RESONANCE FUNCTIONS OF THE THEORY OF BROADENING AND SHIFT OF LINES FOR ACTUAL TRAJECTORIES

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Effect of trajectory bending in calculations of shifts of the rovibrational lines of molecules is studied. The exact solutions of classical dynamic equations are used for calculating the second— order term of interruption function. The universal function of two arguments have been obtained which is independent of the parameters of potential and initial conditions of collision allowing one to take actual trajectories into consideration.

Generally accepted approximation for calculating the integrals defining the resonance functions of the collisional theory of broadening and shift of spectral lines is the use of straight— line trajectories of relative motion of colliding particles.[1–5] This approximation makes it possible to simplify calculations of integrals over time[1] and is appropriate for "strong" collisions, when the long— range anisotropic portion of the intermolecular potential "interrupts" the process of absorption or emission at a relatively large value of the impact parameters.

On the other hand, there is a number of examples when this approach introduces large errors into calculations of the coefficients of spectral line broadening. In Refs. 6— 8 the methods have been proposed to account for the trajectory bending within the framework of semiclassical collisional theory. These methods are based on the model representations of the trajectory and, in the approximation of effective straight— line trajectory, they result in the same resonance functions, but after certain redefinition of the parameters. Thus obtained corrections to the broadening coefficients turn out to be too large for weakly broadened lines.[9] For this reason more detailed study is needed concerning the effect of the collisional bending of a trajectory for calculating the collisional parameters of the line shape.

Bykov et al.[10] studied the effect of the trajectory bending on calculation of the first— order summand of the interruption function determining shift of a rovibrational line in the shortwave region. The method is based on exact solutions of classical equations of motion, which, as is well known, can be easily obtained for an isotropic potential. In this paper the method is used for calculating the resonance functions of the electrostatic portion of the potential which determines the second— order terms of an interruption function.

As is shown in Ref. 5, the resonance function $f_{l_1 l_2}$ can be represented in the form of a sum of products of Fourier images of the intermolecular potential

$$f_{l_1,l_2} \simeq \frac{1}{2(2l_1+1)(2l_2+1)} \times \sum_m F_{l_1,l_2}(\omega_{ii'}+\omega_{jj'}) F^*_{l_1,l_2}(\omega_{ii'}+\omega_{jj'}), (1)$$

where

$$F_{l_1,l_2}(\omega) = (-1)^{l_2} \sqrt{\frac{(2L)!}{(2l_1)!(2l_2)!}} \times \int_{-\infty}^{\infty} dt\, e^{i\omega t} \frac{C_{Lm}(\theta(t)\,\varphi(t))}{r(t)^{L+1}},$$

$$L = l_1 + l_2 , \quad - L \le m \le L , \tag{2}$$

$$C_{Lm}(\theta, \varphi) = \sqrt{(L - m)/(L + m)}\; e^{im\varphi(t)} P_L^m (\cos \theta(t)) .$$

Formula (1) defines the resonance function $f_{l_1 l_2}$ for an individual summand in the multipole series expansion of the intermolecular potential; l_1, l_2 denote multipole character of the interaction; $P_L^m(\cos\theta)$ are the associated Legendre polynomials; $\omega_{ii'}$ and $\omega_{jj'}$ are the frequencies of virtual transitions in the absorbing and broadening molecules, respectively; $r(t)$ is the distance between the molecules at the moment t, $\varphi(t)$ and $\theta(t)$ are the azimuthal and polar angles. Relation (1) gives the resonance function the accuracy within to a constant factor.

For calculating the integral over time in Eq. (2) let us specify the coordinate system as follows: (1) let the origin of coordinates be at the center of mass of colliding particles and (2) since some effective isotropic intermolecular potential will be used below for determining $r(t)$, and as a consequence the trajectory will lie entirely in the same plane, let us choose the plane XY to be the plane where collisions occur, i.e., $z(t) = 0$, $\theta(t) = \pi/2$. Then

$$f_{l_1,l_2} \simeq \frac{(2L)!}{(2l_1+1)!\,(2l_2+1)!\,\sqrt{\pi}} \sum_{\substack{m \\ (L+m=2p)}} \frac{2m\,(L - m)!\,((L + m)/2)!}{(L + m)\,((L - m)/2)!} \times$$

$$\times \left[\left(\int_{-\infty}^{\infty} dt\, \frac{\cos[\omega t + m\varphi(t)]}{r(t)^{L+1}}\right)^2 + \left(\int_{-\infty}^{\infty} dt\, \frac{\sin[\omega t + m\varphi(t)]}{r(t)^{L+1}}\right)^2\right]. \tag{3}$$

