

ELECTRONIC SPECTRAL LINESHAPE  
OF A DIATOMIC MOLECULE

Reza Islampour and Ali Maghari

Department of Chemistry  
University of Teacher Education

Tehran-Iran

(Received 13th June, 1988)

ABSTRACT

The electronic absorption spectral lineshape of a diatomic molecule with harmonic potential curves is calculated using the time correlation function formalism. Both the equilibrium shift and the frequency shift of the two linking electronic states are taken into account. The spectrum is also calculated using the cumulant expansion which is related to the correlation function of the time-dependent energy gap between the two electronic states.

INTRODUCTION

In general, the vibrational structure of an electronic spectrum is determined by two quantities: the dependence of the electronic transition moment upon the nuclear coordinates and the change in molecular dimensions upon electronic excitation. Given the change in the molecular dimensions, and the force fields for the two linking electronic states, the Franck-Condon principle

(1,3) allows the intensity distribution to be calculated.

Within the Born-Oppenheimer approximation(2), the vibronic matrix-element (which determines the intensity of an optical transition) is given by

$$\langle av'' | \hat{M} | bv' \rangle = \int \chi_{v''}^*(q'') \left[ \int \phi_a^*(\underline{r}, q'') \hat{M}(\underline{r}) \phi_b(\underline{r}, q') d^3 \underline{r} \right] \chi_{v'}(q') dq'' \quad 1$$

where  $\underline{r}$  and  $q$  denote the electronic and vibrational variables, respectively, and  $\hat{M}(\underline{r})$  is the electric dipole operator. We adopt the common spectroscopic notation, whereby we label lower state quantities by a double prime and the upper state quantities by a single prime. It is customary to assume that the electronic transition moment

$$\mu_{ab}(q) = \int \phi_a^*(\underline{r}, q'') \hat{M}(\underline{r}) \phi_b(\underline{r}, q') d^3 \underline{r} \quad 2$$

is a slowly varying function of nuclear displacement and to expand the transition moment about the equilibrium configuration of one of the two electronic states as power series in the displacement coordinate  $q'$  or  $q''$

$$\begin{aligned} \mu_{ab}(q) &= \mu_{ab}(0) + (d\mu_{ab}/dq'')_0 q'' + \dots \\ &= \mu_{ab}(0) + (d\mu_{ab}/dq')_0 q' + \dots \quad 3 \end{aligned}$$

According to the Condon approximation(3), we retain only the first (constant) term in these expansions:  $\mu_{ab}(q) \approx \mu_{ab}(0)$ . (more accurately, the function  $\mu_{ab}(q)$  is replaced by some constant  $\mu_{ab}(\bar{R})$ , where  $\bar{R}$  is some sort of average internuclear distance for one transition. The appropriate value of  $\bar{R}$  is called the R-centroid for the

transition(4). The vibronic matrix element is then given by

$$U_{ab}(0) \langle v'' | v' \rangle$$

It is the purpose of this article to formulate the absorption spectral lineshape of a diatomic molecule within the Condon approximation.

### General formulation

In this section we shall attempt to relate the transition probability obtained by calculation to the molecular absorption coefficient, the quantity obtained by experiment.

Consider a sample of length  $l$ , of unit cross section, and containing  $N_i$  molecules per unit volume in the state  $|i\rangle$ . In a layer of thickness  $dl$  the number of molecules is  $N_i dl$ . When light of frequency  $\omega$  passes through the sample some is absorbed owing to transitions it induces in the molecules and the number of photons absorbed is equal to the number of molecules excited: the decrease in the number of molecules per second in the state  $|i\rangle$  is  $-dN_i(\omega)$ , where  $N_i(\omega)$  is the number of molecules which respond to the radiation of frequency  $\omega$ . The number of transitions per second at frequency  $\omega$  is equal to the transition probability  $W_{if}$  times the number of molecules in the layer of the sample,  $N_i dl$ . Therefore

