METHODOLOGICAL NOTES

Contents

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Radiative transitions in the molecular H_2^+ ion

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Abstract. A theoretical analysis was made of continuous light absorption in the visible, IR, and UV spectral ranges in a quasiequilibrium hydrogen plasma with an effective temperature between 1500 and 25000 K. The light absorption is caused by the photodissociation of molecular H₂⁺ ions from a large group of excited vibrational - rotational levels of the ground electronic term and by free-free radiative transitions at the collisions of protons (H $^+$) with hydrogen atoms H(1s). The phototransitions under consideration take place with a change of the electronic state $^{2}\Sigma_{g}^{+}\rightarrow^{2}\Sigma_{u}^{+}$ of the molecular (quasi-molecular) H_{2}^{+} ion. Quantum and quasi-classical descriptions of partial photodissociation cross sections and effective photoabsorption cross sections at particle collisions were accomplished on the basis of the theory of nonadiabatic transitions between the potential energy curves of a diatomic molecule. An analytical approach is set forth to calculate the integral contribution from all possible vibrational-rotational levels to the photodissociation cross section averaged over the Boltzmann distribution function. A detailed study was made of the contribution of bound - free and free - free transitions to the total optical absorption coefficient by the H_2^+ system as a function of temperature and wavelength. The recently calculated values of effective phototransition cross sections and photoabsorption coefficients are presented and compared with previously available data. Emphasis is placed on considering the relative contribution of positive molecular

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Received 23 September 2002 Uspekhi Fizicheskikh Nauk **173** (5) 491–510 (2003) Translated by E N Ragozin; edited by A Radzig H_2^+ ions and negative atomic H^- ions to the total photoabsorption coefficient of quasi-equilibrium hydrogen plasmas.

1. Introduction

The investigation of bound-free and free-free radiative transitions in hydrogen plasmas under conditions of local thermodynamic equilibrium makes it possible to gain important information on the most efficient sources of continuous photoabsorption in stellar atmospheres. It has been known that the main contribution to light absorption in the visible spectral range in a quasi-equilibrium hydrogen plasma with an effective temperature $T_{\rm eff} \approx 6000$ K (characteristic of the solar photosphere) is made by electron photodetachment from the negative H- ion whose concentration is low and amounts to $N_{\rm H^-}/N_{\rm H} \sim 10^{-8}$ of the number density of neutral hydrogen H(1s) atoms. In the infrared range below the threshold of electron photodetachment from the H⁻ ion, the photoabsorption is determined by free-free electron radiative transitions in the field of a hydrogen H(1s) atom (see, for instance, Refs [1, 2]). Another well-known example is light absorption induced by collisions involving hydrogen molecules: H₂-H₂, H₂-H, and H₂-He, which play the decisive part in the infrared photoabsorption in the dense atmospheres of cool stars with a low content of elements heavier than hydrogen and helium (see the works [3-6] and references cited therein).

In our paper we discuss the part played by the radiative transitions of the simplest diatomic system $H-H^+$ in the photoabsorption of a quasi-equilibrium hydrogen plasma with a temperature lying in the 1400-25000 K range. We note that the total number density $N_{H_2^+}$ of bound hydrogen molecular H_2^+ ions in the ground electronic state $X^2\Sigma_g^+$ at a temperature $T \sim 5000-15000$ K proves to be of the same order of magnitude as the H^- ion number density. With decreasing temperature down to T < 3000-3500 K, it

$$H_2^+(^2\Sigma_g^+, vJ) + \hbar\omega \to H_2^+(^2\Sigma_u^+) \to H(1s) + H^+,$$
 (1)

where v and J are the vibrational and rotational quantum numbers, respectively. Along with the bound – free transition (1), a significant contribution to the photoabsorption is made by free – free radiative transitions

$$H(1s) + H^+ + \hbar\omega \to H(1s) + H^+, \qquad (2)$$

induced by proton collisions with ground-state hydrogen atoms. Both processes (1) and (2) result from the electron transition between the even $X^{2}\Sigma_{g}^{+}$ and odd $A^{2}\Sigma_{u}^{+}$ terms of the molecular (quasi-molecular) H_{2}^{+} ion, which involves a change in symmetry of the electron wave function (see Fig. 1). It is pertinent to note that the number density of neutral hydrogen H_{2} molecules in the ground electronic ${}^{1}\Sigma_{g}^{+}$ state exceeds the H_{2}^{+} -ion number density by several orders of magnitude even for sufficiently high temperatures (in the solar photosphere, for instance, $N_{H_{2}}/N_{H_{2}^{+}} \sim 10^{4} - 10^{5}$). However, the ground (bound) ${}^{1}\Sigma_{g}^{+}$ and first excited (repulsive) ${}^{3}\Sigma_{u}^{+}$ terms of the hydrogen molecule have different multiplicities; the intercombination electron transition between them is strongly suppressed, since it involves a change of spin.

The fundamentals of classical and semiclassical theories of the radiative processes accompanied by transitions between different molecular electronic terms were formulated in the works of Kramers and Ter Haar [7], Jablonski [8], and Bates [9]. The possible role of bound-free (1) and free-free transitions (2) in the $H-H^+$ system for a certain type of the stellar atmospheres was first noted by Wildt [10]. The molecular H_2^+ ion is the simplest of all possible diatomic molecules. That is why many papers have been concerned with its theory.

The most weighty contribution to the theory of H_2^+ ions and ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ radiative transitions was made by Bates and his coworkers [11-13]. Bates et al. [13] calculated the energy splitting of the electronic terms in the H_2^+ system, while Bates [11] calculated the oscillator strengths of the radiative electronic ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ transition, which were also subsequently calculated in Ref. [14]. The first quantitative consideration of the radiative processes (1) and (2) was given by Bates in Ref. [12], where he performed semiclassical calculations of the integral light absorption coefficient $K_T(\omega)$ over a wide range of transition frequencies $(500 \le v/c \le 26000 \text{ cm}^{-1})$ for temperatures ranging from 2500 to 12000 K. Based on the quantum calculations of oscillator strengths for a fixed internuclear distance R and considering the H and H⁺ nuclei as classical particles with a probability distribution $W_T(R) \propto 4\pi R^2 \exp[-U(R)/kT]$ over *R*-coordinate in the bound $U_g(R)$ and repulsive $U_u(R)$ terms, Bates [12] derived a simple analytical formula for the $K_T(\omega)$. Therefore, in the framework of the model of immobile H- and H⁺-centers, which was proposed in Refs [9, 12], and employing the classical distribution function for the internuclear distance R in a diatomic system with a given interaction potential U(R), Bates obviated entirely calculations of the photodissociative absorption cross sections for specific vibrational – rotational states vJ and the consequent summation over these states.

Subsequently the quantum nature effect of the nuclear motion in the course of H_2^+ -ion photodissociation (3) was investigated [15] for the short-wavelength part 22× $10^3 \le v/c \le 115 \times 10^3 \text{ cm}^{-1}$ of the spectrum (i.e., for photon energies $2.7 < \hbar\omega < 14.3$ eV) for relatively low temperatures T = 1000 and 2500 K, and the resultant data on absorption coefficients were compared with semiclassical calculations [12]. Furthermore, light absorption coefficients due to bound-free and free-free ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ transitions of the molecular (quasi-molecular) H_2^+ ion were tabulated and the corresponding approximation formulas were derived [16, 17] using the calculated results from Ref. [12] as the base. Also noteworthy is the work [18], in which a semiclassical estimate was made of the integral energy of the electromagnetic radiation arising from the charge exchange of protons on hydrogen atoms. The contribution of H₂⁺-ion photodissociation (1) and radiative collisional transitions (2) to the photoabsorption of the solar atmosphere was subsequently analyzed in Refs [19-21]. Recently, the role of photoabsorption by the H_2^+ system in a locally equilibrium hydrogen plasma was analyzed in a wide range of wavelengths and temperatures typical for stellar atmospheres [22, 23].

The first measurement data for H_2^+ -ion photodissociation cross sections were given in Refs [24, 25]. Quantum-mechanical calculations of the cross sections for the photodissociation (1) from fixed vibrational levels v were performed for the small rotational quantum numbers J = 0 and 1. For the electronic ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ transition matrix elements, use was made of Bates's data mentioned above. In Ref. [27], the resultant cross sections were summed over v employing the Frank–Condon distribution, which is typical for H_2^+ -ion production in the photoionization of neutral hydrogen molecules or in their electron bombardment [in this case, the H_2 molecules reside at a low (room) temperature]. It is evident that the conditions implied in the calculations like those of Refs [26, 27] have little in common with the conditions inherent in stellar photospheres.

Numerical quantum-mechanical calculations of partial photodissociation cross sections $\sigma_{vJ}(\lambda)$ from fixed vibrational-rotational levels vJ of the $H_2^+(X^2\Sigma_g^+)$ ion were performed for the rotational quantum number $0 \le J \le 8$ in Ref. [28]. The resulting data were employed to calculate the in the Boltzmann-averaged cross sections $\sigma_T(\lambda)$ 2500 < T < 26000 K temperature and $50 \le \lambda \le 2500$ nm wavelength ranges. The behavior of the Boltzmann-averaged cross sections $\sigma_T(\lambda)$ in relation to the optical wavelength λ and the temperature T was comprehensively analyzed in Ref. [29]. Numerical quantum-mechanical calculations [29] for the $H_2^+(X^2\Sigma_g^+)$ ion cover a wide range of wavelengths (from 50 nm to 20μ m) and temperatures (3150–25200 K) and extend the summation of partial cross sections $\sigma_{vJ}(\lambda)$ over a huge number of vibrational-rotational states.

By now a great body of experimental data has been accumulated and a substantial amount of theoretical results has been obtained on the photodissociation of different molecules. The general algorithm for calculating photodissociation cross sections and optical absorption coefficients by molecules, which are of interest for astrophysical applications, was set forth in Ref. [30]. However, detailed quantummechanical calculations of photodissociative optical absorption coefficients that include the aggregate contribution from a large set of vibrational – rotational states were carried out only for a limited number of the simplest diatomic systems (like H_2^+ and He_2^+).

channel:

In Refs [21–23], an analytical approach was developed, making it possible to describe the continuous absorption of light by diatomic molecules and ions in the visible, infrared, and ultraviolet spectral ranges. This approach was used to calculate the cross sections for radiative processes (1) and (2), as well as the integral photoabsorption coefficient with the inclusion of the Boltzmann molecular distribution over vibrational–rotational levels and of the contribution from the continuous spectrum related to the H–H⁺ system. In this case, account was taken of the fact that a large number of vibrational and rotational levels of the ground electronic state $^{2}\Sigma_{g}^{+}$ are simultaneously excited when the temperature is high enough (T > 1500-3000 K).

In our review we outline the main theoretical results on the photodissociation (1) of molecular H_2^+ ions and on free-free radiative transitions (2), which were obtained in recent years. These findings are compared with the previously performed calculations of the effective cross sections and photoabsorption coefficients. We discuss the dependences of partial photodissociation cross sections $\sigma_{vJ}(\omega)$ on the vibrational v and rotational J quantum numbers, including the case of highly excited vJ levels located near the dissociation limit of the ground electronic term for the H_2^+ ion. Analytical formulas are given to correctly describe within a quasi-continuous spectrum approximation the integral contribution of all vibrational-rotational levels to the Boltzmann-distribution-averaged photodissociation cross section $\sigma_T(\omega)$ at a given temperature T in a locally equilibrium hydrogen plasma.

The results of specific calculations presented in our paper cover a wide range of transition wavelengths and temperatures T = 1500-25000 K. Simultaneously, considerable attention was given to the analysis of the relative contribution from bound-free (1) and free-free (2) radiative transitions, as well as to the study of the behavior of the total photoabsorption coefficient in relation to the optical wavelength and plasma temperature. Also considered is the question of the passage of quantum calculations of the total photoabsorption coefficient to the limit of simple analytical expressions corresponding to the semiclassical Bates model [12].

Special emphasis in our work is placed on a comparison of the magnitudes of integral optical absorption coefficients for the processes (1) and (2) involving molecular (quasi-molecular) H_2^+ ions with the corresponding photoabsorption coefficients relating to bound – free transitions of the negative $H^$ ion:

$$H^{-}(1s^{2}) + \hbar\omega \longrightarrow H(1s) + e,$$
 (3)

and free-free electron transitions in the field of a hydrogen atom:

$$H(1s) + e + \hbar \omega \longrightarrow H(1s) + e.$$
(4)

The results arrived at are of interest for astrophysical applications and enable us to gain a more comprehensive idea of the relative role of H_2^+ and H^- ions in different wavelength and temperature ranges in a locally equilibrium hydrogen plasma.

