INFLUENCE OF THE COLLISIONAL BENDING OF TRAJECTORIES ON SHIFTS OF THE MOLECULAR SPECTRAL LINES IN THE VISIBLE REGION

A.D. Bykov, N.N. Lavrent'eva, and L.N. Sinitsa

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

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Influence of the trajectory bending on spectral shifts of rovibrational lines of molecules is studied. The first order term of the interruption function is calculated using rigorous solutions of the classical dynamic equations. A universal function of two dimensionless arguments that is independent of the parameters of intermolecular potential and the initial conditions of a collision is derived. This function enables one to account for actual trajectories in calculations. The errors of calculations caused by the use of a model of linear trajectories are estimated for the water vapor and methane spectral lines broadend by foreign gases.

In recent years a lot of papers have been published (see, for example, Refs. 1–8) that are devoted to measurements and calculations of shifts of the rovibrational absorption lines of atmospheric gases caused by the nitrogen, oxygen, and air pressure. A comparison of measurement data with the calculational ones has shown quite a good agreement. At the same time the necessity to improve the calculational techniques first of all for correct statement of the inverse problem on determining the molecular characteristics from the line shift measurements is evident.

In Refs. 1, 4, and 7 we investigated the effect of intermolecular interactions on the line shifts and showed that the vibrational dependence of constants entering into isotropic component of the polarization potential which, for example, almost completely determines the "red" line shift of water vapor in the near–IR and visible spectral regions should be taken into account. In this paper we investigated the effect of trajectory bending of colliding molecules on contribution of the above–mentioned part of intermolecular interaction potential into the shift of the rovibrational line center.

Earlier calculations of the absorption line shifts used a straight–line trajectory approximation, which, unfortunately, is inapplicable to the case of low temperatures and weakly broadening lines. The "strong collisions" (in accordance with the classification proposed in Ref. 9) correspond to the case of $b_0 > r_c$, where b_0 is the cut off parameter in the Anderson theory and r_c is the distance of the closest approach of colliding molecules. For the strong collisions the broadening coefficients are relatively large and process of absorption is interrupted before the trajectory of the relative motion deviates from the rectilinear one. If the line shape is formed by weak collisions when $b_0 < r_c$, the line is, first of all, weakly broadened with a relatively large shift of the center, and, second, the trajectory bending may be an important factor in calculations.

At low temperatures the fraction of "slow" molecules is large and therefore the trajectory bending shows a stronger effect and weak collisions make a larger contribution to the line center shift.

In earlier studies the trajectory bending effect was taken into account in the calculations of half-widths performed using the Anderson–Tsao–Curnutte–Frost (ATCF)[10,11] method and other semiclassical methods, for example, the Robert–Bonamy[9] method. In the above–mentioned papers the models of effective rectilinear trajectories have been used.

In this paper the exact solutions of classical dynamic equations describing the relative motion of colliding molecules are used to calculate the first order term $S_1(b)$ of the interruption function.

1. CONTRIBUTIONS OF DIFFERENT INTERACTIONS INTO THE FORMATION OF THE MOLECULAR ABSORPTION LINE SHIFTS IN THE VISIBLE SPECTRAL REGION

In the impact theory the half-width and the line shift are determined by the first– and second–order terms of the interruption function.[10] Their relative contributions into the shift are different in different spectral regions: for lines of pure rotational transitions the contribution of $S_1(b)$ is equal to zero and the broadening and shift coefficients are determined by $S_2(b)$, for the lines in the near–IR and visible regions the line shifts are almost completely determined by the first–order term $S_1(b)$.[7]

For example, in Table I the results of calculations of contributions of different interactions to the line shifts of the H_2O $3\nu_1 + \nu_3$ band induced by the nitrogen pressure are given. Earlier such calculations have been done in Ref. 4.

