

# Morse Oscillators, Birge-Sponer Extrapolation, and the Electronic Absorption Spectrum of I<sub>2</sub>

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## The Absorption Spectrum of I<sub>2</sub>

The visible spectrum of gaseous I<sub>2</sub> affords a most interesting and instructive experiment for advanced undergraduates. Analysis of the electronic absorption spectrum, measured at intermediate resolution (vibrational progressions resolved; rotational fine structure unresolved), was described in *this Journal* by Stafford (1), improving the initial presentation of Davies (2). (Assignment of vibrational quantum numbers  $v'$  to the bands of the excited B electronic state of I<sub>2</sub> was corrected in two key papers, by Steinfeld et al. (3) and by Brown and James (4).) Improvements both in experimental techniques and in data analysis applied to the I<sub>2</sub> absorption spectrum continued to be presented in *this Journal* (5-9). Instructions for the I<sub>2</sub> experiment also appear in several physical chemistry laboratory manuals (10-14). Steinfeld's excellent spectroscopy textbook (15) often reproduces parts of the actual spectrum of I<sub>2</sub> as examples.

Birge-Sponer extrapolation is one method often used to analyze the visible absorption spectrum of I<sub>2</sub>. All measured differences  $\Delta G$  between adjacent vibrational energy levels  $v' + 1$  and  $v'$  are plotted against vibrational quantum number  $v'$ . The differences between all adjacent vibronic band head energies observed in the usual undergraduate laboratory experiment on I<sub>2</sub> give a nicely linear Birge-Sponer plot. Thus, these vibrational energy levels (which do not include 20 to 30 levels at very high values of  $v'$ ) of the excited B electronic state can be accurately described as those of an anharmonic oscillator with a single anharmonic term. This, in turn, implies that the potential well governing the vibrations up to the maximum  $v'$  observed in these experiments is closely approximated by a Morse potential function.

### What is the Correct Procedure for Birge-Sponer Extrapolation?

Unfortunately, many sources, including some in the references, give incomplete, ambiguous, or self-contradictory descriptions of the Birge-Sponer extrapolation method.

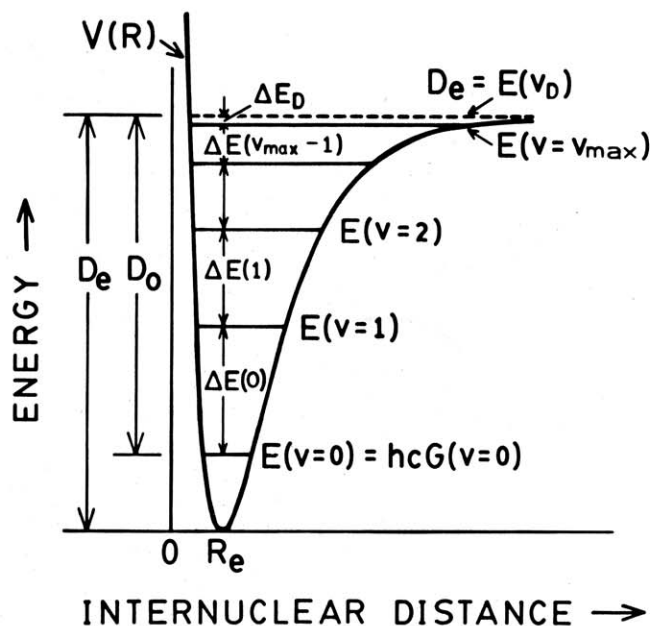


Figure 1. Morse potential curve and vibrational energy levels.

Equations for determining spectroscopic parameters presented in different sources are not consistent with each other. Several erroneous presentations are common. This paper aims to give a complete, correct exposition of Birge-Sponer extrapolation for the special case in which the plot derived from the observed data is taken as exactly linear.

If extrapolation beyond the observable differences is assumed to be strictly linear in both directions, and particularly toward the dissociation limit, then a Morse function would exactly describe the vibrational potential for the diatomic oscillator. For real molecules this is not strictly cor-

rect, but the Morse potential is often a good approximation. Also, the analysis of actual molecular spectral data in terms of this exactly soluble problem in quantum mechanics should be clear and unambiguous.

A schematic diagram of a Morse potential, with its quantized vibrational energy levels, and pictorial definitions of various terms used in the following discussion, is shown in Figure 1.