$$-dN_i(\omega) = W_{if}(\omega) N_i dl \quad 4$$

Let  $dI(\omega)$  be the change in the light intensity at frequency  $\omega$  due to passage through the sample. Be-

cause each photon that is absorbed at a frequency  $\omega$  carries an energy  $\hbar\omega$ , therefore

$$\begin{aligned} -dN_i(\omega)/dl &= -(1/\hbar\omega) dI(\omega)/dl \\ &= N_i I(\omega) k_{if}(\omega)/\hbar \quad 5 \end{aligned}$$

where eq. A2 has been used. The energy density at frequency  $\omega$  is related to  $I(\omega)$  through  $I(\omega) = (c/\eta) \rho(\omega)$ , where  $c$  is the speed of light and  $\eta$  is the refractive index of the medium, so that eq. 5 can be expressed as

$$-dN_i(\omega)/dl = N_i (c/\eta) \rho(\omega) K_{if}(\omega)/\hbar\omega \quad 6$$

Comparing with 4, we may then write

$$K_{if}(\omega) = (\eta/c) (\hbar\omega) W_{if}(\omega) / \rho(\omega) \quad 7$$

From time-dependent perturbation theory, the transition probability per unit time of the system making a transition from a given initial

state  $|i\rangle$  to some final state  $|f\rangle$  due to absorption of isotropic and unpolarized light of frequency  $\omega$  is (5)

$$W_{if}(\omega) = (4\pi^2/3\hbar^2) \rho(\omega) |\langle i | \hat{M} | f \rangle|^2 [\delta(\omega_{if} - \omega) + \delta(\omega_{if} + \omega)] \quad 8$$

where  $\omega_{if} = \omega_f - \omega_i$ , and  $\delta(x)$  is the delta-function. Introducing eq. 8

into eq. 7 we obtain the absorption coefficient of the system  $K_{if}(\omega)$  as

$$K_{if}(\omega) = (\eta/c) \omega (4\pi^2/3\hbar) |\langle i | \hat{M} | f \rangle|^2 [\delta(\omega_{if} - \omega) + \delta(\omega_{if} + \omega)] \quad 9$$

In most physical problems we are not interested in the transition of our system from a given initial state to a given final state, but in transitions to all final states. Moreover, we ordinarily do not know the

precise initial state of the system when perturbation acts on, and the best that we can often do is that to assume that the initial state is given by a canonical distribution

$$P_i = e^{-\beta E_i} / \sum_i e^{-\beta E_i}, \beta = 1/k_B T \quad 10$$

Where  $K_B$  is Boltzman's constant. Eq. 10 can be written in terms of the density matrix  $\hat{\rho}$  as

$$\hat{\rho} = e^{-\beta \hat{H}} / \text{Tr} e^{-\beta \hat{H}} \quad 11$$

With these assumptions we obtain the result that the canonically averaged absorption coefficient of the system  $K(\omega)$  is given by

$$K(\omega) = (n/c) (4\pi^2/3\hbar) \sum_{if} P_i \omega_{if} |\langle i | \hat{M} | f \rangle|^2 [\delta(\omega_{if} - \omega) + \delta(\omega_{if} + \omega)] \quad 12$$

Since the summation  $i$  and  $f$  go over the quantum states of the system, we interchange these indices in the summation over the second delta function, giving

$$K(\omega) = (n/c) (4\pi^2/3\hbar) \sum_{if} (P_i - P_f) \omega_{if} |\langle i | \hat{M} | f \rangle|^2 \delta(\omega_{if} - \omega) \quad 13$$

If we assume that the system is initially in thermal equilibrium, then

$$P_f = P_i \exp(-\beta \hbar \omega_{if})$$

and so

$$K(\omega) = (4\pi^2 n / 3\hbar c) \omega [1 - \exp(-\beta \hbar \omega)] \sum_{if} P_i |\langle i | \hat{M} | f \rangle|^2 \delta(\omega_{if} - \omega) \quad 14$$

Note that the delta function permits to replace  $\omega_{if}$  by  $\omega$ .