2. Initial quantum formulas

We give the input formulas for the cross sections of bound – free and free – free radiative transitions and the coefficients of optical absorption by a diatomic system. Orienting ourselves primarily to applications to the simplest diatomic system H_2^+ , for definiteness we consider the transitions between the initial



Figure 1. Diagram which serves to illustrate light absorption by the molecular H_2^+ ion in the electron transition between its ground (even) ${}^{2}\Sigma_{g}^+$ and first excited (odd) ${}^{2}\Sigma_{u}^+$ terms. R_{ω} is the point of intersection of the potential energy curves $U_g + \hbar \omega$ and U_u .

bound and final repulsive terms which converge to a common dissociation limit. The potential energy curves pertaining to this case are plotted in Fig. 1. We will also assume that no change occurs in the projection Λ of the molecular orbital angular momentum onto the internuclear axis during the radiative transition between the electronic terms U_i and U_f . This also corresponds to the case of ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ transitions considered in our paper. Then, the partial cross section for the photodissociation

$$AB(i, vJ) + \hbar\omega \to AB(f, E') \to A + B$$
(5)

from a given vibrational – rotational energy level vJ of the initial bound molecular electronic term $U_i(R)$ to the continuum of the repulsive term $U_f(R)$ with an energy E' is defined by the following expression (see, for instance, Refs [31, 32]):

$$\sigma_{vJ}^{p.d}(\omega) = \frac{4\pi^2 \omega}{3c(2J+1)} \left[(J+1) \left| d_{E',J+1;vJ}^{(f,i)} \right|^2 + J \left| d_{E',J-1;vJ}^{(f,i)} \right|^2 \right],\tag{6}$$

$$\hbar\omega = |E_{vJ}| + E', \quad E' = \frac{\hbar^2 (q')^2}{2\mu}.$$
 (7)

Here, c is the speed of light in vacuum, $|E_{vJ}|$ is the binding energy of the AB(i, vJ) molecule in the state with a vibrational quantum number v and a rotational quantum number J, and q' and E' are the wave number and kinetic energy (E' > 0) of the flying apart particles A and B in the asymptotic domain of internuclear distances, $R \rightarrow \infty$. The result (6) was summed over two possible values $J' = J \pm 1$ of the orbital angular momentum of the relative motion of atomic particles in the final state f. From this point on we measure the potential energies $U_i(R)$ and $U_f(R)$ from the molecular dissociation limit (i.e., $U_i(\infty) = U_f(\infty) = 0$, since the term splitting for $R \rightarrow \infty$ is absent in the case under consideration). The vibrational – rotational energy E_{vJ} in the state vJ of the discrete spectrum of the molecule is also reckoned from its dissociation limit $U_i(\infty) = 0$ and is related to the energy $\mathcal{E}_{vJ} > 0$, which enters in formula (14) and is measured from the position of the level v = 0, J = 0, by the expression $|E_{vJ}| = D_0 - \mathcal{E}_{vJ}$, where $D_0 \equiv |E_{v=0,J=0}|$ is the dissociation energy of the AB molecule in the initial electronic state *i*. Therefore, the quantity E_{vJ} contains only the total energy of relative nuclear motion in the potential well $U_i(R)$ and varies within the range $-D_0 \leq E_{vJ} < 0$.

well $U_i(R)$ and varies within the range $-D_0 \leq E_{vJ} < 0$. The dipole matrix element $d_{EJ',vJ}^{(f,i)}$ for the transition ${}^2\Sigma_{g}^+, v, J \rightarrow {}^2\Sigma_{u}^+, E, J'$, taken over the radial wave functions $\chi(R)$ of the relative motion of the particles A and B in the discrete spectrum of the initial bound electronic state U_i and in the continuous spectrum of the final repulsive state U_f , is of the form

$$d_{EJ',vJ}^{(f,i)} = \left\langle \chi_{EJ'}^{(u)}(R) \middle| d_{fi}(R) \middle| \chi_{vJ}^{(g)}(R) \right\rangle$$
$$= \int_0^\infty \left(\chi_{EJ'}^{(f)}(R) \right)^* d_{fi}(R) \chi_{vJ}^{(i)}(R) R^2 \, \mathrm{d}R \,. \tag{8}$$

Here, $d_{fi}(R)$ is the electron transition matrix element between the terms $U_i \rightarrow U_f$:

$$\mathbf{d}_{fi}(\mathbf{R}) = \left\langle \phi_f(\mathbf{r}, \mathbf{R}) \middle| \left(e \sum_j \mathbf{r}_j \right) \middle| \phi_i(\mathbf{r}, \mathbf{R}) \right\rangle$$
$$= \int \phi_f^*(\mathbf{r}, \mathbf{R}) \left(e \sum_j \mathbf{r}_j \right) \phi_i(\mathbf{r}, \mathbf{R}) \, \mathrm{d}\mathbf{r}$$
(9)

taken over the adiabatic wave functions $\phi_i(\mathbf{r}, \mathbf{R})$ and $\phi_f(\mathbf{r}, \mathbf{R})$ of the electron shell of the molecule AB, \mathbf{r}_j is the *j*-electron radius vector emanating from the center of mass of the AB molecule (*n* is the total number of electrons; $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_n)$, and $\mathbf{dr} = \mathbf{dr}_1 \times \dots \times \mathbf{dr}_n$), and **R** is the radius vector which connects the nuclei A and B, the electron transition matrix element being aligned with the internuclear axis, i.e., $\mathbf{d}_{fi} || \mathbf{R}$.

The dipole matrix element (9) for the electron transition and the corresponding oscillator strength $f_{fi}(R_{\omega})$ of the transition at a frequency $\omega = \Delta U_{ug}(R_{\omega})/\hbar$ are related as

$$\mathbf{f}_{fi}(\mathbf{R}_{\omega}) = \frac{2}{3} \frac{m_{\rm e}\omega}{\hbar e^2} \left| d_{fi}(\mathbf{R}_{\omega}) \right|^2,\tag{10}$$

where m_e and e are the electron mass and charge, respectively. The nuclear wave functions in expression (8) are normalized as follows

$$\int_{0}^{\infty} \left| \chi_{vJ}^{(i)}(R) \right|^{2} R^{2} dR = 1 ,$$

$$\int_{0}^{\infty} \left(\chi_{E'J}^{(f)}(R) \right)^{*} \chi_{EJ}^{(f)}(R) R^{2} dR = \delta(E - E') .$$
(11)

When the temperature is rather high and the thermal energy kT proves to be of the same order of magnitude as or higher than the energy of the lower molecular vibrational quantum $\hbar\omega_e$, the total photodissociative absorption coefficient $k_T^{\text{p.d}}(\omega)$ (in units of cm⁻¹) is defined by the contribution of a large number of vibrational–rotational levels vJ. For a given photon energy $\hbar\omega$, the quantity $k_T^{\text{p.d}}(\omega)$ can be represented as

$$k_T^{\mathrm{p.d}}(\omega) = \sigma_T^{\mathrm{p.d}}(\omega) N_{\mathrm{AB}}, \qquad N_{\mathrm{AB}} = \sum_{vJ} N_{\mathrm{AB}}^{(vJ)}, \qquad (12)$$

i.e., it is expressed in terms of the total concentration $N_{AB} = \sum_{vJ} N_{AB}(vJ)$ of molecules in the bound electronic state *i*, and the photodissociation cross section $\sigma_T^{p,d}(\omega)$ averaged over the Boltzmann distribution at a given tempera-

ture T is given by

$$\sigma_T^{\text{p.d}}(\omega) = \sum_{vJ} \sigma_{vJ}^{\text{p.d}}(\omega) \frac{N_{\text{AB}}^{(\omega)}}{N_{\text{AB}}}$$
$$= \frac{\exp(-D_0/kT)}{Z_{\text{v.r}}} \sum_{vJ} (2J+1) \sigma_{vJ}^{\text{p.d}}(\omega) \exp\left(-\frac{E_{vJ}}{kT}\right). (13)$$

(a. 1)

Here, D_0 is the molecular dissociation energy, and $Z_{v,r}$ is the vibrational-rotational statistical sum of the molecule in the initial bound electronic state *i*:

$$Z_{v,r} = \sum_{vJ} (2J+1) \exp\left(-\frac{\mathcal{E}_{vJ}}{kT}\right).$$
(14)

It is worth noting that the statistical sum $Z_{v,r}$ pertains here (as usual) to the ground vibrational–rotational level of the diatomic molecule, i.e., $\mathcal{E}_{v=0,J=0} = 0$. The quantity \mathcal{E}_{vJ} in formula (14) and the previously introduced energy E_{vJ} [measured from the dissociation limit of the molecular ion $H_2^+(^2\Sigma_g^+)$] are therefore related as $\mathcal{E}_{vJ} = E_{vJ} + D_0$.

Employing the law of mass action [33]

$$\frac{N_{\rm AB}}{N_{\rm A}N_{\rm B}} = \frac{Z_{\rm v.r} g_{\rm AB}}{\cos g_{\rm A}g_{\rm B}} \left(\frac{2\pi\hbar^2}{\mu kT}\right)^{3/2} \exp\left(\frac{D_0}{kT}\right),\tag{15}$$

the total number density N_{AB} of the AB molecules in the bound state of the initial electronic term *i* can be expressed in terms of the product of the number densities of atoms N_A and N_B residing in the continuous spectrum. Here, the symmetry factor in expression (15) is $\omega = 1$ and $\omega = 2$ for heteronuclear and homonuclear molecules, respectively. It takes into account the fact that the two opposite directions of the internuclear axis of a molecule consisting of identical nuclei actually correspond to the same quantum state of the diatomic system.

We now give the input formulas defining the effective cross sections and free-free radiative transition coefficients for the process

$$\mathbf{A} + \mathbf{B} + \hbar \omega \rightarrow (\mathbf{A} + \mathbf{B})_i + \hbar \omega \rightarrow (\mathbf{A} + \mathbf{B})_f \rightarrow \mathbf{A} + \mathbf{B}.$$
 (16)

As in the case of photodissociation (5), the photon absorption (16) takes place as a result of the electron transition between the initial *i* and final *f* terms of the quasi-molecule AB produced in the course of the collision of atoms A and B. The quantum expression for the optical absorption coefficient $k_T^{\text{fr-fr}}(\omega)$ due to the process (16) can be derived with the use of the general formula for dipole-allowed transitions in the continuum (see, for instance, the book [31]). For radiative transitions (16), which involve colliding particles A and B, from the continuum of the initial electronic state *i* with an energy *E* to the continuum of the final electronic state *f* with an energy *E'*, the absorption coefficient is of the form

$$k_{T}^{\text{fr-fr}}(\omega) = \eta_{T}^{\text{fr-fr}}(\omega) N_{A} N_{B} , \quad \eta_{T}^{\text{fr-fr}}(\omega) = \left\langle V \sigma_{E',E}^{(f,i)} \right\rangle_{T} , \quad (17)$$
$$\sigma_{E',E}^{(f,i)}(\omega) = \frac{1}{\omega} \frac{g_{AB}}{g_{A} g_{B}} \frac{8\pi^{4} \hbar \omega}{3cq^{2}} \sum_{J} \left[(J+1) \left| d_{E',J+1;EJ}^{(f,i)} \right|^{2} + J \left| d_{E',J-1;EJ}^{(f,i)} \right|^{2} \right]. \quad (18)$$

Here, $\sigma_{E',E}^{(f,i)}$ is the effective cross section (in cm⁴ s) $\eta_T^{\text{fr-fr}}$ is the rate constant for the photoabsorption (16) (in cm⁵) $k_{A-B}^{\text{fr-fr}}$ is the corresponding absorption coefficient (in cm⁻¹); $V = (2E/\mu)^{1/2}$ and $q = \mu V/\hbar$ are the relative velocity and

wave number of the colliding particles A and B for $R \to \infty$, and J is the quantum number of the orbital angular momentum of the relative motion of atoms in the initial state (with $J = q\rho$ in the quasi-classical approximation, where ρ is the impact parameter). The electronic statistical weights of the molecule in the initial bound state *i* and of the free particles A and B are denoted respectively as g_{AB} , g_A , and g_B ; μ is the reduced molecular mass, and ∞ is the symmetry factor equal to 1 for heteronuclear molecules and to 2 for homonuclear molecules, respectively. The angle brackets in expression (17) signify averaging over the Maxwellian velocity distribution at a given gas (plasma) temperature T.

We emphasize that formula (18), like the above formula (6) for the photodissociation cross section, applies to the case of transitions between the electronic terms U_i and U_f with $\Delta \Lambda = 0$. In this case, the photoabsorption coefficient in the free-free transition of colliding atoms can be represented in the form (see, for instance, Refs [32, 34])

$$k_{T}^{\rm fr-fr}(\omega) = \frac{1}{\omega} \frac{g_{\rm AB}}{g_{\rm A} g_{\rm B}} N_{\rm A} N_{\rm B} \left(\frac{2\pi\hbar^{2}}{\mu kT}\right)^{3/2} \frac{4\pi^{2}\omega}{3c} \\ \times \int_{0}^{\infty} dE \exp\left(-\frac{E}{kT}\right) \sum_{J} \left[(J+1) \left| d_{E',J+1;EJ}^{(f,i)} \right|^{2} + J \left| d_{E',J-1;EJ}^{(f,i)} \right|^{2} \right].$$
(19)

The energies E and E' obey the energy conservation law for process (16):

$$E' = E + \hbar\omega, \quad E = \frac{\hbar^2 q^2}{2\mu}, \quad E' = \frac{\hbar^2 (q')^2}{2\mu}.$$
 (20)

The dipole matrix elements for the free-free transition, $d_{E'J',EJ}^{(f,i)} = \langle \chi_{E'J'}^{(f)}(R) | d_{fi}(R) | \chi_{EJ}^{(i)}(R) \rangle$, differ from expression (8) only in that the initial nuclear wave function $\chi_{vJ}^{(i)}(R)$ of the discrete spectrum is replaced with the corresponding wave function $\chi_{EJ}^{(i)}(R)$ of the continuous spectrum with normalization to the energy δ function.

3. Bound – free radiative transitions

3.1. Partial cross sections for the photodissociation from an excited vibrational-rotational state

In calculating the partial photodissociation cross section (6) for relatively high vibrational – rotational levels vJ that are of interest to us, the following circumstance should be taken into account. For a given transition frequency ω , the main contribution to the integral taken over the internuclear distances in expression (8) is made by a small neighborhood of the point R_{ω} , which is the point of intersection of potential energy curves $U_i(R) + \hbar \omega$ and $U_f(R)$ of the compound (molecule + photon) system, i.e., when

$$\Delta U_{fi}(R_{\omega}) = U_f(R_{\omega}) - U_i(R_{\omega}) = \hbar\omega.$$
(21)

Thus, the calculation of the radial matrix element of the dipole moment (8) can be performed employing the quasiclassical Landau technique [35] (see also Ref. [36], pp. 399– 401) or in the framework of the approach based on the quantum solution of the problem on nonadiabatic transitions in the model of linear intersecting terms. In the context of this approach, Rice [37] devised the well-known formula for the nonadiabatic transition probability, which includes the Airy function. This formula is equally applicable when the classical turning points $R = a_{vJ}$ are remote from and close to the intersection point R_{ω} of the potential energy curves. We note that the Rice formula was initially constructed in the momentum representation for the slopes of the potential energy curves of the same sign. The corresponding method for calculating the probabilities of nonadiabatic transitions between two different electronic terms of a quasi-molecule was outlined in problem 3 to § 90 in Ref. [36] when considering particle collisions of the second kind.

The result of Ref. [37] was further generalized in Refs [38–43] along the following two lines: (i) the inclusion of a more realistic behavior of potential energy curves at a large distance from the intersection point R_{ω} , and (ii) consideration of potential curves with slopes of opposite signs. A result similar to that of Ref. [37] was borne out in the case of weak coupling irrespective of the signs of the slopes of the potential energy curves. The most significant findings in this field are expounded at length in Ref. [44]. Recent calculations [23] showed clearly that the linear model leads to a good quantitative agreement with the available *ab initio* quantummechanical calculations of photodissociation cross sections for the molecular ion H₂⁺.

