A SIMPLE METHOD TO DETERMINE BOND LENGTHS
AND EXCITED STATE SURFACES FROM ELECTRONIC-VIBRATIONAL SPECTRA

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A fast and efficient method using the spectral moments of an electronic-vibrational spectrum is described to determine the harmonic and Morse potential fits to the excited state potential in the Franck-Condon region. Some of the drawbacks of the Franck-Condon least-squares fitting procedure are overcome by the moment method. The method is applied to some diatomics of current interest, spanning a wide range of bond length change in the electronic transition. The accuracy of the results suggests that the spectral moment method can be a replacement for the traditional and still popular Franck-Condon analysis.

1. Introduction

Franck-Condon (FC) analysis which is an iterative, least-squares fitting procedure is the best-known and most widely used method to determine excited state potential energy surface from an electronic-vibrational spectrum. The procedure makes use of the eigenvalues and eigenfunctions typically of the harmonic and Morse potentials. It is aided by the availability of overlap integrals for displaced harmonic oscillators in closed form [1], and numerous numerical methods for evaluating similar integrals for displaced Morse oscillators [2]. The best fit harmonic or Morse potential is often interpreted as an expansion of the actual excited state potential about its minimum. However, when this minimum falls in the tail end of the FC region, such an interpretation is inappropriate [3]. Moreover, when the harmonic approximation is made, symmetry prevents discriminating between bond lengthening or bond shortening, and additional information of the excited state electronic structure has to be used. Other procedures such as the semiclassical Rydberg-Klein-Rees (RKR) method [4] for diatomics do not have to assume harmonic or Morse potentials. But, unfortunately, many molecules of interest do not give sufficient spectroscopic data to enable accurate RKR potentials to be constructed. Basis set methods, such as the recent discrete variable representation (DVR) approach of Light and coworkers [5] optimizes the potential energy surface by minimizing the difference between the experimental and calculated vibrionic spectra. They can also be classified as FC analysis. Like the RKR method, basis set methods require the observation of a large set of energy levels. Unfortunately, most molecules give limited lines or diffuse spectra which render such methods inapplicable.

The purpose of this paper is to present a simple method that has the same accuracy, and yet can overcome most of the problems associated with FC analysis. The method presented below, uses spectral moments to determine parameters for assumed forms of the excited state potential. Both harmonic and Morse potentials are considered. The simplicity of the approach, and the good quality of the results obtained for a wide range of diatomics indicates that the spectral moment method is a good alternative, if
not a replacement, for the traditional, and still popular Franck–Condon analysis. The method is also applicable to polyatomic molecules with separable modes. At the moment, a direct inversion procedure for polyatomics with non-separable modes is not available; although with sufficient spectral data, the form of the excited state surface in a limited FC region can be determined [6]. Spectral moments have in the past been proposed to provide a qualitative understanding of the potential energy surface that leads to a diffuse absorption spectrum [7,8]. No attempt has been made to use them to determine parameters for a potential energy surface. In the literature, spectral moments are taken with respect to the \( v'' = 0 \) level of the ground electronic state, but in this paper they are taken with respect to the \( v' = 0 \) level of the excited electronic state. The time-frame approach of Heller [9] is used in section 2 to derive the relation between the spectral moments and the excited state vibrational Hamiltonian. It should be stressed that the final equations for the numerical calculation are all in the energy frame, and this should appeal to a wide audience of spectroscopists who very much prefer the energy-frame viewpoint. The harmonic fit to the excited state potential about the ground state minimum is deduced from the first and second spectral moments, and the information derived is used to construct the Morse potential approximation. In section 3 the results of the moment method are reported for a few diatomics of recent interest, spanning a broad range of bond length shift.