TABLE I. Contributions of the intermolecular potential components into the line shift of the H_2O $3\nu_1 + \nu_3$ *band caused by* N_2 *pressure.*

f	i	$S_{dq}10^3$	$S_{qq}10^3$	$S_{du}10^3$	$S_1 10^3$	$\delta_{if}10^3$	Experiment, Ref. 3
422	523	1.15	–0.008	0.005	–11.0	–9.9	–9.4
515	616	–2.00	–0.022	–0.036	–14.8	–16.9	–19.4
505	606	–2.43	–0.030	–0.031	–14.5	–16.9	–15.7
413	514	–3.55	–0.014	0.0007	–10.6	–14.1	–15.5
762	761	2.05	0.003	0.006	–25.9	–23.8	–26.1
330	431	3.34	0.013	–0.006	–13.7	–10.4	–10.3
331	432	3.45	–0.023	–0.003	–14.5	–11.1	–12.0
660	661	1.95	0.006	0.021	–28.1	–26.1	–26.3
321	422	0.64	0.003	–0.002	–10.8	–10.2	–10.6
414	515	–2.46	–0.021	–0.014	–12.5	–14.9	–
404	505	–2.90	–0.038	–0.009	–11.8	–14.7	–
312	413	–0.40	–0.028	0.005	–10.3	–10.7	–13.1
505	524	–2.56	–0.031	–0.027	–13.3	–15.9	–21.1
322	423	–0.42	0.015	–0.005	–11.7	–12.1	–10.5
303	404	–3.37	–0.048	0	–10.3	–13.7	–13.2

Note: The contribution of dipole–hexadecapole interaction is designated as S_{du}.

The calculations were performed by the ATCF method. The developments of the method necessary for the line shift calculations are presented in Refs. 1, 4, and 7. In the calculations we took into account the dipole–quadrupole, quadrupole–quadrupole, and dipole–hexadecapole interactions as well as the contribution from the isotropic component of the potential. Calculating the $S_1(b)$ term we took into account the polarization potential and its constant dependences on the vibrational state of the water vapor molecule.

Table I presents: in the first two columns the quantum numbers, then the contributions to the line shifts coming from the dipole–quadrupole, quadrupole–quadrupole, and dipole–hexadecapole interactions, respectively. Then the contribution from the term $S_1(b)$ is given and, finally, the coefficient of total line shift and its experimental value from Ref. 3 are presented.

It can be seen, that for the band $3\nu_1 + \nu_3$ the contribution from $S_1(b)$ significantly exceeds the contribution coming from the electrostatic component of the potential (for some lines up to 10 times). This is explained by a strong change of the molecular polarizability under the action of vibrational excitation.[1] From this it follows that the line shift in the visible spectral region can be described using an approach similar to the adiabatic one and taking into account only the first–order term of the interruption function related to the vibrational phase shift. Therefore it seems to be useful to investigate the role of the relative motion trajectory bending by a collision when the first–order term of the interruption function is calculated.

Let us note that in the ATCF method the real part of $S_2(b)$ determines the cut off parameter b_0 and therefore it also influences the final result. However, as the calculations for the case of water vapor lines broadening by air have shown, the parameter b_0 weakly depends on the account for the trajectory bending since it is determined by a "strong" dipole–quadrupole interaction. As a result, the trajectory bending can be taken into account only in one term of the interruption function.

2. CALCULATION OF $S_1(b)$ TERM FOR REAL TRAJECTORIES

In the below discussion we assume that the conditions for applicability of the impact approach are satisfied and therefore the model of uncorrelated binary collisions is used. The relative motion of colliding molecules is described by classical trajectories (kinetic energy of molecules is assumed to be sufficiently large) so that the energy exchange between the translational and internal degrees of freedom can be neglected. Under such an assumption, it is natural to assume that the energy and the momentum of relative molecular motion are conserved during the collision.

Within the framework of a semiclassical line broadening theory, irregardless of assumptions on the trajectory and the molecular interaction forces, the first–order term of interruption function can be written in the form:

$$S^{(1)}_{ifj}(b, \upsilon) = \sum_n (C^{(n)}_{ij} - C^{(n)}_{fj}) \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{dt}{r(t, b, \upsilon)^n}, \qquad (1)$$

where b is the impact parameter, υ is the initial relative velocity, $r(t, b, \upsilon)$ is the distance between the center of masses of colliding molecules, i and f are quantum numbers of the initial and final states of a transition, j designates the set of quantum numbers of a foreign gas molecule, $C^{(n)}_{ij}$ and $C^{(n)}_{fj}$ are some combinations of the constants of broadening and absorbing molecules depending on vibrational quantum numbers, and $n = 6, 7, 8, \ldots$, (see Ref. 12). Note that $n = 6$ corresponds to dispersion and induction interaction forces of the dipole–induced dipole type and $n = 8, 10, \ldots$ to the interactions of higher orders like the dipole–induced quadrupole, etc.

Then, it is necessary to determine the dependence of the distance between the centers of masses of colliding molecules on time and to calculate the integral in Eq. (1).