### Morse Oscillators

In 1929, Morse (16) introduced a convenient two-parameter analytical function to approximate the shape of the anharmonic potential energy curve for a diatomic molecular oscillator:

$$V(R) = D_e \left( 1 - e^{-\beta(R - R_e)} \right)^2 \quad (1)$$

The Schrödinger equation for a particle of reduced mass  $\mu$  in this potential can be solved exactly. The energy levels are given by

$$E(v) = h\nu_e(v + 1/2) - h\nu_e x_e(v + 1/2)^2 \quad v = 0, 1, 2, \dots \quad (2)$$

With the conventional spectroscopic units of wavenumber ( $\text{cm}^{-1}$ ), these quantized levels are often written in the following form.

$$\frac{E(v)}{hc} = G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \quad v = 0, 1, 2, \dots \quad (3)$$

There are no higher order terms. The energy levels of a Morse oscillator are given by a harmonic oscillator term plus a single anharmonic correction term, which is precisely what is required for the linear Birge-Sponer extrapolation procedure to be valid.  $D_e$  is the depth of the vibrational potential well;  $\beta$  governs the curvature at  $R_e$ , and thus the force constant  $k_e$ .

$$k_e = 2D_e\beta^2 \quad (4)$$

$D_e$  and  $\beta$  determine the fundamental vibration frequency,  $\nu_e = c\omega_e$ , and the anharmonicity,  $\nu_e x_e = c\omega_e x_e$ :

$$\omega_e = \frac{2\hbar\beta}{hc} \left( \frac{D_e}{2\mu} \right)^{1/2} \quad (5)$$

$$\omega_e x_e = \frac{1}{hc} \left( \frac{\hbar^2 \beta^2}{2\mu} \right) \quad (6)$$

Once  $\omega_e$  and  $\omega_e x_e$  are found from analysis of the spectrum, the well depth  $D_e$  for the Morse oscillator can be determined exactly:

$$\frac{D_e}{hc} = \frac{\omega_e^2}{4\omega_e x_e} \quad (7)$$

The zero-point energy  $E_{(v=0)}$  of the Morse oscillator is given by

$$\frac{E_{(v=0)}}{hc} = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} \quad (8)$$

Subtracting  $E_{(v=0)}$  from  $D_e$  gives the bond dissociation energy  $D_0$ :

$$\frac{D_0}{hc} = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e} \quad (9)$$

A key feature of the vibrational energy levels in a Morse potential is that the number of bound states is finite; the integer vibrational quantum numbers  $v$  for the bound states have a maximum possible value  $v_{\text{max}}$ , governed by the following inequality.

$$v_{\text{max}} < \frac{(2\mu D_e)^{1/2}}{\hbar\beta} - \frac{1}{2}$$

or

$$v_{\text{max}} < \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \quad (10)$$

Moreover, in order to correspond to a finite, normalizable wave function, the highest quantized vibrational energy level must be less than the well depth;  $E(v_{\text{max}})$  cannot be exactly equal to  $D_e$ . The difference  $\Delta E_D$  between the dissociation limit  $D_e$  and the highest quantized level  $E(v_{\text{max}})$  must obey a related inequality:

$$0 < \frac{\Delta E_D}{hc} \leq \omega_e x_e \quad (11)$$

Both inequalities result from the condition put on all physically meaningful bound states: the vibrational wave function must vanish as the internuclear distance  $R$  goes to infinity (17).

As a Morse oscillator approaches dissociation, the density of states does *not* increase without limit, and the energy level spacing does not approach zero, in contrast to the pattern in certain other bound systems, for example, the hydrogen atom. Finally, there is no necessary relationship between the values of the two parameters  $D_e$  and  $\beta$  defining any Morse potential. Thus,  $\omega_e$  and  $\omega_e x_e$  can also have any arbitrary ratio greater than 1.