Using eq. 7, we obtain the canonically averaged absorption coefficient of the system  $K(\omega)$  as

$$K(\omega) = (4\pi^2 n / 3\hbar c) \omega [1 - \exp(-\beta \hbar \omega)] \sum_{if} P_i |\langle i | \hat{M} | f \rangle|^2 \delta(\omega_{if} - \omega) \quad 15$$

To simplify eq. 15, it is convenient to introduce the integral representation of the delta function given by

$$\delta(x) = (2\pi)^{-1} \int_{-\infty}^{+\infty} dt \exp(itx) \quad 16$$

Substituting 16 into 15, we, after a little algebra, find

$$K(\omega) = (4\pi^2 n / 3\hbar c) \omega [1 - \exp(-\beta \hbar \omega)] S(\omega), \quad 17$$

$$S(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} d\tau \exp(-i\omega\tau) \langle \hat{M}(0) \cdot \hat{M}(\tau) \rangle, \quad 18$$

With

$$\hat{M}(\tau) = \exp(i\hat{H}\tau/\hbar) \hat{M} \exp(-i\hat{H}\tau/\hbar), \quad 19$$

and the angular brackets mean

$$\langle A \rangle = \text{Tr}(\hat{\rho} \hat{A}), \quad 20$$

for any operator  $\hat{A}$ . Eq. 17 is the desired result, namely, the lineshape function  $S(\omega)$  is written as the Fourier transform of the time-correlation function of the dipole moment operator of the absorbing system in the absence of the radiation field.

The spectral lineshape of a diatomic molecule

We consider a diatomic molecule with two electronic states:

a ground state  $|a\rangle$ , and an excited state  $|b\rangle$ . The adiabatic hamiltonian of the system is

$$\hat{H} = |a\rangle (E_a + \hat{H}_a) \langle a| + |b\rangle (E_b + \hat{H}_b) \langle b|, \quad 21$$

Where  $E_a$  and  $E_b$  are the electronic energies of the states  $|a\rangle$  and  $|b\rangle$ , respectively: and the vibra-

tional hamiltonians (in harmonic approximation) for the two electronic states are given by

$$\hat{H}_a = P''/2 + \frac{1}{2}\mu\omega''^2 q''^2 \quad 22$$

$$\hat{H}_b = P'/2 + \frac{1}{2}\mu\omega'^2 q'^2 \quad 23$$

We further assume that the displacement of coordinates  $q'$  and  $q''$  are related by the following transformation:

$$q' = q'' + d \quad 24$$

Where  $d$  is a linear displacement of the equilibrium configuration in the two electronic states.

With hamiltonian 21, We may write the correlation-function in eq. 17 within the Condon-approximation as

$$\langle \hat{M}(0) \cdot \hat{M}(\tau) \rangle = |\mu_{ab}(0)|^2 \exp(i\omega_{ab}\tau) G(\tau) \quad 25$$

With

$$G(\tau) = \langle \exp(i\hat{H}_b\tau/\hbar) \exp(-i\hat{H}_a\tau/\hbar) \rangle \quad 26$$

Where the average is over initial (ground)vibrational states.

We shall be interested in calculating  $G(\tau)$  which can be written as

$$G(\tau) = Z^{-1} \sum_{v',v''} \exp[-\lambda''(v''+\frac{1}{2})] \exp[-\lambda'(v'+\frac{1}{2})] | \langle v' | v'' \rangle |^2 = Z^{-1} \int \int dq'' d\bar{q}'' \sum_{v''} \exp[-\lambda''(v''+\frac{1}{2})] \chi_{v''}(q'') \chi_{v''}(\bar{q}'') \times \sum_{v'} \exp[-\lambda'(v'+\frac{1}{2})] \chi_{v'}(q') \chi_{v'}(\bar{q}') \quad 27$$

Where  $\lambda' = -i\omega'\tau$ ,  $\lambda'' = \beta\hbar\omega'' + i\omega''\tau$  and harmonic oscillator eigenfunctions are given by

$$\chi_v(q) = \left[ \frac{\gamma}{\pi} \right]^{1/2} / 2^{v/2} v!^{1/2} H_v(\gamma^{1/2} q) \exp$$

$$(-\gamma q^2/2), \quad \gamma = (\mu\omega/\hbar) \quad 28$$

Here  $Z$  is the canonical partition function of the harmonic oscillator.