The intermolecular potential involves the isotropic and anisotropic components, but since the half–width and the line shift are formed by a large number of collisions for determining $r(t, b, \upsilon)$ let us use some effective isotropic potential. The solution of motion equations for the isotropic potential is well known (see, e.g., Ref. 13):

$$t = \int\limits_{r_c}^{r} \frac{dr'}{\sqrt{2[E - U(r')]/\mu - M^2/\mu^2 r'^2}} + c_1 ; \qquad (2)$$

$$\varphi = \int\limits_{r_c}^{r} dr' \frac{M/\mu r'^2}{\sqrt{2[E - U(r')]/\mu - M^2/\mu^2 r'^2}} + c_2 , \qquad (2a)$$

where $E = \mu\upsilon^2/2$, $M = \mu b\upsilon$, $1/\mu = 1/m_1 + 1/m_2$ are the energy, momentum, and reduced mass, respectively, and $U(r)$ is the molecular interaction potential. Since in the case of an isotropic potential the trajectory is plane, it is defined by two functions: Eq. (2) defines r as an implicit function of t, and Eq. (2a) describes the relationship of r and the polar angle φ. To calculate the integral in Eq. (1) the following coordinate system and initial conditions are chosen: the plane, where collisions take place is the plane (xy), at $t = -\infty$ the coordinate y is infinite, i.e., $y = \infty$ and $\varphi = 0$, the instant $t = 0$ corresponds to the distance of the closest approach r_c. As a result

$$c_1 = 0$$

$$c_2 = -\int\limits_{r_c}^{\infty} dr' \frac{M/\mu r'^2}{\sqrt{2[E - U(r')]/\mu - M^2/\mu^2 r'^2}} .$$

Let us designate

$$\Phi_n = \frac{1}{\hbar} \int\limits_{-\infty}^{\infty} \frac{dt}{r(t, b, \upsilon)^n} \qquad (3)$$

and using Eqs. (2) and (2a) replace the integration variable by r. This gives

$$\Phi_n = \frac{2}{\hbar} \int\limits_{r_c}^{\infty} \frac{dr'}{r'^n \sqrt{2[E - U(r')]/\mu - M^2/\mu^2 r'^2}} . \qquad (4)$$

The parameter r_c is determined from the equation[13]

$$2[E - U(r_c)]/\mu - M^2/\mu^2 r_c^2 = 0$$

or

$$(b/r_c)^2 = 1 - V(r_c) , \qquad (5)$$

where $V(r) = 2U(r)/\mu\upsilon^2$.

By making change of variables in Eq. (4)

$$y = (r/r_c)^2 , \qquad (6)$$

and using relation (5) to transform the integral, we obtain

$$\Phi_n = A_n(\infty)/\upsilon\, r_c^{n-1} ;$$

$$A_n(x) = \int\limits_{1}^{x^2} \frac{dy}{y^{n/2} \sqrt{y - 1 + V(r_c) - yV(\sqrt{y} r_c)}} . \qquad (7)$$

After the change of variables according to Eq. (6), the limits of integration become independent of r_c and the integrand does not contain the impact parameter explicitly.

Generally speaking, the solution of dynamic equations (Eqs. (2) and (2a)) contains not only infinite but also the finite trajectories that correspond to the bound or metastable states of the colliding molecules. The "effective potential" is presented in Fig. 1, in which the classically permissible regions of motion for the collisions of three types are shown as well. Let us note that Eq. (5) that determines the turning points can have one, two, or three solutions depending on the b and υ relation .

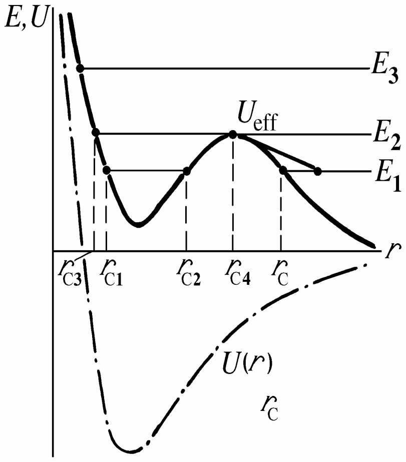

FIG. 1. Intermolecular potential $U(r)$, *the effective potential* $U_{\rm eff}(r) = U(r) + M^2/2\mu r^2$, *turning points* r_{c1}, r_{c2}, *and* r_{c3} *for the collisions of three types. The infinite* ($r_c \le r \le \infty$) *and finite* ($r_{c1} \le r < r_{c2}$) *trajectory correspond to the energy* E_1. *The infinite trajectory* ($r_{c4} \le r < \infty$) *and the region of metastable state* ($r_{c3} \le r \le r_{c4}$) *correspond to the energy* E_2. *A single infinite trajectory corresponds to the energy* E_3.