### Birge-Sponer Extrapolation

Both  $\omega_e$  and  $\omega_e x_e$  are often obtained from spectroscopic data by a graphical method introduced by Birge and Sponer (18). For any two adjacent vibrational energy levels of a Morse oscillator,

$$\begin{aligned} \Delta G(v) &= G(v+1) - G(v) = \omega_e - \omega_e x_e(2v+2) \\ &= (\omega_e - 2\omega_e x_e) - 2\omega_e x_e v \end{aligned} \quad (12)$$

or equivalently,

$$\Delta G(v + 1/2) = (\omega_e - \omega_e x_e) - 2\omega_e x_e(v + 1/2) \quad (13)$$

The spacings between adjacent vibrational energy levels decrease as a linear function of the quantum number  $v$  or, alternatively, of the variable  $v + 1/2$ . The second differences are constant:

$$\Delta(\Delta G) = \Delta G(v+1) - \Delta G(v) = -2\omega_e x_e$$

All the Morse potential parameters can be found analytically, of course, using equally well the line defined by either eq 12 or eq 13. However, a closer look at the geometrical properties of the plot and its commonly presented interpretation shows why it is far better, particularly for pedagogical purposes, to make a Birge-Sponer extrapolation from a plot of  $\Delta G$  vs.  $v + 1/2$  rather than  $\Delta G$  vs.  $v$ . A proper Birge-Sponer plot of  $\Delta G$  vs.  $v + 1/2$ , corresponding to the energy levels of Figure 1, is shown in Figure 2.

The discrete values  $\Delta G$  define a line (eq 13). From its slope,  $-2\omega_e x_e$ , the anharmonicity parameter  $\omega_e x_e$  is found. This value is then used with the ordinate intercept of the line,  $\omega_e - \omega_e x_e$ , to determine the wavenumber  $\omega_e$  corresponding to the fundamental vibration frequency  $\nu_e$  in the harmonic oscillator approximation. All the parameters of

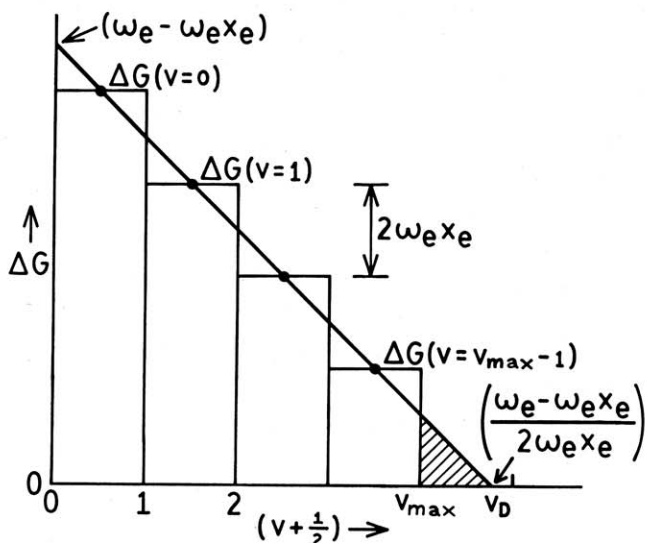


Figure 2. Linear Birge-Sponer plot of  $\Delta G$  vs.  $v + 1/2$ .

the Morse potential can now be determined. In particular, eqs 7 and 9 can be used to calculate  $D_e$  and  $D_0$ .

#### Typical Sources of Error

In the Birge-Sponer plot (Fig. 2) the area of the triangle under the line between the ordinate intercept and the abscissa intercept is exactly equal to  $D_0/hc$  (compare with eq 9):

$$\text{Area} = \frac{1}{2} \left( \frac{\omega_e - \omega_e x_e}{2\omega_e x_e} \right) (\omega_e - \omega_e x_e) = \frac{(\omega_e - \omega_e x_e)^2}{4\omega_e x_e} = \frac{D_0}{hc} \quad (14)$$

This is so because that area corresponds, as Figure 1 makes clear, to the following sum, by which the value of  $D_0$  can be expressed:

$$\frac{D_0}{hc} = \left( \sum_{v=0}^{v=v_{\max}-1} \Delta G(v) \right) + \frac{\Delta E_D}{hc} \quad (15)$$

#### The Contributions

The last term in eq 15 is almost always either omitted, because an unnecessary approximation is made, or erroneously included within the sum, which is incorrectly written to run to  $v = v_{\max}$ . Clearly,  $D_0/hc$ , the area of the large triangle in Figure 2, equals the sum of the areas of all the rectangular strips, each with height  $\Delta G(v + 1/2)$  and unit width, plus the area of the little shaded triangle. I will comment on each contribution in turn.

If the plot were of  $\Delta G$  vs.  $v$  rather than  $\Delta G$  vs.  $v + 1/2$ , the area under the line would not equal  $D_0/hc$ . Then just a bit more than half the value of  $\Delta G(v=0)$ , the area of the first and largest strip in the correct plot, would be left out, and  $D_0$  would be seriously underestimated.

