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Erratum: On improved WKB (uniform asymptotic) quantum conditions, Dunham corrections, the Langer modification, and RKR potentials

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$$\langle i \rangle = S/R + (R-1)^2/4R \quad (7)$$

Notice that $\langle f \rangle - S = \langle i \rangle - S/R$, so that $\langle f \rangle$ in absorption cannot be found from replacement by $R\langle i \rangle$ for emission. For the linear interaction ($R=1$), $\langle i \rangle = \langle f \rangle = S$, a well known result. For the quadratic interaction ($S=0$), $\langle i \rangle = \langle f \rangle = (R-1)^2/4R$. The expressions for $\langle i \rangle$ and $\langle f \rangle$, [Eqs. (4) and (7)] are in agreement with those expected from moment analysis,⁵ namely that

$$M_{\alpha 1} = E_{sp} + \langle f \rangle R \hbar \omega \quad (8a)$$

$$M_{\alpha 1} = E_{sp} - \langle i \rangle \hbar \omega, \quad (8b)$$

where E_{sp} is the zero-phonon energy (the energy of the $i=0 \rightarrow f=0$ transition): $E_{sp} = E_0 + (1/2)[R(1-2S)-1]\hbar\omega$, and the M s are the first moments of the band shapes. The Stokes shift (Δ), the difference between the absorption and emission band centroids, is

$$\Delta = (R^2 + 1)S\hbar\omega R^{-1} + (1/4)(R+1)(R^2-1)\hbar\omega R^{-1} \quad (9)$$

If one defines $S_e = S_\alpha/R$ as the "Huang-Rhys factor" appropriate to emission and S_α (equal to S , as used above) as the "Huang-Rhys factor" appropriate to absorption, then Eqs. (4) and (7) assume the symmetrical form

$$\langle f \rangle = S_\alpha + (R-1)^2/4R$$

$$\langle i \rangle = S_e + (R-1)^2/4R$$

Equation (3) for $\langle f \rangle$ could, in principle, be calculated as a function of temperature by using the finite temperature forms of $\langle \chi_{\alpha i} | \chi_{\beta f} \rangle$ and $B_{\alpha i}$ and noting that the denominator reduces to $C_{\alpha\beta} |\langle \phi_\alpha | R | \phi_\beta \rangle|^2$.

¹M. D. Sturge, Phys. Rev. B 8, 6 (1973).

²M. Lax, J. Chem. Phys. 20, 1752 (1952).

³C. S. Kelley, Phys. Rev. B 6, 4112 (1972).

⁴E. Hutchisson, Phys. Rev. 36, 410 (1930).

⁵J. J. Markham, Rev. Mod. Phys. 31, 956 (1959).

ERRATA

Erratum: On improved WKB (uniform asymptotic) quantum conditions, Dunham corrections, the Langer modification, and RKR potentials [J. Chem. Phys. 57, 4612 (1972)]

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In Eqs. (28) and (29) p should be changed to t .

In the last line of Table I [that for $\text{LiH}(A^1\Sigma^+)$] α_e was miscopied from the reference and should be changed to -0.078305 . This decreases Y_{00} and δ on this line to 7.5033 and 0.03201, respectively. The rest of the paper and the conclusions are unchanged.

Also, an erratum by Tietz¹ brings his solution of the Schrödinger equation for his potential into agreement with mine.

I thank John O. Eaves and Kenneth D. Jordan for calling these things to my attention.

¹T. Tietz, J. Chem. Phys. 43, 1086 (1965).