INFLUENCE OF TURNING POINTS ON THE SHAPE OF PRESSURE BROADENED SPECTRAL LINES*,**

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The region of interatomic distances near the classical turning point is included into the unified Franck-Condon (UFC) treatment of pressure broadening of spectral lines to determine the profile of blue wings. Assuming the radial wave functions in the form of Airy functions a UFC line shape formula is transformed to a form in which both the classically accessible and inaccessible regions are taken into account. In the asymptotic (classical) case this formula yields a quasistatic profile with Boltzmann factor included.

1. Introduction

Since in 1931 Jabłoński [1] recognized the analogy between the pressure broadening of spectral lines and the production of molecular spectra there have been many attempts to describe the line shape in terms of free-free Franck-Condon factors [2–13]. Jabłoński [2, 3] himself and others [6–12] have indicated that in the analysis of line wings the JWKB wave functions may be very useful. The JWKB approximation was also applied in the "unified Franck-Condon" (UFC) treatment developed recently [11, 12] which permits calculations of the intensity distribution in the entire frequency range of the broadened line. The characteristic feature of the UFC treatment is that its line shape function can be expressed by means of Condon points (or stationary phase points) so that each frequncy within the pressure broadened line profile can be associated with corresponding interatomic separations. The JWKB–UFC intensity distribution was shown to be given by a certain universal line shape function (Eq. (5.28) of Ref. [11]), which appeared to be very important in the analysis of profiles of satellite bands.

The JWKB approximation fails, however, when Condon points are near the classical turning points. It is the purpose of this paper to evaluate the UFC line shape formula using

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the wave functions valid in the vicinity of classical turning points. The region of interatomic distances near the classical turning points has recently been taken into account by Bieniek [13] in his calculations of far wing profiles. Using, what he called the uniform JWKB approximation, he derived an analytic expression for the Franck-Condon overlap integral. He did not bother, however, with the analytic angular momentum decomposition. The present paper intends to include the transition occuring in the vicinity of classical turning points to the UFC theory. These transitions are very essential first of all for blue wings of spectral lines, where they can give rise to the appearance of line profiles differing markedly from those resulting from traditional line wings theories. As it will be shown below the method presented here enables us to estimate the influence of such transitions on the line shape. First of all, it makes it possible to determine deviations of the real shape of line wings from the quasistatic profile.

2. The UFC profile for the Airy wave functions

In the UFC treatment the intensity distribution $I(x)$ in the broadened line is found to be of the form (cf. Eq. (2.48) of Ref. [11])

$$I(x) = \frac{1}{\pi} \frac{Nx^2 j(x)}{x^2 + \left(\frac{\gamma}{2}\right)^2}, \tag{1}$$

where $x = \omega - \omega_0 - \Delta$ is the frequency displacement from the impact-shifted line centre, N is the density number of perturbers. Here γ and Δ are the half-width and shift of the impact theory. The function $j(x)$ is given by

$$j(x) = \left\langle \frac{\pi\hbar R^2}{\mathscr{E}_i k_f} \sum_{l=0}^{\infty} (2l+1) \, |A_l(x)|^2 \right\rangle, \tag{2}$$

where the summation is over the quantum numbers l of the angular momentum of the relative motion and the symbol $\langle \ldots \rangle$ indicates the average over initial wave vector k_i of the perturber $\left(\text{or the initial energies } \varepsilon_i = \frac{\hbar^2 k_i^2}{2\mu}, \text{ where } \mu \text{ is the reduced mass of the radiating and perturbing atoms}\right)$.

In Eq. (2) k_f is the wave vector of the perturber for the final level of the radiator and R denotes the radius of a macroscopic container surrounding the radiator such that $4\pi R^3/3$ is the total volume of a gas. $A_l(x)$ is the overlap integral:

$$A_l(x) = \int_0^{\infty} \psi_l^{(i)}(r) \psi_l^{(f)*} dr, \tag{3}$$

where $\psi_l^{(i)}(r)$ and $\psi_l^{(f)}(r)$ are the radial wave functions of the perturbing atom moving in the field of the radiating atom for its initial and final state, respectively. Both wave func-

tions are assumed here to be normalized to unity with the boundary condition: $\psi_l^{(i)}(R) = \psi_l^{(f)}(R) = 0$.