The bound and metastable states correspond to variation of r in some finite region (from r_{c1} to r_{c2}). As is well known, strong collisions and, moreover, the collisions producing a bound pair of molecules interrupt the absorption process and do not contribute to the line shift. Therefore it is necessary to exclude such trajectories from calculations that can be done by using in Eqs. (5), (6), and (7) the largest value of r_c. Thus it is implied that the integration in Eq. (7) is performed from the largest value of r_c determined by Eq. (5) up to $r = \infty$, what corresponds to y varying from 1 to ∞. Moreover, the radicand in Eq. (7) determining the classically permissible region of motion must be nonnegative for all values of y. The integration over the region chosen in such a way, automatically accounts only for contributions from interactions of molecules moving along infinite trajectories into the line shift. Recall that at the turning point the radicand (in Eq. (7)) vanishes but, as it can easily be seen, the integral converges both on the upper and lower limits.

Equation (7) completely takes into account the effect of trajectory bending and it is easily calculated for any model or numerically set potential. The right–hand side of Eq. (7) contains the reduced interaction potential V and may be represented as a universal function of the intermolecular parameters. Equation (7) has been derived using exact solutions of the dynamic equations, what essentially differs it from the results obtained based on model approaches.[14–17] For these reasons, Eq. (7) may be used for determining the applicability limits of approximate methods being used to account for bending, as well as for obtaining new approximate values or estimates of the integral Φ_n values.

3. CALCULATIONS OF Φ_n VALUES AND OF THE TRAJECTORY MODELS

In Refs. 14–17 different models have been proposed which allow one to calculate more accurately the broadening coefficients in the case of "weak collisions". In these models, first, some type of a trajectory is assumed to be valid and then it is used to correct the integral value in Eq. (1). It can be shown that all these models result from some evident approaches used when calculating integral (7). For this purpose it is necessary to expand the radicand entering into Eq. (7) (i.e., the function $yV(r_c\sqrt{y})$ into the Taylor series in the vicinity of the point $y = 1$ and then take the first few terms.

The use of series expansion is justified by the presence of the factor $y^{-n/2}$ in the integrand of Eq. (7) which "cuts" the intermolecular potential on the trajectory portions far from the point $y = 1$, and, it can be stated that the intermolecular interaction potential is mainly formed within certain vicinity of a turning point and the behavior of this potential at large y values can be neglected. In this case the common assumption that the line center shift is formed due to interactions with far–flying broadening particle is used, while the collisions with impact parameter smaller them b_0 are assumed to be inefficient in forming the shift .[10,11]

a) By taking $U(r) = 0$ in Eqs. (5) and (7), we obtain:

$$\Phi_n = \frac{1}{\hbar\upsilon b^{n-1}} \int\limits_1^\infty \frac{\mathrm{d}y}{\sqrt{y^n(y-1)}} = \frac{\sqrt{\pi}}{\hbar u b^{n-1}} \frac{\Gamma((n+1)/2)}{\Gamma(n/2+1)} = a_n/\hbar\upsilon b^{n-1} \quad (8)$$

in a straight line trajectory approximation, where $\Gamma(x)$ is the gamma–function.

This approximation was used in Refs. 1, 4, 5, 7, and 18 for calculations of H_2O rovibrational line shifts. It gives good results in the case of "strong collisions" when the long–range acting anisotropic component of the intermolecular interaction potential interrupts the absorption process when $b_0 \gg r_c$. In the near–IR and visible spectral regions the most strong rotational transitions are observed for small values of J (from 1 to 5). However, in the H_2O 6.3 μm absorption band the broadening and shift coefficients were measured for the lines with J equal to 15–19 (Ref. 20). The shapes of these lines are formed by "weak collisions" and therefore it is necessary to analyze the applicability of the straight line trajectory approximation.

b) As the next approximation, let us take $U(r_c\sqrt{y}) \simeq U(r_c)$ in Eq. (7) and take into account the similar term in Eq. (5). Then we obtain:

$$\Phi_n = a_n/\hbar\upsilon_c\, r_c^{n-1} , \qquad \upsilon_c = \upsilon\sqrt{1 - V(r_c)} = b\upsilon/r_c . \quad (9)$$