2. Theory

The Born–Oppenheimer approximation is assumed to be valid, and the molecule is initially in the \( v'' = 0 \) level of the ground electronic state with eigenenergy \( E_{g0} \) and eigenfunction \( |\chi_{g0}\rangle \). The molecule absorbs a photon of energy \( \hbar \omega \) and makes a transition to the excited electronic state which has vibrational Hamiltonian \( H_e \). The handle for the jump is provided by the transition dipole moment \( \mu \). For a constant damping function (i.e. Dirac delta function lineshape), the photoabsorption intensity as a function of \( \omega \) is given by [9]

\[
I(\omega) = K \omega \sigma(\omega) .
\]

Here \( K \) is a constant and \( \sigma(\omega) \), defined as the absorption profile, in the time-frame viewpoint is given by the Fourier transform of an autocorrelation function,

\[
\sigma(\omega) = (1/2\pi) \int_{-\infty}^{\infty} dt \exp(iEt/\hbar) \\
\times \langle \phi | \exp(-iH_0 t/\hbar) | \phi \rangle,
\]

where the transform energy

\[
E_0 = \hbar \omega + E_{g0}
\]

(3)

and

\[
|\phi\rangle = \mu |\chi_{g0}\rangle.
\]

Taking energies relative to the \( v' = 0 \) level with eigenvalue \( E_{e0} \) in the excited state, we can write the absorption profile as

\[
\sigma(\omega) = (1/2\pi) \int_{-\infty}^{\infty} dt \exp(i\omega t) C(t) ,
\]

(5)

where the transform energy \( \hbar \omega \) here is defined as

\[
\hbar \omega = \hbar \omega + E_{g0} - E_{e0}
\]

(6)

and the autocorrelation function \( C(t) \) is defined to be

\[
C(t) = \langle \phi | \exp[-i(H_e - E_{e0})t/\hbar] | \phi \rangle.
\]

(7)

The reason for this change in reference energy is to permit us to take spectral moments relative to the \( v' = 0 \) level of the excited electronic state, which leads to simpler expressions for the calculation. This is in contrast to other work [7,8] where spectral moments are taken with respect to the \( v'' = 0 \) level of the ground electronic state.

Taking the inverse Fourier transform of eq. (5), the autocorrelation function can be determined from the absorption profile,

\[
C(t) = \int_{-\infty}^{\infty} d\omega \exp(-i\omega t) \sigma(\omega) .
\]

(8)

Defining the \( n \)th moment of the absorption profile by
\[
\langle (\hbar \omega)^n \rangle = \int_{-\infty}^{\infty} d\omega \ (\hbar \omega)^n \sigma(\omega) ,
\]

(9)

it can then be shown by differentiating eq. (8) \( n \) times with respect to \( t \) and setting \( t=0 \) that

\[
\langle (\hbar \omega)^n \rangle = (i \hbar)^n C^{(n)}(0) = \langle \phi | (H_e - E_{co})^n | \phi \rangle ,
\]

(10)

where \( C^{(n)}(0) \) denotes the \( n \)th derivative of \( C(t) \) evaluated at \( t=0 \). In particular, assuming the Condon approximation (\( \mu = \text{constant} \)), the mean energy of the absorption profile (relative to the \( v'=0 \) level) is given by the ratio of the first moment to the zeroth moment,

\[
\frac{\langle \hbar \omega \rangle}{\langle (\hbar \omega)^0 \rangle} = \frac{\langle x_{00} | (H_e - E_{co}) | x_{00} \rangle}{\langle x_{00} | (H_e - E_{co}) \rangle} ,
\]

(11)

and the mean square energy which depends on the width of the absorption profile is given by

\[
\frac{\langle (\hbar \omega)^2 \rangle}{\langle (\hbar \omega)^0 \rangle^2} - 1 = \frac{\langle x_{00} | (H_e - E_{co})^2 | x_{00} \rangle}{\langle x_{00} | (H_e - E_{co}) \rangle} ,
\]

(12)

The moments on the left of eqs. (11) and (12) can be calculated from the observed electronic-vibrational spectrum. Then, by assuming a functional form for the excited state potential, eqs. (11) and (12) can be used to determine the parameters. The simplest situation is to assume harmonic ground and excited state potentials with vibrational Hamiltonians in one dimension given by

\[
H_g = \hbar \omega_g \left( \frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} Q^2 \right) + E_g ,
\]

(13)

and

\[
H_e = \hbar \omega_e \left( \frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} \left( \frac{\omega_{eh}^2}{\omega_e^2} \right) (Q - \delta_h) \right) + E_e ,
\]