In the previous paper [11] the overlap integrals (3) were evaluated using the JWKB wave functions, so that the effects due to transitions in the neighbourhood of classical turning points could not be included. In order to take into account such effects we assume now the radial wave functions in the form [14, 15]:

$$\psi_l^{(i)}(r) = B_l^{(i)} \, \mathrm{Ai}\,(-\eta_l^{(i)}(r)), \tag{4}$$

where $\mathrm{Ai}\,(-\eta)$ is the Airy function and

$$\eta_l^{(i)}(r) = \{\tfrac{3}{2} \int_{r_t^{(i)}}^{r} k_l^{(i)}(r)dr\}^{2/3} \tag{5}$$

with

$$k_l^{(i)}(r) = \frac{1}{\hbar}\left[2\mu(\mathscr{E}_i - V_i(r)) - \frac{\hbar^2 l(l+1)}{r^2}\right]^{1/2}, \tag{6}$$

where $V_i(r)$ is the interaction potential for the initial level of the radiating atom and $r_t^{(i)}$ is the classical turning point for the initial state such that $k_l^{(i)}(r_t^{(i)}) = 0$. In Eq. (4)

$$B_l^{(i)} = \left[\frac{2\pi k_i}{R a_l^{(i)}}\right]^{1/2}, \quad a_l^{(i)} = \left[\frac{2\mu F_l^{(i)}}{\hbar^2}\right]^{1/3}, \tag{7}$$

$$F_l^{(i)} = -\left[\frac{d}{dr} U_l^{(i)}(r)\right]_{r=r_t^{(i)}}, \tag{8}$$

where

$$U_l^{(i)}(r) = V_i(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \tag{9}$$

is the effective interaction potential for the initial level of the radiating atom. The final level wave functions are given by identical expressions with the replacement of index "i" by "f".

Eq. (4) represents the exact solution of the Schrödinger equation in the vicinity of classical turning points, where $\eta_l^{(i)}(r)$ can be approximated by

$$\eta_l^{(i)}(r) = a_l^{(i)}(r - r_t^{(i)}). \tag{10}$$

This approximation strictly holds for distances at which $U_l(r)$ can be expressed as a linear function of r. The normalizing factor $B_l^{(i)}$ is so chosen that for interatomic distances situated far from the classical turning point Eq. (4) becomes identical with the usual JWKB wave functions:

$$\psi_l^{(i)}(r) \approx \left[\frac{2k_i}{R k_l^{(i)}(r)}\right]^{1/2} \cos\left(\int_{r_t^{(i)}}^{r} k_l^{(i)}(r)dr - \frac{\pi}{4}\right). \tag{11}$$

This follows directly from Eq. (4) if one applies the asymptotic form of the Airy function for large values of the argument $\eta_l(r)$:

$$\mathrm{Ai}\,(-\eta_l(r)) \approx \frac{[\eta_l(r)]^{-1/4}}{\sqrt{\pi}} \sin\left[\tfrac{2}{3}\eta_l^{3/2} + \frac{\pi}{4}\right]. \tag{12}$$

By substituting Eq. (4) into Eq. (2) and representing the Airy function in its integral form the overlap integral may be evaluated analytically (cf. Appendix of Ref. [13]):

$$A_l(x) = \frac{2\pi\hbar^{4/3}\sqrt{k_i k_f}}{R(2\mu)^{2/3}} \frac{\mathrm{Ai}\,(-\xi_l)}{[F_l^{(i)}F_l^{(f)}]^{1/6}\,[F_l^{(i)}-F_l^{(f)}]^{1/3}}, \tag{13}$$

where

$$\xi_l = \left[\frac{2\mu F_l^{(i)}F_l^{(f)}}{\hbar^2(F_l^{(i)}-F_l^{(f)})}\right]^{1/3} (r_t^{(i)}-r_t^{(f)}). \tag{14}$$

Here we have also made use of Eq. (10).

Eq. (13) may be reduced to a simpler form if we take into account the Condon points [11] defined as such interatomic separations at which radial momenta in the initial and final state are equal, i. e.

$$k_l^{(i)}(r_c) = k_l^{(f)}(r_c) \equiv k_l(r_c). \tag{15}$$

Because in the vicinity of classical turning points we have

$$k_l^{(i)}(r) = \left[\frac{2\mu}{\hbar^2} F_l^{(i)}(r-r_t^{(i)})\right]^{1/2} \tag{16}$$

and similarly for $k_l^{(f)}(r)$ we obtain from Eq. (15)

$$r_t^{(i)}-r_t^{(f)} = \frac{F_l^{(i)}-F_l^{(f)}}{F_l^{(f)}} (r_c-r_t^{(i)}). \tag{17}$$

Since, according to Eq. (15),

$$r_c-r_t^{(i)} = \frac{\hbar^2}{2\mu}\frac{k_l^2(r_c)}{F_l^{(i)}} \tag{18}$$

Eq. (14) becomes

$$\xi_l = \left[\frac{k_l(r_c)}{q_l}\right]^2, \tag{19}$$

where

$$q_l = \left[\frac{2\mu}{\hbar^2}\frac{F_l^{(i)}F_l^{(f)}}{F_l^{(i)}-F_l^{(f)}}\right]^{1/3}. \tag{20}$$