After the same transformations in Eqs. (2) and (2a) one can see that a real trajectory is replaced by some effective rectilinear one with the impact parameter r_c and the constant velocity υ_c which corresponds to the Herman–Tipping model.[14] In Ref. 15 it was pointed out that in this model there is a physically doubtful point associated with the fact that for small impact parameters the relative velocity is small and at $b = 0$ the effective velocity υ_c vanishes. This approximation was used for calculating the line broadening coefficients of dipole molecules in the atmosphere of inert gases.[14]

c) To obtain the next approximation (which corresponds to the Robert–Bonamy[16] model) let us take into account the first term of the intermolecular interaction potential expansion into the Taylor series in the vicinity of the point $y = 1$. In this case we have

$$A_n(\infty) = \{1 - V(r_c) - r_c V'(r_c)/2\}^{-1/2} a_n . \quad (10)$$

or

$$\Phi_n = a_n/\hbar\upsilon'_c\, r_c^{n-1} , \quad \upsilon'_c = \upsilon\{1 - V(r_c) - r_c V'(r_c)/2\}^{1/2} . \quad (11)$$

Using this same approximation in Eqs. (2) and (2a) it can be shown that in Robert–Bonamy model a real trajectory is replaced by a rectilinear one with the impact parameter r_c and constant velocity υ'_c.

The Robert–Bonamy model gives quite realistic values of mean effective velocity for collisions with small impact parameters. As can be seen from Eq. (11) $\upsilon' \neq 0$ at $b = 0$ and has some finite value. This model was used in calculations of the half-widths of carbon dioxide, water vapor, and ozone.

More accurate expressions for $A_n(\infty)$ (in particular, for a parabolic trajectory model) are obtained by taking into account higher order terms of the intermolecular interaction potential expansion into Taylor series.

4. CALCULATION OF $A_6(\infty)$ FOR THE LENNARD–JONES POTENTIAL

The calculations of water vapor line broadening coefficients for the cases of nitrogen, oxygen, and air as broadening gases performed in Ref. 9, have shown that in the case of the line shape formation by "weak collisions" it is necessary to take into account both the short–range acting component of the potential and the trajectory bending. Moreover, it was found that the Robert–Bonamy "effective rectilinear trajectory" model gives quite satisfactory results. To calculate the line shift coefficients it is necessary not only to determine the values of corrections for the trajectory bendings, but also to verify the applicability of the used models. The simplest way to do such estimations is the direct calculation of integral (7).

To determine $A_n(\infty)$ we shall use the Lennard–Jones potential

$$U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] , \quad (12)$$

where σ and ε are parameters of the potential (σ approximatively corresponds to the radius of action of repulsive forces, and ε is equal to the depth of the potential well). For potential (12) $A_n(\infty)$ takes the form

$$A_n^{LJ}(\infty) = \int\limits_1^\infty \frac{\mathrm{d}y}{y^{n/2}\sqrt{y - 1 + \lambda[\beta^{12}(1 - y^{-5}) - \beta^6(1 - y^{-2})]}} , \quad (13)$$

where $\lambda = 8\ \varepsilon/\mu\upsilon^2$ and $\beta = \sigma/r_c$ are the dimensionless interaction parameters.

Function (13) may be considered as some universal function independent of the parameters of the intermolecular potential and of the initial conditions of a collision and which contains the reduced quantities λ and β. If the values of this function are precomputed that allows one to avoid calculations of integral (13) on each step of integration over the impact parameter and relative velocity when calculating the line shifts for a given pair of molecules.

The classically permissible region depends on λ and β and gives the definition region of $A_6(\infty)$ as a function of λ and β. The latter is determined by the inequalities

$$y - 1 + \lambda[\beta^{12}(1 - y^{-5}) - \beta^6(1 - y^{-2})] \geq 0\ , \quad 1 \leq y \leq \infty\ . \quad (14)$$

For the given initial velocity (i.e., when λ is fixed) the parameter β must satisfy Eq. (14) for any y ($1 \leq y < \infty$), which, according to the accepted assumptions, corresponds to the motion from the infinity to the turning point (the trajectory is symmetric with respect to the vector r_c). If this inequality holds then one can be sure that there is an infinite trajectory, corresponding to the given impact parameter b, velocity υ, and the parameters λ and β. The absence of β satisfying inequality (14) shows the disagreement of λ and β with the initial conditions according to which the trajectory is characterized by four parameters b, υ, ε, and σ and arbitrary λ and β in Eq. (13) can disagree with these parameters. Hence, inequality (14), determining the classically permissible region for the infinite trajectories, only imposes some limitations on λ and β.