By making use of the Mehler's formula (7) :

$$\sum_v \exp[-(v+\frac{1}{2})\xi] \chi_v(q) \chi_v(\bar{q}) = \gamma^{1/2} (2\pi \sinh \xi)^{-1/2} \exp[-\frac{1}{4}\gamma(q+\bar{q})^2 \tanh \xi / 2 - \frac{1}{4}\gamma(q-\bar{q})^2 \coth \xi / 2]$$

We then obtain

$$G(\tau) = Z^{-1} (\gamma' \gamma'')^{-1} (2\pi)^{-1} (\sinh \lambda' \sinh \lambda'')^{-1/2} \int \int dq'' d\bar{q}'' \exp[-\frac{1}{4}\gamma''(q''+\bar{q}'')^2 \tanh \lambda''/2 - \frac{1}{4}\gamma''(q''-\bar{q}'')^2 \coth \lambda''/2] \exp[-\frac{1}{4}\gamma'(q'+\bar{q}')^2 \tanh \lambda'/2 - \frac{1}{4}\gamma'(q'-\bar{q}')^2 \coth \lambda'/2] \quad 29$$

To evaluate the integrals in eq.29, We first use eq. 24 to transform  $q'$  and  $\bar{q}'$  to  $q''$  and  $\bar{q}''$  and then change variables to  $q'' + \bar{q}''$  and  $q'' - \bar{q}''$  and make use of the Gaussian integration formula

$$\int_{-\infty}^{+\infty} dx \exp[-(ax^2 + bx)] = (\pi/a)^{1/2} \exp(b^2/4a) \quad 30$$

The following closed expression for  $G(\tau)$  is obtained

$$G(\tau) = Z^{-1} (\gamma' \gamma'')^{-1/2} (\Omega \Lambda \sinh \lambda' \sinh \lambda'')^{-1/2} \exp(-\gamma' \gamma'' d^2 / \bar{\Omega}) \quad 30$$

where

$$\begin{aligned} \Omega &= \gamma'' \coth \lambda'' / 2 + \gamma' \coth \lambda' / 2 \\ \Lambda &= \gamma'' \tanh \lambda'' / 2 + \gamma' \tanh \lambda' / 2 \\ \bar{\Omega} &= \gamma'' \coth \lambda' / 2 + \gamma' \coth \lambda'' / 2 \end{aligned} \quad 30$$

Equation 30 can be alternatively written in the form

$$G(\tau) = \exp[-\gamma' \gamma'' d^2 / \bar{\Omega} - \frac{1}{2} \text{Ln}(Z^2 \Omega \Lambda \sinh \lambda' \sinh \lambda'' / \gamma' \gamma'')] = \exp[f(\tau)] \quad 31$$

In this form, the connection with the cumulant expansion given in next section is more transparent. Eq. 31 is our time domain electronic spectrum which is converted into its frequency domain (The absorption spectrum) counter part via a Fourier transformation technique.

The integration in eq. 17 can not be carried out without introducing approximations. Let us assume that the modifications of frequency, that is  $\delta = (\omega'' - \omega')$ , and displacement coordinate  $d$  between the two electronic states are small, and expand the function  $f(\delta, d, \tau)$  as a two-variable Taylor series about  $\delta = 0$  and  $d = 0$ .