To find the line shape function in Eq. (2) we replace the sum over angular momenta l by an integral and assume the Maxwellian distribution of initial energies. Then we get from Eq. (2) and (13)

$$j(x) = b \int_0^\infty d\mathscr{E}_i e^{-\frac{\mathscr{E}_i}{kT}} \int_0^\infty \frac{(2l+1)q_l^2}{F_l^{(i)}F_l^{(f)}} |\mathrm{Ai}\,(-\xi_l)|^2 dl, \tag{21}$$

where

$$b = \frac{8\pi^{5/2}\hbar^4}{(2\mu kT)^{3/2}}. \tag{22}$$

Eq. (21) may be further simplified if we assume that the Condon point r_c is close enough to the classical turning points $r_t^{(i)}$ and $r_t^{(f)}$ so that $F_l^{(i)}$ and $F_l^{(f)}$ can be approximated by the derivatives of effective potentials at r_c:

$$F_l^{(i)} \approx -\left(\frac{dU_l^{(i)}}{dr}\right)_{r=r_c}, \quad F_l^{(f)} \approx -\left(\frac{dU_l^{(f)}}{dr}\right)_{r=r_c}. \tag{23}$$

Under these assumptions $F_l^{(i)}$ and $F_l^{(f)}$ may be treated as independent of the initial energy, so that Eq. (21) may be transformed to the following form

$$j(x) = b \int_0^\infty dl(2l+1) \frac{q_l^2}{F_l^{(i)} - F_l^{(f)}} \int_0^\infty d\mathscr{E}_i e^{-\frac{\mathscr{E}_i}{kT}} |\mathrm{Ai}\,(-\xi_l)|^2. \tag{24}$$

Introducing a new integration variable

$$\tau = \frac{2\mu}{\hbar^2 q_l^2}(\mathscr{E}_i - U_l^{(i)}(r)) \tag{25}$$

we get from Eq. (24)

$$j(x) = \frac{\hbar^2 b}{2\mu} \exp\left[-\frac{V_i(r_c)}{kT}\right] \int_0^\infty dl(2l+1) \frac{q_l^4 M(l)}{F_l^{(i)}F_l^{(f)}} \exp\left[-\frac{\hbar^2 l(l+1)}{2\mu r_c^2 kT}\right], \tag{26}$$

where

$$M(l) = \int_{T_l}^\infty d\tau \exp(-\alpha_l \tau) |\mathrm{Ai}\,(-\tau)|^2 \tag{27}$$

with

$$\alpha_l = \frac{\hbar^2 q_l^2}{2\mu kT}, \tag{28}$$

$$T_l = -\frac{2\mu U_l^{(i)}(r_c)}{\hbar^2 q_l^2}. \tag{29}$$

Let us note that according to Eq. (20)

$$F_l^{(i)} - F_l^{(f)} = -\left(\frac{d\Delta V(r)}{dr}\right)_{r=r_c} \equiv -\Delta V'(r_c), \tag{30}$$

where $\Delta V(r) = V_i(r) - V_f(r)$ is the potential difference. Using Eq. (20) and (23) we have

$$\alpha_l = \vartheta[F_l^{(f)}(F_l^{(f)} - \Delta V'(r_c))]^{2/3}, \tag{31}$$

where

$$\vartheta = \left(\frac{\hbar^2}{2\mu|\Delta V'(r_c)|^2}\right)^{1/3} \frac{1}{kT}. \tag{32}$$

Introducing a new variable

$$u \equiv \frac{F_l^{(f)}}{F_0^{(f)}} = 1 + \frac{\hbar^2 l(l+1)}{\mu r_c^3 F_0^{(f)}}, \tag{33}$$

where $F_0^{(f)} = -\left(\frac{dV_f}{dr}\right)_{r=r_c} = -V_f'(r_c)$ the integration over l may be replaced by the integration over u so that Eq. (26) becomes

$$j(x) = \frac{4\pi^{5/2}\hbar^{4/3} r_c^3}{(2\mu)^{1/6}(kT)^{3/2}} \frac{\exp\left[-\frac{V_i(r_c)}{kT} - \frac{r_c V_f'(r_c)}{2kT}\right]}{|\Delta V'(r_c)|^{4/3}} |V_f'(r_c)|^{5/3} S(x), \tag{34}$$