Therefore, to describe the nuclear wave functions of discrete $\chi_{vJ}^{(i)}(R)$ and continuous $\chi_{EJ'}^{(f)}(R)$ spectra in the context of the above approach, advantage is taken of the exact solutions to the problem of a one-dimensional nuclear motion in a uniform field, which reduce, to the corresponding normalizing factors, to the Airy functions (see Ref. [36], § 24). The application of this approach to the calculation of dipole matrix elements for the radiative transitions between the molecular electronic terms and the use of the input formula (6) for a bound-free transition results in the following expression for the cross section of photodissociation (5) from a given vibrational-rotational level vJ [23]:

$$\sigma_{vJ}^{(1)}(\omega) = \frac{8\pi^{3}(2\mu)^{1/2}\omega}{3cT_{vJ}} \frac{|d_{fi}(R_{\omega})|^{2}}{\Delta F_{fi}(R_{\omega})} |\beta(R_{\omega})|^{1/2} \\ \times \operatorname{Ai}^{2} \left\{ -\beta(R_{\omega}) \left[E_{vJ} - U_{i}(R_{\omega}) - \frac{\hbar^{2}(J+1/2)^{2}}{2\mu R_{\omega}^{2}} \right] \right\}.$$
(22)

Here, Ai(x) is the Airy function (see Ref. [45]):

$$\operatorname{Ai}(x) = \frac{1}{\pi} \int_0^\infty \cos\left(\frac{u^3}{3} + ux\right) \mathrm{d}u\,,\tag{23}$$

its presently adopted designation (23) being different from the definition of the function $\Phi(x)$ given by Fock (see, for instance, Ref. [36]) by a factor $\pi^{1/2}$; the quantity T_{vJ} is the period of vibrational-rotational nuclear motion in the bound electronic state $U_i(R)$ at an energy level E_{vJ} , which can be calculated by the formula

$$T_{vJ} = \frac{2\pi\hbar}{|E_{vJ} - E_{v\pm 1,J}|};$$

and $\Delta F_{fi}(R_{\omega})$ is the difference in slopes between the potential energy curves at the point $R = R_{\omega}$ of their intersection:

$$\Delta F_{fi}(R_{\omega}) = \left| \frac{\mathrm{d}U_f(R)}{\mathrm{d}R} - \frac{\mathrm{d}U_i(R)}{\mathrm{d}R} \right|_{R=R_{\omega}}.$$
(24)

The quantity β in expression (22) takes the form

$$\beta(R_{\omega}) = \left(\frac{2\mu}{\hbar^2}\right)^{1/3} \left|\frac{\Delta F_{fi}(R_{\omega})}{F_f^{(J')}(R_{\omega})F_i^{(J)}(R_{\omega})}\right|^{2/3},$$
(25)

where $F_i^{(J)}(R_{\omega})$ and $F_f^{(J')}(R_{\omega})$ are the slopes of potential energy curves in the initial and final electronic states with the inclusion of the centrifugal energy:

$$F_{i}^{(J)}(R_{\omega}) = -\frac{\mathrm{d}}{\mathrm{d}R} \left(U_{i} + \frac{\hbar^{2}(J+1/2)^{2}}{2\mu R^{2}} \right) \Big|_{R=R_{\omega}}$$
$$= F_{i}^{(J=0)}(R_{\omega}) + \frac{\hbar^{2}(J+1/2)^{2}}{\mu R_{\omega}^{3}}, \qquad (26)$$

$$F_{f}^{(J')}(R_{\omega}) = -\frac{\mathrm{d}}{\mathrm{d}R} \left(U_{f} + \frac{\hbar^{2} (J' + 1/2)^{2}}{2\mu R^{2}} \right) \Big|_{R=R_{\omega}}$$
$$= F_{f}^{(J'=0)}(R_{\omega}) + \frac{\hbar^{2} (J' + 1/2)^{2}}{\mu R_{\omega}^{3}} .$$
(27)

The quantum formula (22) for the photodissociation cross section can be rewritten, in view of expressions (24) - (27) and (10), as

where $\alpha = e^2/\hbar c \simeq 1/137$ is the fine structure constant, and the quantity ξ is defined by the expression

$$\xi = \beta(R_{\omega}) \left[E_{vJ} - U_i(R_{\omega}) - \frac{\hbar^2 (J+1/2)^2}{2\mu R_{\omega}^2} \right].$$
 (29)

Further simplifications involve recourse to the wellknown asymptotics of the Airy function:

$$\operatorname{Ai}(-\xi) = \frac{1}{\sqrt{\pi}|\xi|^{1/4}} \sin\left(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4}\right)$$
(30)

in the classically allowed domain $(\xi > 0)$ of motion of the nuclei A and B between the turning points $a_1(vJ) \leq R_{\omega} \leq a_2(vJ)$, i.e., when

$$E_{vJ} - U_i(R_{\omega}) - \frac{\hbar^2 (J+1/2)^2}{2\mu R_{\omega}^2} \ge 0$$

With the aid of formula (30) we average the result (22) over the period of the rapidly oscillating part of the function $Ai^2(-\xi)$ in the classically allowed domain:

$$\langle \operatorname{Ai}^{2}(-\xi) \rangle = \frac{1}{2\pi |\xi|^{1/2}} \,.$$
 (31)

Owing to the exponentially rapid decay of the Airy function in the classically forbidden domain, we neglect its contribution to the photodissociation cross section in the domain $\xi < 0$.

Then, from expressions (22) and (29) there directly follows a simple quasi-classical expression for the partial cross section of molecular photodissociation from a fixed vibrational– rotational level vJ, averaged over the oscillation period:

$$\sigma_{vJ}^{\text{p.d}}(\omega) = \frac{8\pi^2\omega}{3cT_{vJ}} \frac{|d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega})V_{vJ}(R_{\omega})} \,. \tag{32}$$

Here, the quantity

$$V_{vJ}(R_{\omega}) = \sqrt{\frac{2}{\mu}} \left[E_{vJ} - U_i(R_{\omega}) - \frac{\hbar^2 (J+1/2)^2}{2\mu R_{\omega}^2} \right]$$
(33)

is the relative velocity of motion of the molecular nuclei at the intersection point R_{ω} of potential energy curves (21).

Expression (32) is applicable in the classically allowed domain $(\xi > 0)$ of internuclear distances $a_1(vJ) \leq R_{\omega} \leq a_2(vJ)$ far from the turning points (i.e., for relatively large values of the energy difference $E_{vJ} - U_i(R_{\omega}) - \hbar^2(J+1/2)^2/2\mu R_{\omega}^2$). Here, $a_1(vJ)$ and $a_2(vJ)$ are respectively the left and right turning points in the motion along the potential energy curve $U_i(R)$ of the initial (bound) electronic state of the molecule. We note that the result (32) can also be obtained directly from the input expression for photodissociation cross section (6) by taking advantage of the results of the Landau quasi-classical theory (see Ref. [36], pp. 399–401) to calculate the dipole matrix element for the transition of the nuclei of the H–H⁺ system at the intersection point of potential energy curves.

As may be seen from expressions (22)-(29), the quantum result for the partial photodissociation cross section is different from the quasi-classical one only for small values of the difference

$$E_{vJ} - U_i(R_\omega) - rac{\hbar^2 (J+1/2)^2}{2\mu R_\omega^2}$$
.

In particular, accounting for the quantum nature of nuclear motion makes finite the magnitude of the cross section at the turning points and enables us to describe its rapid decay in the classically forbidden domains $R < a_1(vJ)$ and $R > a_2(vJ)$.

Expression (32) is conveniently written in the form

$$\sigma_{vJ}^{p,d}(\omega) = \frac{2^{3/2} \pi^2 \alpha \hbar^2 \sqrt{\mu} f_{fi}(R_{\omega})}{m_e T_{vJ} \Delta F_{fi}(R_{\omega}) \sqrt{E_{vJ} - U_i(R_{\omega}) - \hbar^2 (J + 1/2)^2 / 2\mu R_{\omega}^2}},$$
(34)

which explicitly depends on the energy E_{vJ} of the vibrational-rotational energy level and the quantum number J.

It is evident that formulas (32) and (34) may be directly obtained from the input expression for the photodissociation cross section (6) in the context of the quasi-classical approximation for nuclear wave functions and the conventional quasi-classical version of the Landau theory (see Ref. [36]) for transition matrix elements. In the quasi-classical approximation, the radial wave functions of the relative motion of particles A and B in the continuous spectrum along the classically allowed domain of internuclear distances are of the form

$$\chi_{EJ}(R) = \frac{C_E}{R\sqrt{V_{EJ}(R)}} \cos \Phi(R) ,$$

$$\Phi(R) = \int_{a_1(E)}^R q_{EJ}(R) \, \mathrm{d}R - \frac{\pi}{4} , \qquad (35)$$

$$q_{EJ}(R) = \frac{\mu V_{EJ}(R)}{\hbar} = \sqrt{\frac{2\mu}{\hbar^2} \left[E - U(R) - \frac{\hbar^2 (J + 1/2)^2}{2\mu R^2} \right]},$$
(36)

where $q_{EJ}(R)$ and $V_{EJ}(R)$ are the radial wave number and the relative velocity of the particles, respectively. The quantities $\Phi(R)$ and $C_E = (2/\pi\hbar)^{1/2}$ are the phase and normalization constant of the wave function in the molecular continuum (E > 0). The result for the wave function $\chi_{vJ}^{(i)}(R)$ of the discrete spectrum $(E_{vJ} < 0)$ differs from expression (35) in only the specific magnitude of the normalization constant $C_{vJ} = 2/\sqrt{T_{vJ}}$ and the energy change $E \to E_{vJ}$. We emphasize that these normalization factors were employed in the derivation of both the quantum (22) and quasi-classical (32) expressions. This ensured perfect consistency of the above relations far from the classical turning points.

For free-free transitions (16) without changing the projection ($\Delta \Lambda = 0$) of the orbital momentum of the electron shell of the quasi-molecule AB, a similar consideration leads to the following result for the sum of the squares of the absolute values of dipole matrix elements [23]:

$$\frac{J+1}{2J+1} |d_{E',J+1;EJ}^{(f,i)}|^2 + \frac{J}{2J+1} |d_{E',J-1;EJ}^{(f,i)}|^2
= \left(\frac{\mu}{2}\right)^{1/2} \frac{|d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega})} |\beta(R_{\omega})|^{1/2}
\times \operatorname{Ai}^2 \left\{ -\beta(R_{\omega}) \left[E - U_i(R_{\omega}) - \frac{\hbar^2(J+1/2)^2}{2\mu R_{\omega}^2} \right] \right\}, \quad (37)$$

calculated from the wave functions of the relative motion of the particles A and B in the continuum $(E = \hbar^2 q^2/2\mu > 0, E' = E + \hbar\omega > 0).$

It is pertinent to note that the quantum and quasi-classical formulas presented in the foregoing are valid provided that the difference in slopes between the potential energy curves is not too small. The special case when the potential energy curves of the initial and final terms differ little in slope was considered in Ref. [46] on the basis of the quasi-classical approximation.

3.2 Averaging over the Boltzmann distribution and the photodissociative absorption coefficient

For sufficiently high temperatures realized in stellar photospheres, simultaneously excited vibrational-rotational levels vJ prove, as a rule, to be large in number. Under these circumstances, the main characteristic of the bound-free transition (5) is the photodissociation cross section $\sigma_T(\omega)$ (13) averaged over the Boltzmann distribution function with the inclusion of all vibrational-rotational levels that contribute to the continuous photoabsorption at a given photon energy $\hbar\omega$. According to formula (12), under the conditions of local thermodynamic equilibrium this quantity makes possible the determination of the total photodissociative absorption coefficient from the known total molecular concentration in the initial bound state. It is noteworthy that the available expressions for $\sigma_T^{p,d}$ were derived [47, 48] in the framework of a purely classical consideration of molecular vibrational motion, assuming that the rotational effects can be completely neglected. The correct way of simultaneous inclusion of vibrational and rotational effects in circumstances when their combined influence is especially significant was shown in Ref. [49]. In a recent paper [23], analytical formulas were obtained for the cross section $\sigma_T^{\text{p,d}}(\omega)$ and the integral photodissociative absorption coefficient $k_T^{\text{p,d}}(\omega)$.

In calculating the photodissociation cross section $\sigma_T^{p,d}(\omega)$ averaged over the Boltzmann distribution, the summation over vibrational–rotational levels vJ in formula (13) may be replaced by integration with respect to dv and dJ. In this case, it can be performed by a method similar to that developed in Ref. [49] when calculating the rate constant of associative ionization of a highly excited atom, summed over all possible vibrational – rotational molecular ion levels in the final reaction channel, and in Ref. [50] during computation of the statistical sum of a molecule. This method of calculation corresponds to the replacement of the discrete spectrum of molecular vibrational – rotational energy levels with the quasi-continuous one. It is also extensively used in the physics of highly excited atomic states (see, for instance, Ref. [51]). In the context of the above approximation, expression (13) can be rewritten as

$$\sigma_T^{\text{p.d}}(\omega) = \frac{\exp(-D_0/kT)}{Z_{\text{v.r}}} \int_0^{v_{\text{max}}} dv$$
$$\times \int_0^{J_{\text{max}}(v)} 2J \, dJ \sigma_{vJ}^{\text{p.d}}(\omega) \exp\left(-\frac{E_{vJ}}{kT}\right). \tag{38}$$

We further follow the paper [49] and invoke the Bohr–Sommerfeld relation

$$dv = \frac{T_{vJ}}{2\pi\hbar} dE_{vJ}, \qquad T_{vJ} = \oint \frac{dR}{V_{vJ}(R)}, \qquad (39)$$

which establishes that the integration with respect to the vibrational quantum number v can be replaced with integration over the energy of the quasi-continuous molecular spectrum ($-D_0 \le E < 0$). This gives

$$\sigma_T^{\text{p.d}}(\omega) = \frac{\exp(-D_0/kT)}{2\pi\hbar Z_{\text{v.r}}} \int_{E_{\text{min}}}^0 dE_{vJ} \exp\left(-\frac{E_{vJ}}{kT}\right)$$
$$\times \int_0^{J_{\text{max}}} 2JT_{vJ} \sigma_{vJ}^{\text{p.d}}(\omega) \, dJ.$$
(40)

In the framework of quasi-continuous spectrum approximation, the quantum numbers v and J (and hence the vibrational-rotational energy E_{vJ} of the molecule) in expressions (38)–(40) are continuous quantities in accordance with the principle of correspondence between quantum and classical quantities. Therefore, the same designation $E_{vJ} \rightarrow E$ (where E < 0) can be used for the bound-state molecular energy and for the case of continuous spectrum (where E > 0). We then substitute the analytical formula (22) for the partial photodissociation cross section $\sigma_{vJ}^{p,d}(\omega)$ from a given vibrational-rotational state into expression (40) to obtain the following expression for the photodissociation cross section averaged over the Boltzmann distribution:

$$\sigma_T^{\text{p,d}}(\omega) = \frac{4\pi^2 \sqrt{2\mu\omega}}{3\hbar c Z_{\text{v,r}}} \frac{|d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega})} \exp\left(-\frac{D_0}{kT}\right) \\ \times \int_{E_{\min}^{\text{p,d}}}^{0} dE \exp\left(-\frac{E}{kT}\right) \int_{0}^{J_{\max}} 2J \, dJ \sqrt{\beta} \\ \times \operatorname{Ai}^2 \left\{ -\beta \left[E - U_i(R_{\omega}) - \frac{\hbar^2 J^2}{2\mu R_{\omega}^2} \right] \right\}.$$
(41)

This formula takes into account the relative nuclear motion along both the classically allowed and the classically forbidden domains of internuclear distance. The integration over the rotational quantum number in expression (41) is performed between the limits $0 \le J < J_{\text{max}}(E)$, where $J_{\text{max}}(E)$ is the greatest possible J value for a given energy E in the quasi-continuous spectrum (E < 0). In the quantum description of relative nuclear motion, the lower limit E_{\min} of integration with respect to energy E in expression (41) is determined from the energy conservation law for the photodissociation process (7), i.e., one finds

$$E_{\min}^{p.d} = \max\{-\hbar\omega, -D_0\} \quad (E_{\min}^{p.d} < 0).$$
(42)

Here, account was taken of the fact that the minimal energy of the molecule in the initial bound state, possible during photodissociation at high photon energies $\hbar\omega$, is limited by the ground vibrational-rotational energy level $E_{v=0, J=0} = -D_0$.