The equation of motion for isotropic potential $U(r)$ can be solved in the general form[11]

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

$$\varphi(t) = \int_{r_c}^{r} \frac{M/\mu\, r'^2}{\sqrt{2[E - U(r')]/\mu - M^2/\mu^2 r'^2}}\, dr' + c_2, \tag{4}$$

where r_c is the distance of the closest approaching, $E = \mu v^2/2$ is the kinetic energy of relative motion; v is the initial velocity, μ is the reduced mass; b is the impact parameter; $M = \mu b v$ is the angular momentum of the relative motion. Here the assumption is admitted that the moment and energy of relative motion are conserved.

Like in Ref. 10, we shall use solutions of equations of motion (4) for transforming the integrals in Eq. (3). The values of constants c_1 and c_2 can be chosen so that the colliding particles approach most closely at the moment $t = 0$ and for $t = -\infty$ the coordinate y is equal to $-\infty$ (the collision occurs "along the y axis"). In this case $c_1 = 0$, while the value of c_2 is nonessential for calculating the resonance functions. Let us introduce into Eqs. (3) and (4) the dimensionless variable $y = r/r_c$ and by substituting variables into the integrands we can represent Eq. (4) in the form

$$f_{l_1,l_2}(k_c) = \frac{2(2L)!\, B}{\sqrt{\pi}\,(2l_1 + 1)!\,(2l_2 + 1)!} \times$$

$$\times \sum_{\substack{m \\ (L+m=2p)}} \frac{2^m(L - m)!\,((L + m)/2)!}{(L + m)!\,((L - m)/2)!} \times$$

$$\times \left[\left(\int\limits_1^\infty dy\, \frac{\cos\,[A_0(y)k_c + m\sqrt{1 - V(r_c)}\,A_2(y)]}{y^L\sqrt{y^2 - 1 + V(r_c) - y^2 V(yr_c)}}\right)^2 + \right.$$

$$\left. + \left(\int\limits_1^\infty dy\, \frac{\sin\,[A_0(y)k_c + m\sqrt{1 - V(r_c)}\,A_2(y)]}{y^L\sqrt{y^2 - 1 + V(r_c) - y^2 V(y\,r_c)}}\right)^2\right], \qquad (5)$$

where

$$A_n(y) = \int\limits_1^y \frac{dz}{z^{n-1}\sqrt{z^2 - 1 + V(r_c) - z^2 V(zr_c)}} \qquad (6)$$

are the functions introduced in Ref. 10 and

$$k_c = 2\pi c r_c \omega/v\,; \qquad (7)$$

$$V(r) = 2U(r)/\mu v^2\,. \qquad (8)$$

In derivation of Eq. (5) the factor $1/v^2 \hbar^2 r_c^{2l_1 + 2l_2}$ entering into the definition of the interrupting function[1] was omitted. The constant b must be chosen so that the value of resonance function at $k_c = 0$ in the approximation of the straight— line trajectories would be equal to unity. The parameter k_c, which is the analog of the Massey parameter, is determined in the same way as for the ordinary resonance functions except when b is replaced by r_c. In deriving Eq. (5) the well— known relation

$$b/r_c = \sqrt{1 - V(r_c)}\,, \qquad (9)$$

was used which defines the turning point of the trajectory. Note that the result is independent of the integration constant.

We can say that the resonance functions for electrostatic portion of the intermolecular potential given by formulas (5) and (6) account for actual trajectories, since

they were deduced with any simplifying assumptions on the trajectory and they contain the intermolecular potential in its general form. Equation (5) enables one to calculate the resonance functions for any $U(r)$, even for a numerically set, for example, for that calculated with the help of the quantum— chemical method. Like ordinary functions,[1] these depend on the balance of energy at the moment of collision and vanish as $k \to \infty$ (see Eqs. (5) and (6)).