(14)

where the subscript \( h \) denotes the harmonic approximation. Here \( \hat{P} \) \( (= -i \frac{\partial}{\partial Q} \) is the momentum operator, \( Q \) the dimensionless coordinate is related to the difference of the bond length \( R \) from the ground state equilibrium \( R_g \) by

\[
Q = (m\omega_g / \hbar)^{1/2} (R - R_g) .
\]

(15)

\( E_g, E_e \) are the energies at the potential minima whose difference can be determined from the spectrum, \( m \) is the reduced mass, and \( \omega_g, \omega_e \), \( \omega_{eh} \) are the angular frequencies of the ground and excited state harmonic oscillators, respectively. Finally, \( \delta_h \) is an estimate of the dimensionless shift in the minima of the two surfaces,

\[
\delta_h = \left( \frac{m \omega_e}{\hbar} \right)^{1/2} (R_{eh} - R_e) \equiv \left( \frac{m \omega_e}{\hbar} \right)^{1/2} \delta_h .
\]

(16)

The parameters for these two harmonic oscillators and their relation to the anharmonic ground and excited state potentials are shown in fig. 1. The vibrational frequency \( \omega_g \) of the ground electronic state is commonly known for most molecules, and the assumption of a harmonic ground state surface is usually good, especially when the molecule is in the \( v'=0 \) vibrational state. The initial vibrational wavefunction is then given by

\[
x_{00}(Q) = \pi^{-1/4} \exp \left( -\frac{1}{2} Q^2 \right) .
\]

(17)
On the other hand, the harmonic approximation for the excited state surface is valid only in a very narrow FC region about $Q=0$. Nevertheless the information on $\omega_{eh}$ and $\Delta_n$ is very useful, as we shall see.

Using the following equations for the operators $\hat{P}$ and $\hat{Q}$ acting on the harmonic oscillator wavefunctions $|\chi_n\rangle$,

$$\hat{P}|\chi_n\rangle = \frac{i}{\sqrt{2}} \left\{ (n+1)^{1/2}|\chi_{n+1}\rangle - n^{1/2}|\chi_{n-1}\rangle \right\},$$

$$\hat{Q}|\chi_n\rangle = \frac{i}{\sqrt{2}} \left\{ (n+1)^{1/2}|\chi_{n+1}\rangle + n^{1/2}|\chi_{n-1}\rangle \right\},$$

it is straightforward to evaluate the matrix elements in eqs. (11) and (12) to yield

$$\frac{\langle \hat{h}\hat{\omega} \rangle}{\langle \hat{h}\omega \rangle^2} = \hbar \omega_{eh} \left( \frac{f^2}{1-f^2} + \frac{a}{1-f} \right),$$

and

$$\frac{\langle \hat{h}\hat{\omega} \rangle^2}{\langle \hat{h}\omega \rangle^2} - \frac{\langle \hat{h}\hat{\omega} \rangle^2}{\langle \hat{h}\omega \rangle^0}^2 = 2(\hbar \omega_{eh})^2 \left( \frac{f^2}{(1-f^2)^2} + \frac{1}{2}a \frac{1+f}{(1-f)^2} \right).$$

Here, we have defined the parameters $f$ and $a$ as

$$f = \frac{\omega_{eh}/\omega_{g} - 1}{\omega_{eh}/\omega_{g} + 1} \quad (22)$$

and

$$a = \frac{1}{2}(1+f)\Delta_n^2 \quad (23)$$

The moments can be calculated from the experimental absorption profile; then, if $\omega_g$ is known, eqs. (20) and (21) can be used to solve for $\omega_{eh}$ and $\Delta_n$ of the excited state oscillator.