To the second order of approximation we find

$$f(\delta, d, \tau) = -\frac{\delta}{2}(i\omega''\tau)\chi(0) - \frac{\delta^2}{8}(i\omega''\tau)^2 [1 - \chi^2(0)] + \frac{\delta^2}{3} [\chi^2(\tau) - \chi^2(0)] + \frac{1}{2}\gamma''d^2 [\chi(\tau) - \chi(0)] + \dots \quad 32$$

Where

$$\chi(\tau) = \text{Coth}\beta\hbar\omega''/2 \text{Cos}\omega''\tau + i\sin\omega''\tau \quad 33$$

The integration in eq. 18 is facilitated if the terms containing  $\delta^2$  in eq. 32 are neglected. To this approximation, we may write eq.18 as

$$S(\omega) = (2\pi)^{-1} |\mu_{ab}(0)|^2 \exp[-S\chi(0)] \int_{-\infty}^{+\infty} d\tau \exp[-i\Delta\tau + S\chi(\tau)] \quad 34$$

Where

$$S = \frac{1}{2}\gamma''d^2 \quad 35$$

$$\Delta = \omega - \omega_{ab} + \frac{1}{2}\delta\omega'' \chi(0) \quad 36$$

The integral in eq. 34 resembles integrals which appear in the definition of Bessel's function. To relate  $S(\omega)$  to these functions, let us write eq. 34 as

$$S(\omega) = (2\pi)^{-1} |\mu_{ab}(0)|^2 \exp[-S\chi(0) + \frac{1}{2}\beta\hbar\Delta] \times \int_{-\infty}^{+\infty} \frac{d\xi}{\omega} \exp\left[ \frac{S\text{Csch}\beta\hbar\omega''}{2} \text{Cos}\xi - i\Delta\xi/\omega'' \right] \quad 37$$

and make use of the identity(9)

$$(2\pi)^{-1} \int_{-\infty}^{+\infty} \exp(\gamma\text{Cos}\xi - i p \xi) d\xi = \sum_{k=-\infty}^{+\infty} \delta(p-k) I_p(\gamma) \quad 38$$

Where  $I_p$  is the modified Bessel function of order  $p$ . Now eq. 37

takes the form

$$S(\omega) = |\mu_{ab}(0)|^2 (1/\omega'') \exp[-S\chi(0) + p(\beta\hbar\omega''/2)] I_p(S\text{Csch}\beta\hbar\omega''/2) \quad 39$$

Eq. 39 requires that  $p$  or  $\Delta/\omega''$  be an integer. In other words, the absorption spectrum is discrete.

The cumulant expansion of  $G(\tau)$

In this section we shall expand our time domain spectrum  $G(\tau)$ , in terms of cumulants(10). To that end we make use of the operator identity(11):

$$\exp(\hat{a} + \hat{b}) = \exp\left[ \int_0^{\tau} d\tau' \hat{b}(\tau') \right] \exp(\hat{a}\tau) \quad 40$$

Where

$$\hat{b}(\tau) = \exp(\hat{a}\tau) \hat{b} \exp(-\hat{a}\tau) \quad 41$$

and  $\exp_{-}$  is a negative time ordering exponential which means that  $\hat{b}(\tau)$ 's in power series expansion of  $\exp_{-} \left[ \int_0^{\tau} d\tau' \hat{b}(\tau') \right]$  should be

ordered so that time increases from left to right:

$$\exp_{-} \left[ \int_{\tau_1}^{\tau} d\tau' \hat{b}(\tau') \right] = 1 + \int_{\tau_1}^{\tau} d\tau_1 \hat{b}(\tau_1) + \int_{\tau_1}^{\tau} d\tau_1 \int_{\tau_1}^{\tau} d\tau_2 \hat{b}(\tau_2) \hat{b}(\tau_1) + \dots$$