Following Ref. [23] we introduce here dimensionless variables

$$\varepsilon = \frac{E - U_i(R_{\omega})}{kT}, \qquad v = \frac{\hbar^2 J^2}{2\mu R_{\omega}^2 kT}.$$
(43)

Then, the cross section averaged over the Boltzmann distribution assumes the form

$$\sigma_T^{\text{p.d}}(\omega) = \frac{16\pi^3}{3c} \frac{\omega R_{\omega}^2 |d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega}) Z_{\text{v,r}}} \left(\frac{\mu kT}{2\pi\hbar^2}\right)^{3/2} \\ \times \exp\left(-\frac{D_0 + U_i(R_{\omega})}{kT}\right) \Theta_T^{\text{p.d}}(\omega),$$
(44)

$$\Theta_T^{\text{p.d}}(\omega) = 2\sqrt{\pi} \int_{\varepsilon_{\min}^{\text{p.d.}}}^{\varepsilon_{\max}^{\text{p.d.}}} d\varepsilon \exp(-\varepsilon) \\ \times \int_0^\infty d\nu \sqrt{\Lambda_\nu} \operatorname{Ai}^2 \left[-\Lambda_\nu(\varepsilon - \nu)\right].$$
(45)

For a given photon frequency ω and gas (plasma) temperature *T*, the quantity Λ_{ν} is defined by the expression [see formula (25)]

$$\Lambda_{\nu} \equiv kT\beta(R_{\omega}) = kT\left(\frac{2\mu}{\hbar^{2}}\right)^{1/3} \left|\frac{\Delta F_{fi}(R_{\omega})}{F_{i}^{(\nu)}(R_{\omega}) F_{f}^{(\nu)}(R_{\omega})}\right|^{2/3}, (46)$$

where the slopes of the potential energy curves $F_i^{(v)}(R_{\omega})$ and $F_f^{(v)}(R_{\omega})$, as well as their difference at the intersection point R_{ω} (21), can be found from formulas (24), (26), (27), and (43). We note that the value of dimensionless centrifugal energy $v' = \hbar^2 (J')^2 / 2\mu R_{\omega}^2 kT$ in the final state was set in Eqn (46) equal to the corresponding value (43) in the initial state. This is justified, since the main contribution to the integral (45) is made by the values $J \ge 1$, so that the differences between the quantities J and $J' = J \pm 1$ in formulas (26) and (27) [and hence between v and v' in expression (46)] are small and can be neglected.

When considering the initial bound state $U_i(R) < 0$ and final repulsive state $U_f(R) > 0$ (which converge to a common dissociation limit $U_i(\infty) = U_f(\infty) = 0$), the lower and upper limits of integration over dimensionless centrifugal energy in expression (45) are equal to, respectively,

$$\varepsilon_{\min}^{p.d} = \frac{E_{\min}^{p.d} - U_i(R_{\omega})}{kT} = -\frac{\hbar\omega + U_i(R_{\omega})}{kT}$$
$$= -\frac{U_f(R_{\omega})}{kT} < 0, \qquad (47)$$

$$\varepsilon_{\max}^{p,d} = -\frac{U_i(R_{\omega})}{kT} \equiv \frac{|U_i(R_{\omega})|}{kT} > 0.$$
(48)

A simple quasi-classical expression for the photodissociation cross section (5) averaged over the Boltzmann distribution can be derived employing the well-known asymptotic expression for the Airy function upon averaging over the period of rapid oscillations. It should also be taken into account that the integration over the dimensionless centrifugal energy v in the quasi-classical approximation should actually be performed between the limits $0 \le v \le \varepsilon$. This corresponds to the consideration of the relative motion of molecular nuclei only within the classically allowed domain of internuclear distance. In this case, the lower limit (47) of integration over the dimensionless energy ε in expression (45) should be put at $\varepsilon_{\min}^{p,d} = 0$, since $E_{\min}^{p,d} = U_i(R_{\omega}) < 0$ (for more details, see Refs [23, 49]). Furthermore, for a given transition frequency ω the upper limit of integration with respect to the rotational quantum number in expression (41) is determined from the relation $\hbar^2 J^2 / 2\mu R_{\omega}^2 = E - U_i(R_{\omega})$. Therefore, in the quasi-classical approximation the upper limit of integration over the dimensionless centrifugal energy is $v_{max} = \varepsilon$ [see formula (43)]. As a result, the passage to the limit from quantum expressions (44) and (45) to the quasi-classical approximation follows directly from the following relation

$$\Theta_T^{\text{p.d}}(\omega) = \frac{1}{\sqrt{\pi}} \int_0^{\varepsilon_{\text{max}}^{\text{p.d}}} d\varepsilon \exp(-\varepsilon) \int_0^{\varepsilon} \frac{d\nu}{(\varepsilon - \nu)^{1/2}} \\ = \frac{2}{\sqrt{\pi}} \int_0^{\varepsilon_{\text{max}}^{\text{p.d}}} \varepsilon^{1/2} \exp(-\varepsilon) d\varepsilon = \frac{\gamma(3/2, |U_i(R_\omega)|/kT)}{\Gamma(3/2)}, (49)$$

where $\gamma(3/2, z)$ is the incomplete gamma function of order 3/2 (see Ref. [45]):

$$\gamma\left(\frac{3}{2}, z\right) = \int_0^z t^{1/2} \exp(-t) dt,$$

$$\Gamma\left(\frac{3}{2}\right) = \gamma\left(\frac{3}{2}, \infty\right) = \frac{\sqrt{\pi}}{2}.$$
(50)

The corresponding quasi-classical result for the photodissociation cross section $\sigma_T^{\text{ph.d}}(\omega)$ (in cm²) averaged over the Boltzmann distribution function can be described by a simple analytical formula

$$\sigma_T^{\text{p.d}}(\omega) = \frac{16\pi^3}{3c} \frac{\omega R_{\omega}^2 |d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega}) Z_{\text{v,r}}} \left(\frac{\mu kT}{2\pi\hbar^2}\right)^{3/2} \\ \times \exp\left(-\frac{D_0 + U_i(R_{\omega})}{kT}\right) \frac{\gamma(3/2, |U_i(R_{\omega})|/kT)}{\Gamma(3/2)} .$$
(51)

Quasi-classical expressions (49) and (51) are applicable in the transition frequency range $\hbar \omega < \Delta U_{fi}(R_0)$, i.e., when $R_{\omega} > R_0$. Here, the point R_0 is found from the relation $U_i(R_0) = 0$. In the opposite case, when $\hbar \omega > \Delta U_{fi}(R_0)$, the quasi-classical description of relative nuclear motion within only the classically allowed domain of internuclear distances leads to a zero value for the integral contribution of discrete molecular spectrum to the photoabsorption due to bound – free transitions. This signifies that the Boltzmann-averaged cross section $\sigma_T^{\text{p.d}}(\omega)$ vanishes for $R_{\omega} < R_0$, i.e., the molecular photodissociation (5) involving high energy transfer $\hbar \omega > \Delta U_{fi}(R_0)$ is impossible when we neglect the nuclear motion in the classically forbidden domain.

The cross section $\sigma_T^{p,d}(\omega)$ defined by formulas (44)–(48) and (51) is a function of the frequency $\omega = \Delta U_{fi}(R_{\omega})/\hbar$ and the temperature *T*. These formulas provide a means of calculating the photodissociative absorption coefficient (12) from the given total concentration of molecules AB in the discrete spectrum of the ground term U_i . Employing the law of mass action (15), the result for the optical absorption coefficient may be expressed in terms of the product of the atomic number densities N_A and N_B in the continuous spectrum. This is especially convenient for astrophysical applications. In this case we proceed from expressions (12), (15), and (44) and take into consideration the well-known relation (10) between the dipole transition matrix element squared and the oscillator strength of the transition. As a result, the quantum formula for the integral photodissociative absorption coefficient $k_T^{p,d}(\omega)$ (in cm⁻¹) in the case of bound – free transitions (5) takes the following form

$$k_T^{\text{p.d.}}(\omega) = \eta_T^{\text{p.d.}}(\omega) N_A N_B$$

= $\frac{1}{\infty} \frac{g_{AB}}{g_A g_B} N_A N_B 8\pi^3 \alpha \frac{\hbar^2}{m_e} \frac{R_{\omega}^2 f_{fi}(R_{\omega})}{\Delta F_{fi}(R_{\omega})}$
× $\exp\left(-\frac{U_i(R_{\omega})}{kT}\right) \Theta_T^{\text{p.d.}}(\omega)$, (52)

where $\alpha = e^2/\hbar c$. The dimensionless factor $\Theta_T^{\text{p.d}}(\omega)$ is defined by expression (45). Formula (52) assumes a particularly simple form in the quasi-classical approximation:

$$k_T^{\text{p.d}}(\omega) = \frac{1}{\omega} \frac{g_{\text{AB}}}{g_{\text{A}}g_{\text{B}}} N_{\text{A}} N_{\text{B}} 8\pi^3 \alpha \frac{\hbar^2}{m_{\text{e}}} \frac{R_{\omega}^2 f_{fi}(R_{\omega})}{\Delta F_{fi}(R_{\omega})} \times \exp\left(-\frac{U_i(R_{\omega})}{kT}\right) \frac{\gamma(3/2, |U_i(R_{\omega})|/kT)}{\Gamma(3/2)}, \quad (53)$$

when the $\Theta_T^{\text{p.d}}(\omega)$ factor reduces to the quasi-classical expression (49). As noted above, expression (53) is valid in the $\hbar\omega < \Delta U_{fi}(R_0)$ range, i.e., when $R_{\omega} > R_0$. Meanwhile, $k_T^{\text{p.d}}(\omega) = 0$ for $\hbar\omega > \Delta U_{fi}(R_0)$, if the nuclear motion is accounted for within the classically allowed domain only.

4. Free-free transitions and the total absorption coefficient

4.1 Contribution of continuous spectrum to the photoabsorption coefficient

The calculation of the optical absorption coefficient (17) due to free-free transitions (16) is performed on the basis of the same method [49] as the derivation of formulas for the photodissociative absorption coefficient (see Ref. [23]). Replacing summation over J with integration over dJ in the input formula (19) gives

$$k_T^{\text{fr-fr}}(\omega) = \frac{1}{\omega} \frac{g_{AB}}{g_A g_B} N_A N_B \left(\frac{2\pi\hbar^2}{\mu kT}\right)^{3/2} \frac{4\pi^2 \omega}{3c} \\ \times \int_0^\infty dE \exp\left(-\frac{E}{kT}\right) \int_0^\infty 2J \, dJ \left|d_{E',J\pm 1;EJ}^{(f,i)}\right|^2.$$
(54)

We note that integration over the quantum numbers J of the orbital angular momentum of the relative motion of colliding atoms is equivalent to integration with respect to the impact parameters $\rho = J/q$ (q is the wave number for $R \to \infty$). The integration with respect to energy in expression (54) is performed over the Maxwellian distribution function.

Upon substitution of the quantum expression (37) for the square of the modulus of the dipole matrix element in expression (54), the integral contribution of the free-free

transitions (16) to the optical absorption coefficient can be written down as

$$k_{T}^{\text{fr-fr}}(\omega) = \frac{1}{\omega} \frac{g_{AB}}{g_{A}g_{B}} N_{A} N_{B} \left(\frac{2\pi\hbar^{2}}{\mu kT}\right)^{3/2} \frac{2\pi^{2}\sqrt{2\mu\omega}}{3c}$$

$$\times \frac{\left|d_{fi}(R_{\omega})\right|^{2}}{\Delta F_{fi}(R_{\omega})} \int_{0}^{\infty} dE \exp\left(-\frac{E}{kT}\right)$$

$$\times \int_{0}^{\infty} d(J^{2})\sqrt{\beta_{J}(R_{\omega})}$$

$$\times \operatorname{Ai}^{2}\left\{-\beta_{J}(R_{\omega})\left[E - U_{i}(R_{\omega}) - \frac{\hbar^{2}J^{2}}{2\mu R_{\omega}^{2}}\right]\right\}. \quad (55)$$

The integral in expression (55) is taken with respect to energy between the limits $0 \le E < \infty$, as opposed to the case of bound-free transitions, for which $E_{\min}^{p,d} \le E < 0$ [see formulas (12) and (41)].