Resonance functions calculated in the approximation of the straight— line trajectories[1] or in the approximation of "the effective rectilinear trajectories"[6–8] are universal functions in the sense that they are explicitly independent of the parameters of trajectory and such quantities as the initial velocity v, impact parameter b, or parameter r_c and determine the adiabatic parameter k, i.e., the argument of function, but not the function itself. Therefore, once being calculated and then tabulated, this function can be used in any other cases. At the same time formulas (5) and (6) defining the function itself contain r_c and intermolecular potential, and, as a result, the resonance functions become dependent on the parameters of potential and the initial conditions of collision. However, for the case of model potentials (for example, the Lennard— Jones potential) the "associated parameters of interaction"[10] can be introduced, that again makes functions (5) and (6) be "universal". In Ref. 7 it was found that for a model with parabolic trajectories the resonance functions depend on the ratio $v_c^2/v_c'^2$, where v_c is the velocity at the moment of maximum approach and v_c' is the effective velocity.[7]

Use of different approximations for calculations of integrals in Eqs. (5) and (6) enables one to obtain different approximate relations for the resonance functions.

The approximation of the straight— line trajectories is appropriate when $U(r) = 0$. In this case

$$A_n(y) = \sqrt{y^2 - 1}\,,\; A_2(y) = \arctan\sqrt{y^2 - 1}\,, \qquad (10)$$

and after the substitution of variables $x = y^2 - 1$ one obtains ordinary equations for the resonance functions[1,5]

$$f_{l_1,l_2} = \frac{2(2L)!\, B}{\sqrt{\pi}\,(2l_1 + 1)!\,(2l_2 + 1)!} \times$$

$$\times \sum_{\substack{m \\ (L+m=2p)}} \frac{2^m(L - m)!\,((L + m)/2)!}{(L + m)!\,((L - m)/2)!} \times$$

$$\times \left[\left(\int\limits_0^\infty dx\, \frac{\cos\,[k_c x + m \arctan x]}{(x^2 + 1)^{L+1/2}}\right)^2 + \right.$$

$$\left. + \left(\int\limits_0^\infty dx\, \frac{\sin\,[k_c x + m \arctan x]}{(x^2 + 1)^{L+1/2}}\right)^2\right]. \qquad (11)$$

Next approximation that can be derived from Eqs. (5) and (6), is the approximation of "the effective rectilinear trajectories".[7] To do this we expand $U(yr_c)$ from Eqs. (5) and (6) in a series over $(1 - y^2)$ powers around the point $y = 1$ and keep only the first term. It can be seen that we again obtain Eq. (8), in which the impact parameter b is replaced by r_c and the velocity v is replaced by $v_c' = v\sqrt{1 - V(r_c) - r_c V'(r_c)/2}$.

In concrete calculations the Lennard–Jones potential is normally used.

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

For this potential the quantities $A_0(y)$ and $A_2(y)$ take the form

$$A_0(y) = \int\limits_1^y \frac{z\,\mathrm{d}z}{\sqrt{z^2 - 1 + \lambda[\beta^{12}(1 - z^{-10}) - \beta^6(1 - z^{-4})]}}, \quad (12)$$

$$A_2(y) = \int\limits_1^y \frac{\mathrm{d}z}{z\sqrt{z^2 - 1 + \lambda[\beta^{12}(1 - z^{-10}) - \beta^6(1 - z^{-4})]}}, \quad (13)$$

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

The representation analogous to that in Eqs. (12) and (13) can be obtained for radicands from formula (5). In this case the resonance functions depend on three variables, that is, the adiabatic parameter k and "the reduced parameters of interaction" λ and β. It is obvious that the resonance functions, having been once calculated for different k, λ, and β and tabulated, can be used for any other molecule and different ε, σ, b, and v. Therefore resonance functions (5) like the functions obtained earlier in the approximation of the straight–line trajectories, can also be regarded as universal.

It can be seen from formulas (5)–(13) that the region of $f_{l_1 l_2}$ definition as functions of λ and β is connected with the classically permissible region of motion. As in Ref. 10 it can be shown here that the requirement of nonnegativity of radicands in Eqs. (5)–(13) is supplemented by the inequality $y \geq 1$ (or $z \geq 1$ for Eqs. (12) and (13)) that corresponds to the infinite trajectories. In so doing, as in

Ref. 10, it is assumed that the finite trajectories, corresponding to the bound or metastable states do not contribute to the shifts and broadening of spectral lines.

Thus, an account of the trajectory bendings does not alter the basic relations of the collision theory (within the framework of the admitted assumptions) but requires redefining of the resonance functions. In this connection, exact solutions of the equation of motion can be used without any model representation of the trajectory. New resonance functions exhibit "universality" because they depend on the "reduced parameters of interaction", i.e., λ and β.

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