If we choose  $\hat{a} = i\hat{H}_a/\hbar$  and  $\hat{b} = i[(\hat{H}_b - \hat{H}_a) - \langle \hat{H}_b - \hat{H}_a \rangle] / \hbar = i\hat{U}/\hbar$  in eq. 40, we can then write eq. 26 as

$$G(\tau) = \exp \left[ i \langle \hat{H}_b - \hat{H}_a \rangle \tau / \hbar \right] \langle \exp_{-} \left[ (i/\hbar) \int_{\tau_1}^{\tau} d\tau' \hat{U}(\tau') \right] \rangle = \exp \left| i \langle \hat{H}_b - \hat{H}_a \rangle \tau / \hbar \right| \exp \{ \text{Ln}(1 + \langle \exp_{-} \left[ (i/\hbar) \int_{\tau_1}^{\tau} d\tau' \hat{U}(\tau') \right] - 1 \rangle) \}. \quad 42$$

We note that  $\hat{U}(\tau)$  (which is related to the time dependent energy gap of the two electronic states) is the quantity which determines the resulting line shape.

Upon expanding the logarithm in eq. 24 and collecting terms according to the power of  $\hat{U}$ , we obtain (6):

$$\text{Ln}(1 + \langle \exp_{-} \left[ (i/\hbar) \int_{\tau_1}^{\tau} d\tau' \hat{U}(\tau') \right] - 1 \rangle) = (i/\hbar)^2 \int_{\tau_1}^{\tau} d\tau_1 \int_{\tau_1}^{\tau} d\tau_2 K_2(\tau_2, \tau_1) + (i/\hbar)^3 \int_{\tau_1}^{\tau} d\tau_1 \int_{\tau_1}^{\tau} d\tau_2 \int_{\tau_1}^{\tau} d\tau_3 K_3(\tau_3, \tau_2, \tau_1) + (i/\hbar)^4 \int_{\tau_1}^{\tau} d\tau_1 \int_{\tau_1}^{\tau} d\tau_2 \int_{\tau_1}^{\tau} d\tau_3 \int_{\tau_1}^{\tau} d\tau_4 \left[ K_4(\tau_4, \tau_3, \tau_2, \tau_1) - K_2(\tau_4, \tau_3) K_2(\tau_2, \tau_1) - K_2(\tau_4, \tau_2) K_2(\tau_3, \tau_1) - K_2(\tau_4, \tau_1) K_2(\tau_3, \tau_2) \right] + \dots \quad 43$$

Where the cumulants  $K_n(\tau_1, \tau_2, \dots, \tau_n)$  are defined by (10)

$$K_n(\tau_1, \tau_2, \dots, \tau_n) = \langle \hat{U}(\tau_1) \hat{U}(\tau_2) \dots \hat{U}(\tau_n) \rangle \quad 44$$

Note that we have

$$K_1(\tau) = \langle \hat{U} \rangle = 0.$$

The simplest approximation is obtained by terminating the series at the second order; to this approximation we may write eq.42 as

$$G(\tau) = \exp \left[ (i/\hbar) \langle \hat{H}_b - \hat{H}_a \rangle \tau + (i/\hbar)^2 \int_{\tau_1}^{\tau} d\tau_1 \int_{\tau_1}^{\tau} d\tau_2 \langle \hat{U}(\tau_2) \hat{U}(\tau_1) \rangle \right] \quad 45$$

$$G(\tau) = \exp \left[ (i/\hbar) \langle \hat{H}_b - \hat{H}_a \rangle \tau + (i/\hbar)^2 \int_{\tau_1}^{\tau} d\tau_1 (\tau - \tau_1) \langle \hat{U}(0) \hat{U}(\tau_1) \rangle \right], \quad 46$$

where the second line of eq.46 is justified in appendix 2.