Taking advantage of dimensionless variables (43), formula (55) can be rewritten as

$$k_T^{\text{fr-fr}}(\omega) = \eta_T^{\text{fr-fr}}(\omega) N_A N_B$$

= $\frac{1}{\varpi} \frac{g_{AB}}{g_A g_B} N_A N_B \frac{16\pi^3}{3c} \frac{\omega R_{\omega}^2 |d_{fi}(R_{\omega})|^2}{\Delta F_{fi}(R_{\omega})}$
× $\exp\left(-\frac{U_i(R_{\omega})}{kT}\right) \mathcal{O}_T^{\text{fr-fr}}(\omega)$. (56)

The dimensionless factor for free-free transitions assumes the form

$$\Theta_{T}^{\text{fr-fr}}(\omega) = 2\sqrt{\pi} \int_{\varepsilon_{\min}^{\text{fr-fr}}}^{\infty} d\varepsilon \exp(-\varepsilon) \\ \times \int_{0}^{\infty} d\nu \sqrt{\Lambda_{\nu}} \operatorname{Ai}^{2} \left[-\Lambda_{\nu}(\varepsilon - \nu) \right]$$
(57)

with the following lower limit of integration:

$$\varepsilon_{\min}^{\text{fr-fr}} = \varepsilon_{\max}^{\text{p.d}} = \frac{\left| U_i(R_{\omega}) \right|}{kT} > 0.$$
(58)

As in the case of bound-free radiative transitions, the values of integrals in expression (57) can be computed in the analytical form with the use of the quasi-classical approximation (for more details, see the paper [49]). This gives [23]

$$\Theta_T^{\text{fr-fr}}(\omega) = \frac{1}{\sqrt{\pi}} \int_{\varepsilon_{\min}}^{\infty} d\varepsilon \exp(-\varepsilon) \int_0^{\varepsilon} \frac{d\nu}{(\varepsilon - \nu)^{1/2}} = \frac{\Gamma(3/2, |U_i(R_{\omega})|/kT)}{\Gamma(3/2)}$$
(59)

for $\hbar \omega < \Delta U_{fi}(R_0)$. Here, $\Gamma(3/2, z)$ is the incomplete gamma function of order 3/2 defined by the expression [45]

$$\Gamma\left(\frac{3}{2},z\right) = \int_{z}^{\infty} t^{1/2} \exp(-t) \,\mathrm{d}t = \Gamma\left(\frac{3}{2}\right) - \gamma\left(\frac{3}{2},z\right). \tag{60}$$

Therefore, a simple analytical expression for the absorption coefficient $k_T^{\text{fr-fr}}(\omega)$, which depends explicitly on the potential energy, is of the form

$$k_T^{\text{fr-fr}}(\omega) = \eta_T^{\text{fr-fr}}(\omega) N_A N_B = \frac{1}{\omega} \frac{g_{AB}}{g_A g_B} N_A N_B 8\pi^3 \alpha$$
$$\times \frac{\hbar^2}{m_e} \frac{R_{\omega}^2 f_{fi}(R_{\omega})}{\Delta F_{fi}(R_{\omega})} \exp\left(-\frac{U_i(R_{\omega})}{kT}\right)$$
$$\times \frac{\Gamma(3/2, |U_i(R_{\omega})|/kT)}{\Gamma(3/2)}. \tag{61}$$

Quasi-classical expressions (59) and (61) are applicable in the frequency range $\hbar \omega < \Delta U_{fi}(R_0)$, i.e., for $R_{\omega} > R_0$. For high transition frequencies $\hbar \omega > \Delta U_{fi}(R_0)$, the factor $\Gamma(3/2, |U_i(R_{\omega})|/kT)/\Gamma(3/2)$ in expression (61) should be replaced by unity. Since the integral contribution of bound – free transitions (5) to photoabsorption is absent in this case (ignoring nuclear motion in the classically forbidden domain, see Section 3.1), this signifies that the total optical absorption coefficient at frequencies $\hbar \omega > \Delta U_{fi}(R_0)$ is, in the approximation under consideration, entirely determined by free – free transitions (16).

4.2 Integral contribution of bound – free and free – free transitions

Let us consider in greater detail the problem of the integral optical absorption coefficient due to processes (5) and (16). A comparison of formulas (52) and (56) shows that the final quantum expressions for the integral optical absorption coefficients $k_T^{\text{p.d}}$ and $k_T^{\text{fr-fr}}$ due to bound – free and free – free transitions differ from one another only by the specific values of the lower and upper limits of integration with respect to dimensionless energy. In particular, both contributions prove to be proportional to the product of number densities $N_A N_B$ of atoms A and B in the continuum. This circumstance permits the derivation of a more compact expression for the total optical absorption coefficient due to processes (5) and (16) than for each term taken separately. In the quasicontinuous spectrum approximation, the general formula for the total absorption coefficient $k_T(\omega)$ (in cm⁻¹) is of the form

$$k_T(\omega) = \eta_T(\omega) N_{\mathbf{A}} N_{\mathbf{B}} = k_T^{\mathrm{p,d}}(\omega) + k_T^{\mathrm{fr-fr}}(\omega) \,. \tag{62}$$

Here $\eta_T(\omega)$ is the total photoabsorption rate constant (in cm⁵). We make use of expressions (45) and (57) to obtain

$$k_{T}(\omega) = \frac{1}{\omega} \frac{g_{AB}}{g_{A}g_{B}} N_{A}N_{B}8\pi^{3} \alpha \frac{\hbar^{2}}{m_{e}} \frac{R_{\omega}^{2} f_{fi}(R_{\omega})}{\Delta F_{fi}(R_{\omega})}$$
$$\times \exp\left(-\frac{U_{i}(R_{\omega})}{kT}\right) \Theta_{T}^{\text{tot}}(\omega) .$$
(63)

The dimensionless factor $\Theta_T^{\text{tot}} = \Theta_T^{\text{p.d}} + \Theta_T^{\text{fr-fr}}$ can be written down as

$$\Theta_T^{\text{tot}}(\omega) = 2\sqrt{\pi} \int_{\varepsilon_{\min}^{\text{p,d}}}^{\infty} d\varepsilon \exp(-\varepsilon) \int_0^{\infty} d\nu \sqrt{\Lambda_{\nu}} \\ \times \operatorname{Ai}^2 \left[-\Lambda_{\nu}(\varepsilon - \nu) \right].$$
(64)

We note that the ratio between the factors $\Theta_T^{\text{p.d.}}(\omega)$ and $\Theta_T^{\text{fr-fr}}(\omega)$ defines the relative contributions of bound-free and free-free radiative transitions (5) and (16) to the total photoabsorption as functions of photon frequency and temperature.

The passage to the limit from the general quantum expression (63) for the photoabsorption coefficient to the corresponding quasi-classical expression for $k_T(\omega)$ follows directly from the relation

$$\Theta_T^{\text{tot}}(\omega) = \Theta_T^{\text{p.d}}(\omega) + \Theta_T^{\text{tr-tr}}(\omega)$$
$$\rightarrow \frac{1}{\sqrt{\pi}} \int_0^\infty d\varepsilon \, \exp(-\varepsilon) \int_0^\varepsilon \frac{d\nu}{(\varepsilon - \nu)^{1/2}} = 1$$
(65)

in full accordance with formulas (49) and (59). Note that the result (63) has a clear physical meaning for $\Theta_T^{\text{tot}}(\omega) = 1$,

namely, the optical absorption coefficient at a frequency ω is proportional both to the oscillator strength $f_{fi}(R_{\omega})$ of the $i \rightarrow f$ electron transition at the point of intersection of the terms (21) and to the probability $W_T(R_{\omega}) \propto 4\pi R_{\omega}^2 \times \exp[-U_i(R_{\omega})/kT]$ that the particles A and B are separated by a distance R_{ω} and reside in the initial bound state $U_i(R)$. The Boltzmann factor $\exp(-U_i/kT)$ in expression (63) defines the temperature dependence of the total absorption coefficient.

Formula (63) gives the total contribution of direct processes (5) and (16) to the photoabsorption coefficient of the molecular (quasi-molecular) system AB. With the inclusion of stimulated emission, the resultant coefficient $K_T(\omega)$ (in cm⁻¹) and the corresponding rate constant $\zeta_T(\omega)$ (in cm⁵) for the absorption of light at a frequency ω under conditions of thermodynamic equilibrium are defined by the well-known relation

$$K_T(\omega) = \zeta_T(\omega) N_{\rm A} N_{\rm B} = k_T(\omega) \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right]. \quad (66)$$

The expression for the photoabsorption coefficient $K_T(\omega)$ assumes, in view of formulas (63) and (66), the simple form

$$K_{T}(\omega) = \frac{1}{\omega} \frac{g_{AB}}{g_{A}g_{B}} N_{A}N_{B} 8\pi^{3} \alpha \frac{\hbar^{2}}{m_{e}} \frac{R_{\omega}^{2} f_{fi}(R_{\omega})}{\Delta F_{fi}(R_{\omega})}$$
$$\times \left[\exp\left(-\frac{U_{i}(R_{\omega})}{kT}\right) - \exp\left(-\frac{U_{f}(R_{\omega})}{kT}\right) \right] \mathcal{O}_{T}^{\text{tot}}(\omega) .$$
(67)

This result can also be obtained directly from formulas (52) and (56) for the contributions of bound – free and free – free radiative transitions employing relation (66).

The result (67) for the total continuous photoabsorption coefficient $K_T(\omega)$ with a quasi-classical factor $\Theta_T^{\text{tot}}(\omega) = 1$ is in complete agreement with the well-known semiclassical expression obtained by Bates [12] in the quasi-static approximation. Therefore, the dimensionless factor $\Theta_T^{\text{tot}}(\omega)$ describes the ratio between the quantum result of Ref. [23] and the semiclassical result of Ref. [12], i.e., $\Theta_T^{\text{tot}}(\omega) = K_T^{(q)}(\omega)/K_T^{(cl)}(\omega)$. It is noteworthy that the quantum result [see formulas (63) and (67)] takes into account the relative nuclear motion both in the classically allowed and in the classically forbidden domains of internuclear distances and provides a correct description of the true behavior of radiative transition probability in the immediate vicinity of the turning points.

5. Discussion of results

We now turn to a discussion of recent results on the continuous optical absorption by the simplest diatomic system H_2^+ due to radiative transitions (1) and (2) in the visible, IR, and UV spectral ranges. Figure 1 shows the potential energy curves $U_g(R)$ and $U_u(R)$, which correspond to the even and odd electronic terms of the molecular H_2^+ ion, to explain the physical mechanism of the radiative transitions under consideration. As noted above, these transitions take place in the vicinity of the intersection point R_{ω} of the potential energy curves $U_g(R) + \hbar\omega$ and $U_u(R)$ [see formula (21)]. The internuclear distance R_0 [which is determined from the relation $U_g(R_0) = 0$] is equal to $1.12a_0$ (where a_0 is the Bohr radius comprising an atomic unit of length). The minimum $U_g(R_e) = -2.79$ eV of the potential energy curve of the ground electronic state $X^2 \Sigma_g^+$ is reached for $R_e = 2.0 a_0$.

The energy splitting of the even and odd terms is $\Delta U_{gu} = 11.84 \text{ eV}$ for $R = R_e$. That is why the bound-free transitions $X^2 \Sigma_g^+$, $vJ \rightarrow A^2 \Sigma_u^+$, E, and $J \pm 1$ from low-lying vibrational-rotational states vJ with small v and J values [i.e., $R_\omega \sim (1.6-2.6)a_0$ near the bottom of the potential well] correspond to relatively high photon energies ($\hbar\omega \approx 8-16 \text{ eV}$) and short wavelengths ($\lambda \approx 800-1600 \text{ Å}$). On the other hand, photodissociative absorption in the near-infrared, visible, and near-ultraviolet spectral ranges with photon energies $0.25 < \hbar\omega < 6 \text{ eV}$ (i.e., $0.2 < \lambda < 5 \mu$ m) occurs primarily from the excited and highly excited vibrational-rotational states vJ of the H₂⁺ ion. The main contribution to the cross sections of such transitions like (1) and (2) is made by the domain of attraction ($R_e < R_\omega$) of the potential energy curve $U_g(R)$ for $3 < R_\omega < 7a_0$.

A comprehensive notion of the correlation between the photon energy $\hbar \omega = \Delta U_{ug}(R_{\omega})$, the corresponding radiation wavelength λ , and the internuclear distance R_{ω} [see formula (21)] can be gained from Table 1. Also collected in this table are the values of the potential energy $U_g(R_{\omega})$ of the ground electronic state of the molecular H_2^+ ion at the point R_{ω} and the oscillator strengths $f_{ug}(R_{\omega})$ of the electron $X^2\Sigma_g^+ \rightarrow A^2\Sigma_u^+$ transition. The relationship between the internuclear separations R_{ω} and the photon energies $\hbar \omega$ (transition wavelengths λ) given in Table 1 was obtained

Table 1. Photon wavelength $\lambda = 2\pi c/\omega$ and energy $\hbar\omega = \Delta U_{ug}(R_{\omega})$, potential energy $U_g(R_{\omega})$ of the lower electronic state $X^2\Sigma_g^+$, and oscillator strength $f_{ug}(R_{\omega})$ of the $X^2\Sigma_g^+ \rightarrow A^2\Sigma_u^+$ electron transition at the intersection point R_{ω} of the terms $U_g + \hbar\omega$ and U_u of the compound system H_2^+ + photon (a_0 is the Bohr radius).