where

$$S(x) = \int_1^\infty du[u(u+f(r_c))]^{1/3} M(u) \exp(-g(r_c)u) \tag{35}$$

with

$$f(r_c) = \frac{\Delta V'(r_c)}{V_f'(r_c)}, \tag{36}$$

$$g(r_c) = -\frac{r_c V_f'(r_c)}{2kT}, \tag{37}$$

and

$$M(u) = \int_{T_u}^\infty d\tau \exp[-\alpha(u)\tau] \,|\, \mathrm{Ai}(-\tau)|^2, \tag{38}$$

where

$$\alpha(u) = \frac{1}{kT}\left(\frac{\hbar^2 |V_f'(r_c)|^4}{2\mu|\Delta V'(r_c)|^2}\right)^{1/3} [u(u+f(r_c))]^{2/3}. \tag{39}$$

The relation between T_u and the variable u may be found using Eqs. (29) and (33).

3. *Quasi-static limit*

Let us consider now the case when the initial potential curve is strongly repulsive. This may correspond, for instance, to the blue wing of a spectral line arising due to transitions between repulsive branches of potential curves. In such a case the Condon points r_c are situated very close to calssical turning points.

For transitions between repulsive branches of potential curves the lower limit of integration T_u in Eq. (38) is negative ($T_u < 0$) so that $M(u)$ may be written as the sum

$$M(u) = M_>(u) + M_<(u), \tag{40}$$

where

$$M_>(u) = \int_0^\infty d\tau \exp\left[-\alpha(u)\tau\right] \mid \mathrm{Ai}\,(-\tau)|^2, \tag{41}$$

and

$$M_<(u) = \int_0^{|T_u|} d\tau \exp\left[\alpha(u)\tau\right] \mid \mathrm{Ai}\,(\tau)|^2. \tag{42}$$

The integral $M_<(u)$ takes into account effects originated in the classically inaccessible region ($r < r_t$). Since for large positive τ the function $\mathrm{Ai}(\tau)$ decreases exponentially, the contribution to the integral (40) coming from the function $M_<(u)$ is much smaller than that given by the function $M_>(u)$. Hence in the first approximation we can take $M(u) \approx M_>(u)$.

The next simplification may be achieved if we apply the asymptotic form of the Airy function $\mathrm{Ai}(-\tau)$ for large positive τ (cf. Eq. (12)). In such a case one obtains from Eq. (41)

$$M(u) \approx \frac{1}{\pi} \int_0^\infty d\tau \frac{e^{-\alpha(u)\tau}}{\sqrt{\tau}} \sin^2\left(\tfrac{2}{3}\tau^{3/2} + \frac{\pi}{4}\right). \tag{43}$$

By replacing $\sin^2\left(\frac{2}{3}\tau^{3/2} + \frac{\pi}{4}\right)$ by its average value 1/2 we get the asymptotic form of the $M(u)$ function:

$$M(u) \approx \frac{1}{2\sqrt{\pi\alpha(u)}}. \tag{44}$$

After substitution of this formula into Eq. (35) one obtains

$$S(x) \approx \tfrac{1}{2}\sqrt{\frac{kT}{\pi}}\left(\frac{2\mu|\Delta V'(r_c)|}{\hbar^2 V_f'(r_c)}\right)^{1/6} \frac{\exp\left(-g(r_c)\right)}{g(r_c)}. \tag{45}$$

With this $S(x)$ Eq. (34) yields

$$j(x) \approx 4\pi\hbar r_c^2 \frac{\exp\left[-\dfrac{V_i(r_c)}{kT}\right]}{|\Delta V'(r_c)|}. \tag{46}$$

This is the usual one-perturber quasistatic distribution [11].

Let us emphasize that for the blue wing, arising due to transitions between repulsion parts of interaction potentials, the Boltzmann factor usually plays a very essential role. Sometimes it can give rise to the exponential decrease of the intensity distribution in the blue wing as observed in some molecular bands (cf. e. g. the high frequency wing of the 4.3 μ band of CO_2 [16]). The inaccuracy involved by the quasistatic approximation in the line shape analysis of blue wings can be estimated by investigating the deviations of the total function $M(u)$ (or even $M_{>}(u)$ only) from its asymptotic "quasistatic" form given by Eq. (44).

4. Summary

Assuming the wave functions in the vicinity of classical turning points in the form of the exact solution of Schrödinger equation for the linear potential the UFC shape of line wings has been derived. It was shown that in the asymptotic case (when only classically accessible region is included) this formula yields the well-known quasistatic intensity distribution. This quasistatic distribution contains the Boltzmann factor, which for transitions between repulsive parts of potential curves (blue wings) may lead to the line shape of an exponential type.

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