As an example, let us give the definition region of the Φ_6 function: at $\lambda < 2.6767$ this function exists for any β, for other values of λ and for any $y > 1$ the values of β must satisfy two conditions:

$$\beta^6 > \frac{y^2}{2(y^4 + y^3 + y^2 + y + 1)} \times$$

$$\times \left[y(y+1) + \sqrt{\frac{\lambda y^2(y+1)^2 - 4y(y^4 + y^3 + y^2 + y + 1)}{\lambda}} \right]; \quad (15)$$

$$\beta^6 < \frac{y^2}{2(y^4 + y^3 + y^2 + y + 1)} \times$$

$$\times \left[y(y+1) - \sqrt{\frac{\lambda y^2(y+1)^2 - 4y(y^4 + y^3 + y^2 + y + 1)}{\lambda}} \right].$$

It can easily be seen, that these conditions must be satisfied for minimum and maximum values of the right–hand sides of the inequality and for small λ the right–hand sides of inequalities have complex values. In this case the definition region β is $\beta \geq 0$. Note that if inequality (15) is valid only for y from some interval that means that the motion occurs in some finite region, what corresponds to bound or metastable states.

To estimate the effect of trajectory bending on the line shifts integral (13) was calculated numerically for $0.1 \leq \lambda \leq 10$. The dependences of $A_6(\infty)$ on β for $\lambda = 0.2$, 1.0, 2.6, and 6 is shown in Fig. 2.

In the Robert–Bonamy approximation[17] we have

$$A_6(\infty) = a_6/\sqrt{1 + \lambda\,\beta^6(5\beta^6 - 2)}\ . \quad (16)$$

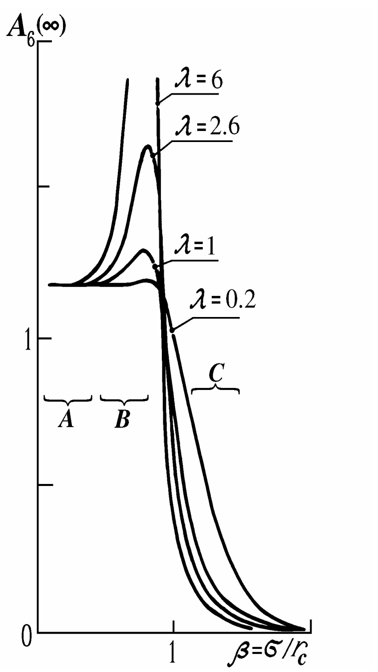

FIG. 2. Dependence of $A_6(\infty)$ on $\beta = \sigma/r_c$ and $\lambda = 8\varepsilon/\pi\upsilon^2$ (σ and ε are parameters of the Lennard–Jones potential, r_c is the distance of the closest approach, υ is the velocity, and μ is the reduced mass of a molecule). The trajectory portion A *corresponds to distant flights of molecules,* B *to collisions occurring at distances approximatively equal to* σ, and C *to the head–on collisions.*

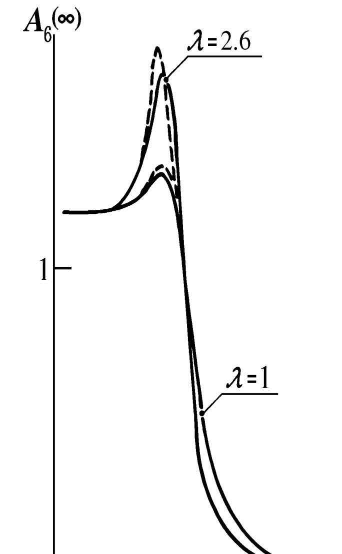

FIG. 3. The $A_6(\infty)$ calculated in accordance with the approximate (dashed curves) and exact (solid curves) formulas.

A comparison of $A_6(\infty)$ calculated using the Robert–Bonamy approximation with the results of exact calculations shows, that a relation similar to Eq. (16) can be a convenient approximation of integral (13).