There is a significant difference between the harmonic approximation here and the one used in FC analysis. In harmonic FC analysis, it is an average potential that is obtained which usually does not fit the actual potential at any point. Moreover, by reflection symmetry, the sign of the bond length shift is undetermined. Here, the spectral moments are related to the derivatives of the autocorrelation function evaluated at $t=0$ when the wavepacket prepared on the excited state surface is centred about $Q=0$. Hence, it is the harmonic fit to the excited state surface near $Q=0$ that is determined. We can therefore use the curvature to determine the sign of the bond length shift. We do this by comparing $\omega_{eh}$ with the spectroscopic frequency $\omega_g$ at the minimum of the excited state potential. The frequency $\omega_g$ can be determined by a Birge–Sponer plot of the electronic-vibrational spectrum, but in almost all cases it suffices to use the Morse approximation,

$$\hbar \omega_g \approx 3E(\nu' = 1) - 2E(\nu' = 0) - E(\nu' = 2),$$

where $\omega_M$ is defined as the Morse frequency. In the case of bond lengthening, $\Delta_n > 0$, the excited state anharmonic potential about the ground state minimum $Q=0$ is a hard wall and $\omega_{eh} > \omega_g$. This is shown in fig. 2. It is also evident that $\Delta_n < \Delta_s$; thus a lower bound to the actual shift in bond length $\Delta$ is given by the moment method. On the other hand, for bond short-
ening, $\Delta_n < 0$, it is the soft wall of the excited state potential that is reached at $Q = 0$, and $\omega_{nh} < \omega_n$. Moreover, $-\Delta_n > -\Delta_e$ and an upper bound to the actual decrease in bond length is obtained in this case. This is shown in fig. 3. Thus, even though the harmonic approximation here may be a good fit for the excited state potential only in a very small region of space about $Q = 0$, nevertheless we see that $\omega_{nh}$ can be used to determine the sign of the bond length shift and $\Delta_n$ provides one bound on the actual bond length shift. This is useful for refinements beyond the harmonic approximation. The slope of the excited state potential $V_e(Q)$ at $Q = 0$ is also an important quantity determined by the harmonic approximation,
\[
\left( \frac{dV_e}{dQ} \right)_{Q=0} = -\left( \hbar \omega_{nh} / \omega_n \right) \Delta_n ,
\]
\[
\equiv \Delta_h . \tag{25}
\]

A better model is to assume a Morse potential for the excited state oscillator,
\[
V_e(Q) = D_{em} \left[ 1 - \exp \left[ -\alpha(Q - \Delta_m) \right] \right]^2 + E_e . \tag{26}
\]
The energy $E_e$ at the potential minimum can be determined by a Birge–Sponer plot. The remaining three parameters $D_{em}$, $\alpha$, and $\Delta_m$ can be determined in various ways. But one procedure that yields consistently good results for a wide range of molecules uses the following three conditions: (a) The slope at $Q = 0$ matches the harmonic result eq. (25),
\[
2\alpha D_{em} y(1-y) = \Delta_h , \tag{27}
\]
where we define,
\[
y = \exp (\alpha \Delta_m) . \tag{28}
\]
(b) The Morse frequency deduced from eq. (26) matches the spectroscopic frequency given by eq. (24),
\[
2(\hbar \omega_n)D_{em} \alpha^2 = (\hbar \omega_m)^2 . \tag{29}
\]
(c) The calculated first moment matches the observed result, as given by eq. (11). It is straightforward to show that the matrix element for the first moment of the Morse potential can be evaluated in closed form,
\[
\langle \chi_{\mathbf{g}} \mid (H_e - E_{eo}) \mid \chi_{\mathbf{g}} \rangle = D_{em} \left[ 1 - 2y \exp \left( \frac{1}{2} \alpha^2 \right) + y^2 \exp (\alpha^2) \right] + \frac{\hbar \omega_n}{2} \left( 2 + \alpha^2 \right) - \frac{1}{2} \hbar \omega_m . \tag{30}
\]
Now, $\alpha$ is typically of the order of 0.1 and this permits a Taylor expansion of the exponential functions, with the following result,
\[
\langle \chi_{\mathbf{g}} \mid (H_e - E_{eo}) \mid \chi_{\mathbf{g}} \rangle = D_{em} (1-y)^2 + \frac{\hbar \omega_n}{2} \left[ 1 - (\omega_m/\omega_n)^2 y \right] - \frac{1}{2} \hbar \omega_m \left[ 1 - (\omega_m/\omega_n)^2 y \right] + \frac{1}{2} \hbar \omega_n \alpha^2 
\approx D_{em} (1-y)^2 . \tag{31}
\]
We have neglected the smaller terms, which often cancel one another, and have retained only the principal, classical result. This is simply the energy difference between $Q = 0$ and the equilibrium configuration of the Morse potential. The third condition to determine the Morse parameters is thus taken to be
\[
\frac{\langle \hbar \omega \rangle}{\langle \hbar \omega \rangle_0} = D_{em} (1-y)^2 . \tag{32}
\]
It is straightforward to solve for $D_{cm}$, $\alpha$, and $\Delta_\alpha$ using eqs. (27), (29) and (32). The Morse oscillator so determined is again a fit to the excited state potential in the FC region, and is expected to be valid over a wider range about $Q=0$ than the harmonic fit. The Morse shift $\delta_{M}$ (or $\delta_\alpha$) should be a better estimate of the bond length shift. We do not expect to be able to correctly predict the actual dissociation energy with $D_{cm}$, because this is an asymptotic property of the potential that usually does not affect the first few spectral moments. Moreover, a single Morse potential may not be a good representation over the whole range of the actual potential. In such a situation, a piecewise construction of the excited state potential is recommended.