To apply eq. 46 to our case (a diatomic molecule) we need, as a first step, to calculate  $\hat{H}_b - \hat{H}_a$ . From eqs. 21, we obtain  $(\hat{H}_b - \hat{H}_a) / \hbar = \gamma \omega \left[ -\frac{1}{2} \delta(2 - \delta) q^2 + (1 - \delta)^2 dq + \frac{1}{2} (1 - \delta)^2 d^2 \right]$ . 47

To evaluate the cumulant  $\langle \hat{U}(0) \hat{U}(\tau) \rangle$  we make use of the rule which holds for the harmonic systems(12): the expectation value of an odd number of  $q$ 's vanishes and the expectation value of an even number of  $q$ 's is equal to the sum of products of pair expectation values, the sum being over all pairings which preserves the order of the pair. For example

$$\langle q_i q_j q_k q_l \rangle = \langle q_i q_j \rangle \langle q_k q_l \rangle + \langle q_i q_k \rangle \langle q_j q_l \rangle + \langle q_i q_l \rangle \langle q_j q_k \rangle.$$

The pair correlations are given by (12)

$$\langle q^2(0) q^2(\tau) \rangle = \frac{1}{2} (\gamma \omega)^{-1} \chi(\tau), \quad 48$$

Where  $\chi(\tau)$  is given by eq. 33.

Resulting in

$$(i/\hbar) \langle \hat{H}_b - \hat{H}_a \rangle = -\frac{1}{4}(i\omega''')\delta(2-\delta) \chi(0) + \frac{1}{2}(i\omega''')\gamma''(1-\delta)^2 d^2 \quad 49$$

$$(i/\hbar)^2 \langle \hat{U}(0)\hat{U}(\tau) \rangle = \frac{1}{8}(i\omega''')^2 \delta^2 (2-\delta)^2 \chi^2(\tau) + \frac{1}{2}(i\omega''')^2 \gamma'' d^2 (1-\delta)^4 \chi(\tau) \quad 50$$

Introducing eqs. 49 - 50 into eq. 46 and making use of eq. 33, after straightforward integration we obtain

$$G(\tau) = \exp \left\{ \frac{1}{16}(i\omega''')\tau \delta(2-\delta) (\delta^2 - 2\delta - 4) \chi(0) - \frac{1}{2}(i\omega''')\tau \delta(2-\delta)(1-\delta)^2 \gamma'' d^2 - \frac{1}{32}\delta^2(2-\delta)^2 (i\omega''')^2 \tau^2 \left[ 1 - \chi^2(0) \right] + \frac{1}{32}\delta^2(2-\delta)^2 \left[ \chi^2(\tau) - \chi^2(0) \right] + \frac{1}{2}\gamma'' d^2 (1-\delta)^4 \left[ \chi(\tau) - \chi(0) \right] \right\} \quad 51$$

Inserting eq. 32 into eq. 31 and comparing the result with eq. 51, we conclude that to the same order of expansion, the cumulant expansion contains more terms than the Taylor expansion. If those terms in eq. 51 which are linear in  $\tau$  are kept and the rest are neglected, then eq. 51 exactly reduces to the Taylor expansion. However, the cumulant expansion is much simpler and the calculation is done just by considering the energy gap  $\hat{U}$  between the two electronic states and evaluating its correlation function. The method has been used to calculate line broadening in clusters(6), molecular electronic spectra(8), and overtone line shapes(13).

#### CONCLUSION

As a result of making the Born-

Oppenheimer and harmonic oscillator approximations to the molecular Hamiltonian, and making the Condon approximation to the electronic transition moment, we have derived an easily calculable expression for the vibronic absorption spectrum of a diatomic molecule within the first order time dependent perturbation theory. We have explicitly included the equilibrium shift and the frequency shift in our calculations. The calculations are done exactly, resulting in eq. 31; and perturbatively (using the second order cumulant expansion), resulting in eq. 51. A numerical calculation for our theory will be postponed to a new communication.