In our studies we revealed that the equation

$$A_6^{LJ}(\infty) = a_6/\sqrt{1 + \lambda(\beta - \beta_0)^6[5(\beta - \beta_0)^6 - 2]} \qquad (17)$$

with $\beta_0 = 0.042$ gives an approximation accurate to several percent for λ varying from 0.2 to 10. Similar approximations can also be obtained for other values of n. The dependences of $A_6(\infty)$ on β obtained using approximate formula (17) and exact relation (13) are shown in Fig. 3. It should be noted that good agreement (within 1 % accuracy) occurs between the values Φ_6 calculated by the exact and approximate (Eq. (17)) formulas what allows one to use quite a simple approximation to calculate the shift coefficients of the absorption spectral lines.

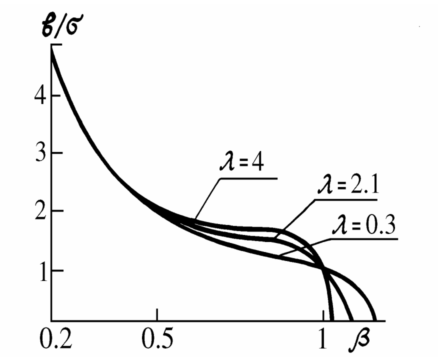

FIG. 4. The dependence of $\beta = \sigma/r_c$ *on the parameter* b/σ.

The dependence of the impact parameter b on β (and, hence, on r_c) is shown in Fig. 4. From Figs. 2–4 it follows that small values of β correspond to large distances (($b \gg \sigma$) when $r_c \simeq b$ (see Eq. (5)) between interacting molecules, each molecule flying along its own trajectory. In this case, as it could be expected, the corrections are small and the straight line trajectory approximation is applicable, $A_6^{LJ}(\infty) = 3\pi/8$ (the section A of the curve in Fig. 2).

Figure 3 shows that for the impact parameters approximately corresponding to the radius of attractive forces action ($\beta = 0.75$) r_c is smaller than b. In this case the trajectory is determined by the attractive potential and its bending leads to an increase of the interaction time and to the Φ_6 growth (interval B in Fig. 2). In this case the corrections depend on the ε to kinetic energy ratio. Thus for small energies the parameter λ takes large values and the values of $A_6(\infty)$ can increase several times. For collisions occurring at large initial velocities the parameter λ is small and the corrections are not large. Thus one can draw a conclusion, that at high temperatures, when the fraction of rapid molecules is large, the trajectory bending may be neglected. At the same time at low temperatures the effect of trajectory bending must be taken into account.

The values $\beta \gg 1$ correspond to molecular collisions occurring at short distances (the impact parameters ($b < \sigma$)). In this case the interaction time corresponds to the time of molecule travel to the turning point whose position is determined by the repulsive forces. Small values of r_c and the velocities of the relative motion of molecules exceeding the average one correspond to large values of β. In this case the time of the interaction between molecules decreases and contributions from such a type of collisions (i.e., when $b < \sigma$ and $\upsilon > \upsilon_{av}$) to the line shift are small and, as a consequence, Φ_6 vanishes.

5. ESTIMATIONS OF THE TRAJECTORY BENDING EFFECT ON THE LINE SHIFTS

The dependences of $\beta^5 A_6(\infty)$ on the impact parameter calculated using several models and the exact formula are shown in Fig. 5. For large impact parameters the calculations made using a simple model of a straight line trajectory give the results, which, as it could be anticipated, well agree with the results obtained using any other model. For the impact parameters near 1.8 σ the results of calculations by the exact formula differ from those obtained using the calculation of model trajectories. When $b \simeq \sigma$ the calculations performed using all the model trajectories give wrong results. As was pointed out above, the Herman–Tipping model underestimates velocity of the relative motion along the trajectory in the vicinity of the turning point, what, in turn, gives overestimation of the molecular interaction time. As a result, the values of Φ_6 for this model exceed the actual ones by several times. The results of calculations by the Robert–Bonamy model qualitatively agree with the results of calculations by exact formula but at small values of the impact parameter the difference reaches 20 %.