3. Application to diatomic electronic-vibrational spectra

The moment method is applied to several diatomic electronic-vibrational spectra spanning a broad range of bond length shifts. First, we consider the vibrationally resolved photoelectron (PE) spectra of the transitions $\text{Se}_{2}^+ \rightarrow \Pi_{u1/2}^+ \rightarrow \text{Se}_{2}^+ \rightarrow \Sigma^+_g$ and $\text{Te}_{2}^+ \rightarrow \Pi_{u1/2}^+ \rightarrow \text{Te}_{2}^+ \rightarrow \Sigma^+_g$, which were recently measured using a supersonic molecular beam source [10]; and second, the laser-induced fluorescence spectrum of $\text{ZnAr}$ van der Waals molecules for the transition $C^+ \rightarrow \Pi_1^+ \rightarrow X^+ \rightarrow \Sigma_0^+$. Recent experimental advances have resulted in both low and high resolution spectra [11]. We only need the low resolution spectra for our analysis. In this example, the decrease in bond length is very large ($\approx -1 \text{ Å}$), and serves as a severe test of the theory. Third, we consider the PE spectrum for the classical transition $\text{H}_2^+ \rightarrow X^+ \rightarrow \text{H}_2 \rightarrow X^+ \rightarrow \Sigma^+_g$. This example [12] where the increase in bond length is relatively large ($\approx 0.3 \text{ Å}$) is the converse of the previous case. The observed energies $E_{\nu}$ and relative peak intensities $I_{\nu}$ as a function of the excited state vibrational quantum number $\nu$ for the various species are collected in table 1. For such well-resolved vibronic spectra which can be treated as discrete, the zeroth, first, and second moments of the absorption profile are simply given by

$$\langle \hbar \omega \rangle = \sum_{\nu} \frac{(E_{\nu} - E_0)I_{\nu}}{E_{\nu}} ,$$

$$\langle (\hbar \omega)^2 \rangle = \sum_{\nu} \frac{(E_{\nu} - E_0)^2I_{\nu}}{E_{\nu}} .$$

These moments are used in eqs. (20) and (21) to solve for $\omega_{ch}$ and $\Delta_\alpha$ (or $\delta_\alpha$). The sign of the bond length shift is determined by comparing $\omega_{ch}$ with $\omega_{M}$ given by eq. (24). In table 2, the results of the harmonic approximation together with the slope $S_h$ at
Table 2
Harmonic approximation to the excited state potential