R_{ω}, a_0	$\Delta U_{ m ug}, { m eV}$	$U_{\rm g}, {\rm eV}$	\mathbf{f}_{ug}	λ, μm
0.2	38.804	97.181	0.150	0.0320
0.4	35.103	32.633	0.175	0.0353
0.6	31.212	13.474	0.207	0.0397
0.8	27.525	5.320	0.240	0.0450
1.0	24.137	1.312	0.269	0.0514
1.2	21.048	-0.788	0.292	0.0589
1.4	18.286	-1.904	0.309	0.0678
1.6	15.851	-2.474	0.317	0.0782
1.8	13.701	-2.728	0.321	0.0905
2.0	11.840	-2.793	0.319	0.1047
2.2	10.226	-2.744	0.315	0.1212
2.4	8.836	-2.627	0.310	0.1403
2.6	7.633	-2.472	0.304	0.1624
2.8	6.596	-2.295	0.297	0.1880
3.0	5.701	-2.110	0.289	0.2175
3.2	4.925	-1.925	0.281	0.2517
3.4	4.256	-1.744	0.271	0.2913
3.6	3.676	-1.570	0.261	0.3372
3.8	3.173	-1.407	0.250	0.3908
4.0	2.735	-1.254	0.238	0.4533
4.2	2.356	-1.113	0.225	0.5261
4.4	2.027	-0.984	0.213	0.6116
4.6	1.744	-0.866	0.200	0.7108
4.8	1.497	-0.760	0.188	0.8284
5.0	1.282	-0.665	0.175	0.9673
5.5	0.865	-0.469	0.145	1.4328
6.0	0.580	-0.326	0.116	2.1390
6.5	0.386	-0.224	0.093	3.2086
7.0	0.253	-0.152	0.070	4.8991
7.5	0.166	-0.103	0.052	7.4691
8.0	0.109	-0.070	0.039	11.3904
8.5	0.071	-0.047	0.028	17.5236
9.0	0.046	-0.032	0.021	26.8009
10.0	0.019	-0.016	0.011	65.0878



Figure 2. Oscillator strength $f_{ug}(R_{\omega})$ of the electron ${}^{2}\Sigma_{g}^{+} \rightarrow {}^{2}\Sigma_{u}^{+}$ transition in the molecular H_{2}^{+} ion as a function of internuclear distance R_{ω} reproduced from the data of quantum-mechanical calculations in Refs [11, 14].

from the results of quantum-mechanical calculations of the splitting $\Delta U_{ug}(R_{\omega})$ of the even and odd H₂⁺-ion terms [13]. The values of the potential energy $U_g(R_{\omega})$ of the ground electronic term were determined employing the comprehensive calculations of Refs [13, 52], and the oscillator strengths of the electron $X^2\Sigma_g^+ \rightarrow A^2\Sigma_u^+$ transition were calculated in Refs [11, 14]. The $f_{ug}(R_{\omega})$ curve is plotted in Fig. 2. It is pertinent to note that the values of the energy of the lower vibrational quantum, the rotational constant, and the dissociation energy of the molecular H₂⁺ ion in the ground electronic state are, according to the data of Ref. [53], $\hbar\omega_e = 0.288 \text{ eV}$, $B_e = 3.74 \times 10^{-3} \text{ eV}$, and $D_0 = 2.651 \text{ eV}$, respectively.

5.1 Photodissociation cross sections

As shown in Ref. [23], an analytical expression (22) makes it possible to describe the dependence of partial photodissociation cross sections on the wavelength λ for excited vibrational-rotational levels. In particular, with the aid of this expression it is possible to quantitatively reproduce the results of the first numerical calculations [26, 27] of the photodissociation cross sections $\sigma_{vJ}^{(1)}(\lambda)$ of the molecular $\mathrm{H}_2^+(v, J=0)$ ion from the states with vibrational quantum numbers v = 7, 8, and 9 for J = 0, as well as the calculated results of Ref. [28] produced for v = 7 for rotational quantum numbers J = 0and J = 8. Furthermore, in addition to the available numerical cross-sectional data for small and medium J values, recently calculations [23] were also done for excited vibrational-rotational states with large rotational quantum numbers. In these computations, the energy values E_{vJ} of vibrational-rotational levels of the $H_2^+(X^2\Sigma_g^+)$ ion were borrowed from Refs [52, 54].

Figure 3 shows the typical dependences of partial photodissociation cross sections $\sigma_{vJ}^{p,d}$ of the molecular H₂⁺ ion on the optical wavelength λ . The calculations of Ref. [23] were performed for a fixed vibrational quantum numbers J = 0, J = 10 (Fig. 3a), J = 15, and J = 20 (Fig. 3b). Curves I correspond to quantum results obtained employing formula (28). Curves 2 are the results of quasi-classical computations of partial photodissociation cross sections (averaged over oscillations) obtained with the aid of a simple formula (34) in the classically allowed wavelength range $\lambda < \lambda_{cl}$. For given v and J values, the vertical lines 3 indicate the positions of the



Figure 3. Partial cross sections σ_{vJ}^{vJ} of $H_2^+(^2\Sigma_g^+, vJ)$ -ion photodissociation from a given vibrational (v = 10) state and different rotational states as a function of wavelength λ : (a) J = 0 and J = 10, (b) J = 15 and J = 20.

wavelengths $\lambda_{cl} \equiv \lambda_{cl}(v, J)$ for which the point of intersection R_{ω} of potential energy curves (21) coincides with the right classical turning point $a_2(v, J)$ in the relative nuclear motion of the molecule in its ground electronic state (i.e., $U_g[a_2(v, J)] = E_{vJ}$). A characteristic feature of the photodissociation from excited vibrational – rotational states is the oscillatory behavior of the partial cross sections $\sigma_{vJ}^{p,d}$ as functions of wavelength λ . Figures 3a and 3b demonstrate only several such oscillations located to the left of the $\lambda_{cl}(v, J)$ point. The overall number of peaks in the $\sigma_{vJ}^{p,d}(\lambda)$ dependence equals v + 1 for a given vibrational – rotational state vJ.

A comparison of curves *1* and *2* shows that the quasiclassical and quantum photodissociation cross sections (averaged over the period of oscillations) are little different for $\lambda \ll \lambda_{cl}(v, J)$, i.e., in the classically allowed domain away from the right turning point $R_{\omega} \ll a_2(v, J)$. On the other hand, a simple formula (34) leads to qualitatively incorrect behavior of the partial cross section in the immediate vicinity of the $\lambda_{cl}(v, J)$ point. In particular, the photodissociation cross section defined by expression (34) tends to infinity as $\lambda \rightarrow \lambda_{cl}(v, J)$ with $\lambda < \lambda_{cl}(v, J)$. Moreover, ignoring nuclear motion in the classically forbidden domain beyond the right turning point, the quasi-classical approach (34) results in a zero value of the cross section $\sigma_{vJ}^{p,d}(\lambda)$ in the wavelength range $\lambda > \lambda_{cl}(v, J)$ (see Fig. 3).

Figure 3 gives a clear idea of how the partial cross section $\sigma_{vJ}^{p,d}(\lambda)$ depends on the rotational quantum number J. In particular, it follows from Figs 3a and 3b that this dependence becomes pronounced for highly excited vibrational–rotational states [particularly for the vJ states resided near the dissociation limit of the $H_2^+(X^2\Sigma_g^+)$ ion]. For a fixed v value, increasing the rotational quantum number results in a significant shift of λ_{cl} towards longer wavelengths. For instance, for a vibrational quantum number v = 10 the values of λ_{cl} are equal to 1.09, 1.36, 2.20, and 4.75 µm for J equal to 0, 10, 15, and 20, respectively (Figs 3a and 3b). In this case, the general pattern of the oscillatory behavior of the partial cross section as a function of λ is significantly shifted to the long-wavelength domain (see the data for J = 15 and J = 20).

We now discuss the behavior of photodissociation cross sections $\sigma_T^{p,d}(\omega)$ of the molecular H_2^+ ion, averaged over the Boltzmann distribution, as functions of photon energy. Referring to Figs 4a and 4b, for every given value of *T*, the cross section $\sigma_T^{p,d}(\omega)$ exhibits a clearly defined maximum



Figure 4. Photodissociation cross sections $\sigma_T^{p,d}$ of the molecular $H_2^+(^2\Sigma_g^+)$ ion, averaged over the Boltzmann distribution, as functions of the photon energy $\hbar\omega$. Solid curves — calculated data of Ref. [23] for different temperatures: 1500 K (1), 2500 K (2), 3150 K (3), 4200 K (4), 5040 K (5), 6300 K (6), 8400 K (7) (Fig. 4a), and 12600 K (8), 16800 K (9), 25200 K (10) (Fig. 4b). The points in Fig. 4a correspond to the data of Ref. [29] for temperatures in the 3150–8400 K range. The asterisks indicate the calculated data of Ref. [15] for T = 2500 K. The squares, diamonds, and triangles in Fig. 4b represent the data of Ref. [29] calculated for temperatures of 12600, 16800, and 25200 K, respectively.

whose position, ω_{max} , shifts to lower frequencies with increasing temperature. This is explained by an increase in the contribution of high energy levels vJ with increasing T. Typical peak values of photodissociation cross sections $\sigma_T^{\text{p,d}}(\omega)$ prove to be on the order of $10^{-18} - 10^{-17}$ cm² in the T = 1500 - 25200-K range investigated.

Of special interest is the verification of the validity of the above-outlined analytical technique for calculating the photodissociation cross section $\sigma_T^{p,d}(\omega)$ of equilibrium hydrogen plasmas in a broad temperature range. Figures 4a and 4b give a detailed comparison of the cross sections $\sigma_T^{p,d}(\omega)$ calculated in the framework of the theory developed in Ref. [23] with ab initio quantum calculations [29] for the H_2^+ ion for T = 3150 - 25200 K, as well as with the results of the first quantum calculations [15] for T = 2500 K. It is pertinent to note that the numerical computations of Ref. [29] were performed with the inclusion of the contributions from all vibrational levels ($0 \le v \le 18$); the maximum number J_{max} of rotational levels was 35, and the total number of vibrational-rotational levels in Ref. [29] was 423. The first calculations done in Ref. [15] took into account only seven vibrational levels with rotational quantum numbers $J \leq 8$ typical for relatively small temperatures.

On the whole, the data obtained with the simple formula (51) are in good agreement with the *ab initio* numerical calculations in Ref. [29] for all temperatures in the 3150-25200-K range investigated by Stancil [29]. For instance, the photodissociation cross sections $\sigma_T^{p,d}(\omega)$ computed for $3150 \leq T \leq 8400$ K in Ref. [23] agree with the calculation data of Ref. [29] to within several percent throughout the entire photon energy range investigated (Fig. 4a). At high temperatures (12600 $\leq T \leq$ 25200 K) there is some difference between our findings [23] and the data calculated in Ref. [29], which, however, does not exceed 10% (Fig. 4b). These minor distinctions show up only in the vicinity of the peak ($\omega \approx \omega_{\text{max}}$) of the photodissociation cross section, where the quantities $\sigma_T^{\text{p.d}}(\omega)$ evaluated in Ref. [29] for temperatures $T \ge 12600$ K exhibit some irregular behavior. We note that our theory results in a smooth frequency dependence of the cross section (the neighborhood of ω_{max} inclusive) for all temperatures in the 1500-25000-K range considered. Furthermore, the validity of our approach was additionally verified in Ref. [50], in which the statistical sum for the molecular H_2^+ ion (calculated in the quasi-continuous approximation for the spectrum of vibrational-rotational levels) was directly compared with ab initio quantum calculations. This comparison suggests that the accuracy of this approach rises with temperature. This is natural: the larger the number of levels that make a contribution to the sum over all states, the more appropriate the quasi-continuous spectrum approximation.

The results of Ref. [23], depicted in Fig. 4a, also include the case of relatively low temperatures T = 2500 K and 1500 K and cover a broad wavelength range, including the visible and IR spectral ranges. Previous quantum computations [15] for T = 2500 K were performed only for several wavelengths λ in the $87 \leq \lambda \leq 455$ nm range. Referring to Fig. 4a, the calculation results of Refs [23] and [15] for T = 2500 K agree to within 25% for wavelengths in the $100 \le \lambda \le 455$ nm range. As noted in Ref. [23], for the molecular H_2^+ ion the validity range of the approach outlined here is bounded below by temperatures of the order of 1000 K. However, it is well to bear in mind that its accuracy depends strongly on the transition wavelength. In particular, at moderate values of T it proves to be more justified in the long-wavelength range, which larger internuclear separations are responsible for (and where highly excited vibrational-rotational levels make the main contribution).

5.2 Photoabsorption coefficients

Here we discuss the main features of the behavior of the integral optical absorption coefficient of the H₂⁺ system due to processes (1) and (2). The total photoabsorption rate constant $\eta_T = k_T/N_{\rm H}N_{\rm H^+}$ calculated by formula (63) in Refs [22, 23] is plotted in Fig. 5 with solid curves for different temperatures in the 1500–4000 K (Fig. 5a) and 5000–20000 K (Fig. 5b) ranges. One can see that the curves exhibit a qualitatively similar dependence of the photoabsorption rate constant η_T on the wavelength λ , with the exception of the case of high temperatures T > 9000 K. In particular, the $\eta_T(\lambda)$ dependence proves to be very sharp in the neighborhood of the peak in the UV spectral range for temperatures lying in the range $T \sim 1500-6000$ K. Depending on the specific value of T, the



Figure 5. Total H₂⁺-ion photoabsorption rate constants due to bound – free and free – free transitions as functions of wavelength λ for different temperatures *T*. Solid curves [1500 K (*1*), 2000 K (*2*), 3000 K (*3*), 6000 K (*4*), 12000 K (*5*) (a), and 6000 K (*6*), 7000 K (*7*), 8000 K (*8*), 9000 K (*9*), 10000 K (*10*), 12000 K (*11*), 20000 K (*12*) (b)] represent the quantity η_T calculated by formulas (63) and (64) in Refs [22, 23]. The dashed lines show the corresponding photoabsorption rate constants ζ_T calculated with the inclusion of stimulated emission (66).

peaks in the $\eta_T(\lambda)$ curves appear for $\lambda_{\text{max}} \approx 0.11 - 0.13 \ \mu\text{m}$. On the other hand, our attention is drawn to the strong variations in magnitude of the absorption coefficient: the peak values of η_T vary by several orders of magnitude with increasing temperature T from 1500 to 6000 K. In this case, the integral photoabsorption rate constant proves to be particularly large for moderate temperatures (see curves 1 and 2 in Fig. 5a). At the same time, typical values of η_T in the IR spectral range for $\lambda > 1.5 \,\mu\text{m}$ turn out to be on the order of $10^{-39} - 10^{-38}$ cm⁵ throughout the 1500 - 20000 K temperature range. In the 1500 < T < 6000 K temperature range, the photoabsorption rate constant decreases dramatically with an increase in λ in the visible region. However, this behavior becomes less pronounced for high temperatures $T \sim 7000 - 8000$ K. Moreover, the peaks in the UV spectral range disappear, as does the decrease of η_T in the visible region itself, beginning with T > 9000 K (Fig. 5b). In this case, the characteristic values of the photoabsorption rate constant vary over the range of about 2×10^{-40} – 2×10^{-39} cm⁵ for 7000 < T < 20000 K.