#### Appendix 1: The Beer-Lambert law

The reduction of radiation intensity due to passage through the layer is proportional to the thickness of the layer, the concentration of the absorbing molecules, and the intensity itself. If the constant of proportionality is written  $k_{if}(\omega)$ , we may then write

$$-dI(\omega) = N_i I(\omega) k_{if}(\omega) dl \quad A1$$

Which by integrating over the length of the sample, it gives

$$I(\omega) = I_0(\omega) \exp[-N_i k_{if}(\omega) l] \quad A2$$

where  $I_0(\omega)$  is intensity of the initial beam. Expressing the concentration of the sample  $c_i$  in moles per liter, and the thickness  $l$  in meter, we may then write A2 as

$$\log[I(\omega)/I_0(\omega)] = -100c_i [(10/\ln 10)$$

$$N_A k_{if}(\omega)] \quad A3$$

Where  $N_A$  is the Avogadro's number, and the molar extinction coefficient  $\epsilon_{if}(\omega)$  is defined by

$$\epsilon_{if}(\omega) = (10/\ln 10) N_A k_{if}(\omega). \quad A4$$

Appendix 2: Justification of eq.46

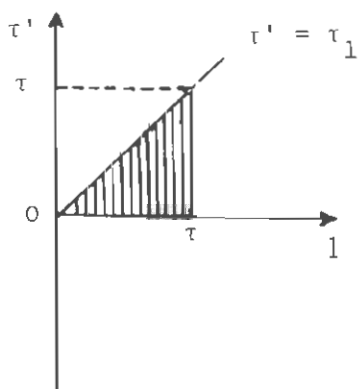
Using the symmetry property

$$\langle \hat{U}(\tau) \hat{U}(\tau+t) \rangle = \langle \hat{U}(\tau-t) \hat{U}(\tau) \rangle$$

we may write

$$\begin{aligned} I &= \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \hat{U}(\tau_2) \hat{U}(\tau_1) \rangle \\ &= \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \hat{U}(0) \hat{U}(\tau_1 - \tau_2) \rangle \\ &= \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau' \langle \hat{U}(0) \hat{U}(\tau') \rangle. \end{aligned}$$

The domain of the last integral extends over the shaded area in the following figure



Changing the order of integration we may then write the integral as

$$\begin{aligned} I &= \int_0^\tau d\tau' \int_{\tau'}^\tau d\tau_1 \langle \hat{U}(0) \hat{U}(\tau') \rangle \\ &= \int_0^\tau d\tau' (\tau - \tau') \langle \hat{U}(0) \hat{U}(\tau') \rangle. \end{aligned}$$

## REFERENCES

- 1 -J.Franck,Trans.Faraday Soc.21, 536(1925)
- 2 -M.Born and R.E.Oppenheimer,Ann. Physik.84,457(1927)
- 3 -E.U.Condon,Phys.Rev. 32 , 858 (1928)

- 4 -R.W.Nicholls and W.R.Jarman , Proc.Phys.Soc.A,68,253(1955)
- 5 -See, for instance,J.J. Sakurai, Modern Quantum Mechanics ( The Benjamin/Cummings Publishing Company,Inc.,1985),P. 334
- 6 -R.Islampour and S.Mukamel , J. Chem. Phys. 80 ,5487 (1984) ; Chem. Phys.Lett.107 ,239(1984)
- 7 -R.C.O'Rourke,Phys.Rev.91, 265 (1953); H.D.Vasileff,Phys .Rev. 96 , 603(1954)
- 8 -S.Mukamel,S.Abe, Y.J.Yan , and R.Islampour,J.Phys. Chem . 89, 201(1985)
- 9 -M.Lax , J.Chem.Phys.20 , 1752 (1952)
- 10-R.Kubo, in Fluctuation,Relaxation,and Resonance in magnetic systems,Edited by Ter Haar(Oliver and Boyd , Edinburgh,1962),P.23
- 11-R.P. Feynman,Phys.Rev.84, 108 (1951)
- 12-G.W.Ford,M.Kac,and P.Mazur,J. Math. Phys. 6 ,504(1965)
- 13-S.Mukamel and R.Islampour,Chem. Phys.Lett. 29 , 161(1984)