<table>
<thead>
<tr>
<th>Species</th>
<th>( \omega_{\text{th}} ) (cm(^{-1}))</th>
<th>( \omega_{\text{ft}} ) (cm(^{-1}))</th>
<th>( \delta_{\text{e}} ) (Å)</th>
<th>( S_{\text{b}} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(<em>2) (^2\Pi</em>{3/2})</td>
<td>427.38</td>
<td>464.57</td>
<td>-0.0989</td>
<td>1002.13</td>
</tr>
<tr>
<td>Te(<em>2) (^2\Pi</em>{3/2})</td>
<td>258.38</td>
<td>304.07</td>
<td>-0.0789</td>
<td>460.97</td>
</tr>
<tr>
<td>ZnAr (^C\Pi_1)</td>
<td>10.55</td>
<td>61.57</td>
<td>-3.302</td>
<td>69.63</td>
</tr>
<tr>
<td>H(_2^+) X (^2\Sigma_u^+)</td>
<td>3588.29</td>
<td>2318.826</td>
<td>0.2635</td>
<td>-6306.03</td>
</tr>
</tbody>
</table>

Table 3
Morse approximation to the excited state potential

<table>
<thead>
<tr>
<th>Species</th>
<th>( D_{\text{om}} ) (eV)</th>
<th>( \alpha )</th>
<th>( \delta_{\text{m}} ) (Å)</th>
<th>( \delta_{\text{t}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(<em>2) (^2\Pi</em>{3/2})</td>
<td>20.26</td>
<td>0.0414</td>
<td>-0.095</td>
<td>-0.094±0.005</td>
</tr>
<tr>
<td>Te(<em>2) (^2\Pi</em>{3/2})</td>
<td>2.156</td>
<td>0.1037</td>
<td>-0.072</td>
<td>-0.068±0.005</td>
</tr>
<tr>
<td>ZnAr (^C\Pi_1)</td>
<td>0.0808</td>
<td>0.3767</td>
<td>-1.21</td>
<td>-1.21</td>
</tr>
<tr>
<td>H(_2^+) X (^2\Sigma_u^+)</td>
<td>2.867</td>
<td>0.1626</td>
<td>0.329</td>
<td>0.318</td>
</tr>
</tbody>
</table>

\( Q=0 \) are presented for the various species. The Morse parameters are then determined using eqs. (27), (29), and (32). The results are given in table 3. Over a broad range of bond length shifts, the calculated results \( \delta_{\text{e}} \) here are in excellent agreement with the literature values \( \delta_{\text{e}} \) determined by FC analysis using a Morse potential. For the ZnAr complex, where it has been postulated that a single Morse potential is adequate to describe the excited state potential, even the dissociation energy \( D_{\text{om}} \) and anharmonicity \( \frac{1}{2}\hbar \omega_{\text{c}}\alpha^2 \) agrees with the literature [11]. In the case of H\(_2^+\) \((X\ ^2\Sigma_u^+)\) and Te\(_2\) \((^2\Pi_{3/2})\), the calculated \( D_{\text{om}} \) gives a good estimate of the experimental dissociation energy. But, in the case of Se\(_2\) \((^2\Pi_{3/2})\), the large value of \( D_{\text{om}} \) and the small value of \( \alpha \) for the Morse fit is an indication that the FC region of the excited state surface is close to being harmonic. This is in contrast to Te\(_2\) \((^2\Pi_{3/2})\) where the FC region is better described by a Morse fit, even though the two molecular ions are quite similar.

4. Conclusion

In principle, we should use as much information as possible to determine the excited state potential energy surface. But if we seek a harmonic (or Morse) approximation to the excited state surface then clearly there are only two (or three) parameters to determine, excluding the minimum energy of the potential which usually can be read off the spectrum. Just two (or three) pieces of information would suffice. We have presented a method using the minimum information – the first and second spectral moments of the absorption profile – to determine the harmonic approximation to the excited state potential in the FC region. This method gives the harmonic fit to the excited state potential at \( Q=0 \), in contrast to the harmonic FC analysis which gives only an average potential whose interpretation is unclear. The moment method has been shown to be able to give the sign of the bond-length change even with the harmonic approximation. The information from the harmonic fit is used to construct the Morse potential. The three conditions used for the Morse approximation are the slope at \( Q=0 \), the Morse frequency, and the classical result for the first moment. The method described in this paper is computationally more efficient than a FC analysis to fit the absorption spectrum, and the excellent results for a wide range of bond length shift indicate that it can be a replacement for FC analysis.
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References