To demonstrate the role of stimulated emission in different wavelength and temperature ranges for locally equilibrium hydrogen plasma, we plotted in Figs 5a and 5b the calculated results [23] for the photoabsorption rate constant ζ_T (dashed curves), which additionally take into account the factor $[1 - \exp(-hc/kT\lambda)]$ [see relation (66)]. As expected, the correction for stimulated emission becomes most pronounced in the long-wavelength spectral range at high temperatures. For short λ and low T, the solid and dashed curves in Fig. 5a are practically coincident.

It is worth noting that our findings for the total rate constant $\zeta_T(\lambda)$ of optical absorption by the H⁺₂ ion, obtained with the aid of formulas (64) and (67), are in good agreement with the results of semiclassical calculations [12, 29] performed in the framework of the Bates theory [9] for the 2500-15000-K temperature range. This comes as no surprise, since (as shown in Section 5.1) the quasiclassical approach provides a high accuracy in the calculation of the integral contribution of photodissociation from all possible vibrational-rotational levels. The same conclusion is drawn from a comparison of our data for the integral contribution of free-free radiative transitions to the optical absorption coefficient (17) with the corresponding semiclassical calculations. This implies that a reliable determination of the contributions from bound-free and free-free transitions to photoabsorption permits us to employ simple analytical expressions from Sections 3.1 and 3.2 in lieu of more complex formulas containing integrals of the Airy function.

In addition to the previously investigated T and λ ranges, a series of new data for the photoabsorption rate constant is depicted in Figs 5a and 5b. In particular, we give the calculated results obtained in Refs [22, 23], which cover the range of relatively low temperatures T = 1500 K and 2500 K, whereby the H₂⁺-ion photoabsorption rate constants prove to be especially large (see curves *I* and *2* in Fig. 5a). These results hold significance for the comparison of the relative roles of photoabsorption by the H₂⁺ and H⁻ ions in low-temperature hydrogen plasmas. Furthermore, the data on H₂⁺-ion photoabsorption rate constants η_T and ζ_T for very high temperatures (T = 20000 K) are depicted in Fig. 5b. One can see that the role of stimulated emission effects in photoabsorption by a thermodynamically equilibrium plasma becomes most pronounced (see the solid and dashed curves in Fig. 5b).

It would be instructive to discuss the wavelength dependence of the contribution of free – free radiative transitions (2) to the total photoabsorption by the H_2^+ system in proton collisions with atomic hydrogen H(1s). Figure 6 exhibits the ratio $\delta = k_T^{\text{fr-fr}}/k_T$, calculated for different temperatures *T* in Refs [22, 23], between the optical absorption coefficient $k_T^{\text{fr-fr}}$ due to process (2) and the total quantity $k_T = k_T^{\text{b-fr}} + k_T^{\text{fr-fr}}$ which additionally takes into account the integral contribution of the bound – free transitions (1). One can see that the δ ratio at relatively low temperatures T = 1500 K and 2500 K amounts to about 10-15% near the corresponding peak $(\lambda_{max}\approx 2~\mu m$ and $\lambda_{max}\approx 1~\mu m)$ of the Planck distribution curve. However, with an increase in temperature and wavelength the contribution of the free-free transitions (2) increases rapidly to become dominant. For instance, the relative contribution of free-free H₂⁺-system transitions to the photoabsorption of equilibrium hydrogen plasma for T = 5000, 10000, and 20000 K is $\delta \approx 40$, 68, and 86% at $\lambda = 1 \ \mu m$, and $\delta \approx 66, 85$, and 94% at $\lambda = 2 \ \mu m$. Furthermore, Fig. 6 suggests that the part played by free-free radiative transitions at high temperatures becomes quite significant, not only in the IR range, but also in the visible spectral range.



Figure 6. Ratio between the optical absorption coefficient $k_T^{\text{fr-fr}}$ due to the free-free radiative transitions (2) of the H-H⁺ system and the total absorption coefficient $k_T = k_T^{\text{pd}} + k_T^{\text{fr-fr}}$ as a function of wavelength λ . Curves 1, 2, 3, 4, and 5 correspond to temperatures of 1500, 2500, 5000, 10000, and 25000 K.

5.3 Relative absorption of light by H_2^+ and H^- ions in a locally equilibrium hydrogen plasma

In this section we make a comparative analysis of the relative role of processes (1) and (2) of optical absorption by the H_2^+ ion and photoabsorption by the H^- ion due to radiative transitions (3) and (4), which are the subject of our studies in this work. Note that the dominant role of process (3) of electron photodetachment from the negative H^- ion in the visible spectral range in a locally equilibrium hydrogen plasma with a temperature $T \approx 6000$ K (characteristic of the solar photosphere) is well known. However, in the IR range for $\lambda > \lambda_{\rm H^-}^{\rm th}$ [where $\lambda_{\rm H^-}^{\rm th} = 1.644 \,\mu{\rm m}$ is the wavelength corresponding to the threshold of electron photodetachment (3)] the main contribution to optical absorption in plasmas with $T \approx 6000 \,{\rm K}$ is made by free-free radiative electron transitions (4) in the field of hydrogen atoms.

As follows from the findings of Refs [16, 17, 19, 20] and from recent calculations [21], in the solar photosphere the total contribution from radiative processes (1) and (2) involving the molecular (quasi-molecular) H_2^+ ion is small ($\leq 8\%$) in comparison with the contribution from the H^- ion. Several results concerning the role of H^- and H_2^+ ions in stellar atmospheres with a moderate temperature are outlined in Refs [4, 22]. A comprehensive analysis of the relative role of processes (1), (2) and (3), (4) in continuous optical absorption by quasi-equilibrium hydrogen plasmas was performed in Ref. [23] for a broad range of the parameters λ and *T*.

The total optical absorption coefficient $k_T^{H^-}$ (in cm⁻¹) of the H⁻ system may be represented in the form

$$k_T^{\mathrm{H}^-}(\omega) = k_T^{(3)}(\omega) + k_T^{(4)}(\omega) = \eta_T^{\mathrm{H}^-}(\omega)N_{\mathrm{H}}N_{\mathrm{e}},$$

$$k_T^{(3)} = \sigma_{\mathrm{H}^-}N_{\mathrm{H}^-}, \quad k_T^{(4)} = \eta_T^{(4)}N_{\mathrm{H}}N_{\mathrm{e}}.$$
(68)

Here, $\sigma_{\rm H^-}$ is the cross section of electron photodetachment from the negative H⁻(1s²) ion (in cm²), $\eta_T^{(4)}$ is the rate constant of the photoabsorption process (4) (in cm⁵), $\eta_T^{\rm H^-}$ is the total rate constant (in cm⁵), and correspondingly $k_T^{\rm H^-}$ is the total optical absorption coefficient due to the H⁻ ion (in cm⁻¹), and $k_T^{(3)}$ and $k_T^{(4)}$ are the optical absorption coefficients due to the bound – free (3) and free – free (4) transitions. Note that the cross section of process (3) and the rate constant of the photoabsorption (4) are presently known with a high degree of precision (see, for instance, Refs [55, 56]).

The number density of $H^{-}(1s^2)$ ions can be calculated by the formula

$$N_{\rm H^-} = \frac{g_{\rm H^-}}{g_{\rm e} g_{\rm H}} \left(\frac{2\pi\hbar^2}{m_{\rm e}kT}\right)^{3/2} \exp\left(\frac{\epsilon_{\rm H^-}}{kT}\right) N_{\rm H} N_{\rm e} \,, \tag{69}$$

where $\epsilon_{\rm H^-} = 0.754$ eV is the electron binding energy of the negative $\rm H^-(1s^{2\,1}S_0)$ ion, $g_{\rm H^-} = 1$ is the statistical weight of the $1s^2$ state, $g_e = 2$, and $g_{\rm H(1s)} = 2$ is the statistical weight of a hydrogen atom in the ground state 1s.

The total number density $N_{\text{H}_2^+} = \sum_{vJ} N_{vJ}$ of positive molecular H_2^+ ions can be found with recourse to the law of mass action (15):

$$N_{\rm H_2^+} = \frac{Z_{\rm v.r} g_{\rm H_2^+}}{\exp_{\rm H} g_{\rm H^+}} \left(\frac{2\pi\hbar^2}{\mu kT}\right)^{3/2} \exp\left(\frac{D_0}{kT}\right) N_{\rm H} N_{\rm H^+} \,. \tag{70}$$

Here, $g_{\rm H(1s)} = 2$, $g_{\rm H^+} = 1$, $g_{\rm H_2^+} = 2$, $\omega = 2$, and $D_0 = 2.651 \, {\rm eV}$. For the internal statistical sum $Z = (g_{\rm H_2^+}/\omega)Z_{\rm v,r}$ we take advantage here of the quantum result [50] obtained using the available energy values of all vibrational – rotational levels of the ${\rm H_2^+}({\rm X}\,^2\Sigma_{\rm g}^+)$ ion [52, 54]. The calculated ${\rm H_2^+}$ and ${\rm H^-}$ ion concentrations are collected in Table 2. One can see from this table that the total number density $N_{{\rm H_2^+}}$ of the molecular ${\rm H_2^+}$ ion and the ${\rm H^-}$ -ion number density prove to be of the same order of magnitude when the temperature is high enough ($T \sim 5000-15000 \, {\rm K}$). However, with decreasing temperature in the $T < 3000-3500 \, {\rm K}$ range, the ${\rm H_2^+}$ -ion number density $N_{{\rm H_2^+}}$ rises steeply and significantly exceeds the $N_{{\rm H}^-}$ value (Fig. 7).

As follows from formulas (62) and (68), in a thermodynamically equilibrium hydrogen plasma with equal con-

Table 2. Relative number densities of positive molecular $H_2^+(X^2\Sigma_g^+)$ ions $(N_{H_2^+} = \sum_{vJ} N_{vJ})$ and negative atomic $H^-({}^1S_0)$ ions as functions of equilibrium hydrogen plasma temperature. The electron and proton number densities are assumed to be equal: $N_e = N_{H^+}$. The number densities are given in units of cm⁻³.

<i>Т</i> , К	$N_{{ m H}_2^+}/N_{ m H}N_{{ m H}^+},{ m cm}^3$	$N_{\mathrm{H}^-}/N_{\mathrm{H}}N_{\mathrm{e}},\mathrm{cm}^3$	$N_{{ m H}_2^+}/N_{{ m H}^-}$
1500	4.50×10^{-15}	$6.09 imes 10^{-19}$	7390
2000	2.63×10^{-17}	9.20×10^{-20}	286
2500	1.24×10^{-18}	2.74×10^{-20}	45.3
3000	1.67×10^{-19}	1.16×10^{-20}	14.3
3500	$4.08 imes 10^{-20}$	6.09×10^{-21}	6.69
4000	1.44×10^{-20}	3.65×10^{-21}	3.96
5000	3.50×10^{-21}	1.69×10^{-21}	2.08
6000	1.40×10^{-21}	9.58×10^{-22}	1.46
8000	4.52×10^{-22}	4.32×10^{-22}	1.05
10000	2.26×10^{-22}	2.48×10^{-22}	0.91
15000	$8.18 imes 10^{-23}$	1.01×10^{-22}	0.81



Figure 7. Ratio between the total number density $N_{\text{H}_{2}^{+}} = \sum_{vJ} N_{vJ}$ of positive molecular $\text{H}_{2}^{+}(\text{X}^{2}\Sigma_{g}^{+})$ ions and the number density of negative $\text{H}^{-}(^{1}\text{S}_{0})$ ions as a function of equilibrium hydrogen plasma temperature. The electron and proton number densities are assumed to be equal: $N_{e} = N_{\text{H}^{+}}$.

centrations of electrons and protons $(N_{\rm H^+} = N_{\rm e})$ the ratio

$$\rho_T(\lambda) = \frac{k_T^{\mathrm{H}_2^+}(\lambda)}{k_T^{\mathrm{H}_-}(\lambda)} = \frac{\eta_T^{\mathrm{H}_2^+}(\lambda)}{\eta_T^{\mathrm{H}_-}(\lambda)} = \frac{\zeta_T^{\mathrm{H}_2^+}(\lambda)}{\zeta_T^{\mathrm{H}_-}(\lambda)}$$
(71)

between the optical absorption coefficients $k_T^{H_2^+} = \eta_T^{H_2^-} N_H N_{H^+}$ and $k_T^{H^-} = \eta_T^{H^-} N_H N_e$ is a dimensionless quantity which depends only on the radiation wavelength λ and the temperature *T*. We note that the last equality in expression (71) follows directly from relation (66), because the correction for stimulated emission [i.e., the factor in the square brackets in relation (66)] under conditions of local thermodynamic equilibrium appears in the same way in all formulas for the resultant optical absorption coefficient due to direct and inverse processes.

Let us we compare the coefficients of optical absorption by the H_2^+ and H^- ions. The behavior of photoabsorption rate constants $\zeta_T^{H_2^-}(\lambda)$ and $\zeta_T^{H^-}(\lambda)$ of the H_2^+ and H^- systems is shown in Figs 8a-d for different temperatures (1400, 2800, 6300, and 10080 K) of an equilibrium hydrogen plasma. The calculations of the integral photoabsorption coefficient of the molecular (quasi-molecular) H_2^+ ion were performed employing formulas (64) and (67) with the inclusion of the contributions from bound-free (1) and free-free (2) transitions. The calculations of the total absorption coefficient of



Figure 8. Comparison of the total optical absorption rate constants $\zeta_T^{H_1^+}$ and $\zeta_T^{H_1^-}$ of the H₂ and H⁻ systems at temperatures T = 1400 K (a), 2800 K (b), 6300 K (c), and 10080 K (d). The calculations were performed using formula (67) with the inclusion of the correction for stimulated emission [see relation (66)] and take into account the aggregate contributions of bound – free and free – free radiative transitions.

the H⁻ system were done using formulas (68) and (69), employing the available data [55, 56] for the electron photodetachment cross section σ_{H^-} (in cm²) [process (3)] and the rate constant $\eta_T^{(4)}$ (in cm⁵) of the radiative process (4). We note that the correction for stimulated emission [the factor in the square brackets in relation (66)] was also included in the calculation of the total optical absorption rate constant $\zeta_T^{\text{H}^-}$ for the H⁻ system, plotted in Figs 8a – d. Referring to Figs 8a – d, the relative position of the $\zeta_T^{\text{H}^+_2}(\lambda)$

Referring to Figs 8a – d, the relative position of the $\zeta_T^{\rm H_2}(\lambda)$ and $\zeta_T^{\rm H^-}(\lambda)$ photoabsorption curves changes radically in going over from low to high temperatures. It is also evident that the characteristic values of the optical absorption rate constants by both the H₂⁺ and H⁻ ions depend heavily on the optical wavelength. We emphasize that the total H⁻-system photoabsorption coefficient is determined only by free–free transitions (4) below the threshold $\hbar\omega < \epsilon_{\rm H^-} = 0.754$ eV of electron photodetachment from the H⁻ ion (i.e., in the IR range for $\lambda > \lambda_{\rm H^-}^{\rm th} = 1.644 \,\mu{\rm m}$).