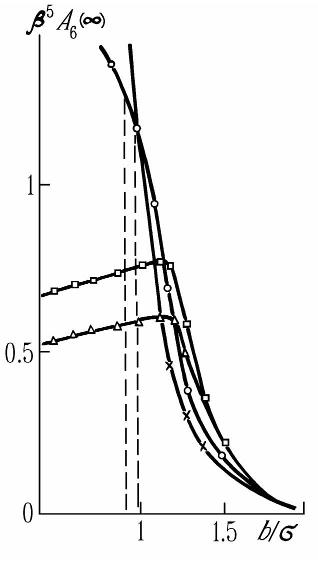

FIG. 5. The dependence of $\beta^5 A_6(\infty) \sim S_1(b)$ *on the impact parameter calculated using exact formula (13) (squares) and models: triangles is the Robert–Bonnamy model, circles is the Herman–Tipping model, crosses is the straight line trajectory model. Dashed lines show the values of* b_0 *for* $j_2 = 11$ *and* 13 *for the line* $7_{62} \to 6_{61}$ *of* H_2O *perpendicular band broadened by nitrogen pressure.*

Dashed curve in Fig. 5 corresponds to the values of cut off parameter b_0 for the line of the transition 7_{62}–6_{61} with $j = 11$ and 13 from the water vapor molecule perpendicular absorption band broadened by collisions with nitrogen molecules. The half–width of this line is formed by "weak collisions" and "the interruption does not succeed" to remove the effect of trajectory bending. In this case the calculations that use model trajectories can give large errors.

The values of $A_6(\infty)$ calculated for different pairs of molecules by formula (17) are given in Table II. As the initial parameters the average velocity of relative motion of molecules and impact parameter b_0 from Anderson theory determined in the exact resonance approximation (the resonance parameter k for virtual transitions in $S_2(b)$ is equal to zero) were used. The Φ_6 value in this case is presented as a correction to the line shift calculated by the ATCF technique. The values of multipole moments of water–vapor, methane, and other molecules, the Lennard–Jones potential parameters were taken from the literature, the calculations were carried out for room temperature.

TABLE II. Corrections to the line shifts for the trajectory bending.

Molecules	ε, K	s, A	b_0, A	λ	β	Correction (%)	
$H_2O–H_2O$	92.20	3.23	11.38	0.98	0.28	0	0
$–SO_2$	152.43	3.76	11.79	1.62	0.32	0	0
$–N_2$	93.61	3.46	4.70	0.99	0.80	+10	+12
$–CO_2$	132.01	3.86	6.70	1.40	0.57	+ 4	+ 3
$–O_2$	104.31	3.35	3.05	1.11	1.01	–42	–42
–He	30.70	2.89	2.05	0.33	1.10	–44	–45
–Ne	56.73	3.01	2.59	0.60	1.04	–40	–40
–Ar	105.10	3.32	3.44	1.11	0.99	–35	–34
–Kr	125.56	3.42	3.78	1.33	0.97	–32	–30
–Xe	142.75	3.67	4.16	1.51	0.95	–26	–23
CH_4–He	38.92	3.19	1.86	0.41	1.12	–52	–52
–Ne	72.00	3.30	2.35	0.77	1.06	–49	–50
–Ar	133.25	3.61	3.09	1.41	1.02	–49	–50
–Kr	159.19	3.71	3.37	1.69	1.01	–49	–50
–Xe	180.98	3.96	3.68	1.92	1.01	–51	–52

Note: in column 7 there is the correction equal to $(\Phi_6/\Phi_6^{str} - 1)\cdot 100$, where Φ_6 is the result obtained by formula (13), and Φ_6^{str} is the same quantity in the straight line trajectory approximation; in column 8 the quantity Φ_6 was calculated using Eq. (17).

The analysis of data presented in Table II shows that the effect of trajectory bending on the first–order term may be neglected in the case of "strong collisions" (for example, for $H_2O–H_2O$ and $H_2O–SO_2$ collisions). Actually, for the "strong" dipole–dipole interaction the collisions forming the line shift have the impact parameter $b > b_0$ and Anderson's cut off parameter b_0 is much greater than σ. The water vapor line shifts may vary within the limits 3–12 % for the collisions with nonpolar molecules which have large quadrupole moments (e.g., N_2 and CO_2). For the collisions with atoms of light inert gases (He, Ne, and Ar) or with molecules having small quadrupole moments (O_2), the corrections are found to be significant both in the case of methane and water vapor molecules. In these cases the parameter b_0 is determined by short–range forces (the polarization and repulsion potentials) and is smaller than σ. As a consequence, the line shifts decrease. For heavy atoms the basic interactions determining b_0 are the induction and dispersion interactions and, moreover, the interruption in this case takes place at the impact parameter values exceeding σ. This means that in this case the trajectory bending plays less essential role in the formation of line shifts.

The methane molecule has neither dipole nor quadrupole moments and therefore the interaction forming the half-width are weak, the parameter b_0 is small, and the trajectory bending becomes an important factor of formation of the line shifts and should be taken into account in calculations.

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