in a flat gap between a semi-infinite medium and a well conducting nonradiating (cold) mirror was obtained already in Ref. 3 in connection with the question of experimental observation of the near field. There were pointed out, in particular, interference deviations from homogeneity of the field at

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