Figure 9 gives a comprehensive idea of the relative role of positive molecular (quasi-molecular) H_2^+ ions and negative atomic H^- ions in the photoabsorption by a locally equilibrium hydrogen plasma. The results of recent calculations [21, 23] of the relative optical absorption $\rho_T = \eta_T^{H_2^+}/\eta_T^{H^-}$ (71) by the H_2^+ and H^- systems in different wavelength and temperature ranges between 1400 and 10080 K are depicted in Fig. 9. It is obvious that the wavelength dependences of the relative absorption are qualitatively similar in shape at quite different temperatures *T*. However, the specific ρ_T values at low, medium, and high plasma temperatures are radically different.



Figure 9. Ratio $\rho_T = k_T^{\rm H_2^+}/k_T^{\rm H_-}$ between the total optical absorption coefficients by positive molecular (H[±]) and negative atomic (H⁻) hydrogen ions as a function of wavelength λ . Curves *1*, *2*, *3*, *4*, and *5* correspond to temperatures of 1400, 2800, 4200, 6300, and 10080 K of a hydrogen plasma in local thermodynamic equilibrium.

We first consider the low-temperature case T = 1400 K, when the peak of the Planck distribution curve is reached for $\lambda_{\text{max}}^{\text{P}} = 2.07 \,\mu\text{m}$, and its full width at half maximum is

Table 3. Relative photoabsorption ρ_T by the H₂⁺ and H⁻ ions at the peak $\lambda = \lambda_{\text{pax}}^{\text{p}}$ of the Planck distribution curve and at the points $\lambda = \lambda_1^{\text{P}}$ and $\lambda = \lambda_2^{\text{p}}$ which correspond to the half maximum $[P_T(\lambda_1^{\text{P}}) = P_T(\lambda_2^{\text{P}}) = 0.5P_T(\lambda_{\text{max}}^{\text{m}})]$ of the Planck distribution function $P_T(\lambda)$ at a given temperature *T*.

Т, К	1400	2800	3150	4200	6300	8400	10080
$\lambda_1^{\rm P}, \mu m$	1.269	0.634	0.564	0.423	0.282	0.212	0.176
$ ho_T(\lambda_1^{\mathrm{P}}),$ %	0.18	2.6	3.92	8.9	20.2	27.8	30.4
$\lambda_{max}^{P}, \mu m$	2.07	1.035	0.920	0.690	0.460	0.345	0.287
$\rho_T(\lambda_{\max}^{\mathrm{P}}), \%$	98.6	1.1	1.5	3.2	8.2	13.9	18.1
$\lambda_2^{\mathrm{P}}, \mu m$	3.761	1.880	1.671	1.254	0.836	0.627	0.522
$ ho_T(\lambda_2^{\mathrm{P}}),$ %	15.2	26.0	28.4	3.0	4.3	7.0	9.4
$ ho_T(\lambda_{ m H^-}^{ m th}),$ %	215	36.7	29.6	19.2	12.5	10.2	9.3

 $\Delta \lambda_{1/2}^{P} = 2.49 \ \mu m$ (see Table 3). The most substantial part of the spectrum is therefore located in the IR spectral range between 1 and 4 μ m. From Fig. 9 it is evident that the contributions of ions H_2^+ and H^- to the total absorption coefficient for T = 1400 K (curve 1) are equal in the neighborhood of the peak $\lambda\approx 2~\mu m$ of the Planck curve. In the wavelength range 1.644 $< \lambda < 2 \ \mu m$, which lies below the threshold $\lambda_{H^-}^{th} = 1.644 \ \mu m$ of electron photodetachment from the negative hydrogen ion (3) ($\hbar\omega < \epsilon_{\rm H^-}$), the integral H₂⁺-ion optical absorption coefficients exceed the corresponding H⁻-system photoabsorption coefficients. Note that the relative photoabsorption $\rho_T(\lambda) \approx 2$ at $\lambda = \lambda_{\rm H^-}^{\rm th}$. With decreasing wavelength ($\lambda < \lambda_{\rm H^-}^{\rm th}$), a sharp decrease of the $\rho_T(\lambda)$ in the visible spectral range occurs, which results from a strong increase in the coefficient of optical absorption by weakly bound negative H⁻ ions due to process (3). A significant rise of the H_2^+ -ion optical absorption coefficient in comparison with H⁻ takes place in the short-wavelength part of the spectrum as well (in particular, the ρ_T value becomes greater than unity for $\lambda < 0.35 \,\mu$ m). However, this circumstance has only a minor effect on the magnitude of the absorption coefficient integrated over the entire spectrum.

Curve 2 in Fig. 9 corresponds to our results for relative photoabsorption ρ_T for T = 2800 K, when the peak of the Planck intensity distribution curve and its width at half maximum are $\lambda_{max}^P = 1.04 \ \mu m$ and $\Delta \lambda_{1/2}^P = 1.25 \ \mu m$, respectively. Referring to this curve, for $\lambda > \lambda_{H^-}^{th}$ the infrared absorption by the H₂⁺ ion becomes weaker than the photoabsorption by the H⁻ ion due to free – free transitions. But the relative role of H₂⁺-ion absorption above the threshold of electron photodetachment from the H⁻ ion ($\hbar \omega > \epsilon_{H^-} = 0.754 \ eV$ or $\lambda < 1.644 \ \mu m$) is somewhat greater. Nevertheless, for $T < 3000 \ K$ (when the IR absorption is especially significant) the optical absorption by the H₂⁺ ion makes a significant contribution in comparison with H⁻-ion photoabsorption in the $\lambda > \lambda_{H^-}^{th}$ wavelength range. For instance, the relative photoabsorption for $\lambda = 1.644$, 2, 2.5, and 3 μm amounts respectively to 37, 22, 13, and 9% for $T = 2800 \ K$, and to 30, 19, 11, and 8% for $T = 3150 \ K$.

Curves 3 and 4 in Fig. 9 serve to illustrate the behavior of the ρ_T ratio at temperatures T = 4200 K and 6300 K. For T = 6300 K, the major part of the integral radiation intensity corresponds to the visible spectral range, since the peak of the Planck distribution curve and its width at half maximum are $\lambda_{\text{max}}^{\text{P}} = 0.46 \,\mu\text{m}$ and $\Delta \lambda_{1/2}^{\text{P}} = 0.55 \,\mu\text{m}$, respectively. As follows from Table 3, the relative contribution ρ_T of the ions H_2^+ and H^- proves to be equal to 20, 8, and 4% at wavelengths of $\lambda = 0.28$, 0.46, and 0.83 µm, respectively. In the UV spectral range for $\lambda \approx 0.1 - 0.2$ µm, this contribution is $\rho_T \approx 40 - 70\%$.

A further increase in temperature leads to an increase in the integral contribution of the H₂⁺ ion to the value of ρ_T averaged over the entire spectrum. This follows directly from our calculations [21, 23] for T = 8400 K and T = 10080 K. At these values of T, the peaks of the Planck distribution function shift towards shorter wavelengths to the UV spectral range and are $\lambda_{\text{max}}^{\text{P}} = 0.35 \,\mu\text{m}$ and $\lambda_{\text{max}}^{\text{P}} = 0.29 \,\mu\text{m}$, respectively. That is why significant values of the ratio $\rho_T \approx 25-30\%$ are attained even within the half-width $\Delta \lambda_{1/2}^{\text{P}}$ of the Planck curve (see Table 3). For T = 10080 K, the behavior of relative optical absorption ρ_T as a function of wavelength λ is demonstrated by curve 5 in Fig. 9.

6. Conclusions

This paper is devoted to the comprehensive analysis of continuous optical absorption arising from bound-free and free-free radiative transitions between two different electronic terms of a diatomic molecule. Our consideration was oriented primarily to the application of results to the radiative processes (1) and (2) involving the simplest diatomic system H_2^+ . We have pointed out the main accomplishments in this field since the emergence of Bates's fundamental work on photoabsorption [9, 12], which was performed employing the quasi-classical method in the context of the quasi-static approximation. We have set forth the recently developed theoretical approach [21-23] based on the input quantum formulas for the efficient cross sections of the processes under consideration and on the theory of nonadiabatic transitions between the potential energy curves of a diatomic molecule. We have demonstrated the feasibility of analytical description of the integral contribution from all possible vibrationalrotational molecular levels to the cross section of photodissociation process (5), averaged over the Boltzmann distribution, and to the corresponding optical absorption coefficient. In this case, advantage was taken of a quasicontinuous spectrum approximation for vibrational-rotational levels and of the calculation technique developed in Ref. [49]. The photoabsorption due to free-free radiative transitions (16) was considered in a similar way. This allowed us to obtain compact formulas for the total optical absorption coefficients due to processes (5) and (16) in a thermodynamically equilibrium medium containing atomic and molecular components.

For the example of the molecular H_2^+ ion it was shown that the expressions for partial photodissociation cross sections $\sigma_{vJ}^{p,d}(\omega)$ given in our paper provide an adequate explanation of their behavior in relation to the vibrational and rotational quantum numbers of excited molecular levels (including levels located near the dissociation limit of the ground term). Simple analytical formulas were given for the photodissociation cross sections $\sigma_T^{p,d}(\omega)$ averaged over the Boltzmann distribution for a given gas (plasma) temperature. Over a wide range of frequencies and temperatures of a quasiequilibrium hydrogen plasma, the H_2^+ -ion photodissociation cross sections $\sigma_T^{p,d}(\omega)$ calculated in Refs [22, 23] were compared with available numerical quantum-mechanical *ab initio* calculations [29] pertaining to this case.

The analytical method outlined in our paper was shown to provide a high accuracy throughout the temperature and frequency ranges investigated. Furthermore, it was found that the data for the H₂⁺-ion photodissociation cross section $\sigma_T^{p,d}(\omega)$, obtained employing a simple quasi-classical formula (51), are little different from the quantum calculations in the $kT > \hbar\omega_e$ temperature range most interesting for applications. This opens good prospects for the application of the above method to the calculation of total photodissociation cross sections in the case of heavier diatomic molecules and ions, for which the pursuance of such *ab initio* quantum calculations is a challenge.

Special consideration was given to the problem of the integral contribution from bound-free (5) and free-free (16) radiative transitions in the molecule (quasi-molecule) to the total optical absorption coefficient. The expression for the total absorption coefficient given in this case takes into account the motion of molecular nuclei both along the classically allowed and classically forbidden internuclear distance intervals. In the passage to the limit of the classical description of nuclear motion in the H_2^+ system, this expression leads to the well-known semiclassical Bates formula, which he obtained in the framework of a quasistatic approximation. Therefore, the approach outlined in our paper makes it possible to entirely reproduce the most significant results of the semiclassical Bates theory for the total photoabsorption coefficient.

In the example of specific calculations for the H_2^+ system we have demonstrated that the quasi-classical theory of light absorption is inappropriate for the adequate description of the behavior of the partial cross sections $\sigma_{vJ}^{\rm p.d}(\omega)$ of photodissociation from selectively excited levels vJ in the immediate vicinity of the $\lambda_{cl}(vJ)$ wavelength and at wavelengths $\lambda \ge \lambda_{cl}$ corresponding to the classically forbidden domains of motion of molecular nuclei. However, a simple quasi-classical formula (34) faithfully reproduces the oscillations-averaged cross sections $\sigma_{vJ}^{p,d}(\omega)$ that are away from the turning points (i.e., in the domain which makes the decisive contribution to the photodissociation cross section averaged over the Boltzmann distribution and to the total photodissociative absorption coefficient). That is why the differences between quantum and quasi-classical results for the integral characteristics of photodissociation prove to be extremely small throughout the wavelength range investigated. A similar conclusion is drawn when the general expressions for the integral contribution of free-free transitions to photoabsorption are compared with the results of Bates's semiclassical calculations.

The results of calculations for the molecular (quasimolecular) H_2^+ ion outlined in our paper give a rather comprehensive idea of the behavior of the integral contribudoi>8. tion from bound – free (1) and free – free radiative transitions (2) to the total optical absorption coefficient. These calculations encompass the IR, visible, and UV spectral ranges and a broad temperature range of quasi-equilibrium hydrogen plasma between 1500 and 25000 K. One can infer from the analysis conducted that the main contribution to the total <u>doi></u>14. photoabsorption coefficient in the neighborhood of the peak of the Planck distribution curve is, as a rule, made by the bound-free transitions (1) from a large number of vibrational-rotational states. However, the contribution of freefree transitions (2) at high temperatures becomes dominant in the long-wavelength spectral range.

A comparative analysis of the total rate constants of continuous optical absorption by different components of hydrogen plasmas is of interest for astrophysical applications. Here, we confine ourselves to the consideration of the relative contribution to photoabsorption made only by the ion components: H₂⁺ and H⁻. In doing so, in addition to the already available results on the solar photosphere (see Refs [16, 17, 19, 20]) and the individual models for relatively cool stars (see Ref. [4] and references cited therein), we have outlined detailed calculations [21-23] of the relative photoabsorption ρ_T by the H₂⁺ and H⁻ ions as a function of wavelength for temperatures in the 1400-10080 K range. However, it should be borne in mind that a large number of diverse radiative processes should be included to give a realistic idea of the behavior and magnitude of the total photoabsorption coefficient in stellar atmospheres. In particular, as already noted in the Introduction, the decisive role in infrared radiation absorption in the dense atmospheres of cool stars with a low content of elements heavier than hydrogen and helium is played by the processes of collisionally induced light absorption involving hydrogen molecules: H_2-H_2 , H_2-H , and H_2-He (see Refs [3-5]). This is due to the fact that neutral hydrogen under these conditions is primarily in the H₂ molecular state and the concentrations of ion components are significantly lower than in the case of the solar photosphere or atmospheres of hotter stars. However, for the solar photosphere and photon energies $\hbar\omega > 4.93$ eV, the dominant role is played by the radiation absorption from the triplet 3s3p³P level of atomic Mg (see Ref. [2]). A notion of the role of different photoprocesses in stellar atmospheres can be gained from Refs [1-6].

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