The error in  $D_0/hc$  would in general be

$$\frac{\omega_e}{2} - \frac{3\omega_e x_e}{4}$$

For the B state of  $I_2$  this is  $\approx 65 \text{ cm}^{-1}$ . If students are told to calculate the area of the triangle in the Birge-Sponer plot to find  $D_0/hc$ , the plot must be made correctly.

The area of the little shaded triangle in Figure 2 is equal to  $(D_e - E(v_{\max}))/hc$ . It corresponds exactly to the energy

difference  $\Delta E_D$ , shown in Figure 1, between the well depth  $D_e$  and the highest quantized vibrational energy level  $E(v_{\max})$ . Recall that  $\Delta E_D$  bears no necessary relation to the pattern of quantized  $E$  values, or the corresponding  $\Delta G$  values, for integral  $v$ . For the special case when  $D_e$  accidentally equals exactly  $E(v_{\max} + 1)$ , the numerical value of  $\Delta E_D/hc$  is expressed by  $\omega_e x_e = \Delta G(v_{\max})$ . The highest bound state in this case, however, is still the one with  $v = v_{\max}$ ; there is no Morse oscillator wave function corresponding to  $E(v_{\max} + 1) = D_e$ . Therefore, no rectangular strip is drawn for  $\Delta E_D/hc$  in Figure 2, and it is treated as a distinct separate term in eq 15.

The highest vibrational quantum number  $v_{\max}$  is the largest integer less than  $(\omega_e - \omega_e x_e)/2\omega_e x_e$ , the value of the abscissa intercept. To what value does the abscissa intercept (which is generally nonintegral) itself correspond?

#### Extrapolation in Incorrect Terms

Birge-Sponer extrapolation is often incorrectly explained in terms of the intercept at  $\Delta G = 0$  and the supposed significance of the corresponding  $v_{(\Delta G=0)}$ , with  $v$  treated as a continuous variable:

$$\Delta G = 0$$

when

$$v + 1/2 = \frac{\omega_e - \omega_e x_e}{2\omega_e x_e} = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \quad (16)$$

or equivalently, when

$$v = v_{(\Delta G=0)} = \frac{\omega_e}{2\omega_e x_e} - 1 \quad (17)$$

The value  $v_{(\Delta G=0)}$  does not correspond to  $v_{\max}$ , except accidentally for the special case when

$$\Delta E_D/hc = \omega_e x_e/4$$

In general,  $v_{(\Delta G=0)}$  is a noninteger in the range

$$(v_{\max} - 1/2) < v_{(\Delta G=0)} \leq (v_{\max} + 1/2)$$

Moreover,  $v_{(\Delta G=0)}$ , treating  $v$  as a continuous variable, does not correspond to  $v_D$ , defined as the value of  $v$  at the dissociation limit, because

$$G_{(v=v_{(\Delta G=0)})} = \frac{D_e}{hc} - \frac{\omega_e x_e}{4} \quad (18)$$

In short, the quantity  $v_{(\Delta G=0)}$  has no physical significance at all.

The correct value  $v_D$  corresponding exactly to the dissociation limit, at which  $G_{(v=v_D)} = D_e/hc$ , is

$$v_D = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} = \frac{\omega_e - \omega_e x_e}{2\omega_e x_e} = v_{(\Delta G=0)} + \frac{1}{2} \quad (19)$$

This is also clearly shown by the proper Birge-Sponer plot (Fig. 2) of  $\Delta G$  vs.  $v + 1/2$ , where  $v_D$  exactly equals the value of the abscissa intercept. In this plot, each strip is bounded left and right by successive integer values of  $v$ . The abscissa intercept is simply the upper bound of a hypothetical last strip, with integer lower bound  $v_{\max}$ , and an area  $\Delta E_D/hc$  equal to the area of the shaded triangle. Generally,  $v_D$  is nonintegral, except for the special case when  $\Delta E_D/hc = \omega_e x_e$ , its maximum possible value.

The distinction between  $v_{(\Delta G=0)}$  and  $v_D$  can also be understood analytically. Equations 12 and 13 for  $\Delta G$  are by definition expressions for finite differences  $\Delta v = 1$ . Thus, the

condition  $\Delta G = 0$  does not correspond exactly to  $D_e/hc$ , the maximum value of  $G$ . Then  $v_D$  is defined as that value of  $v$ , treated as a continuous variable, for which  $G(v) = D_e/hc$ , the maximum in the parabolic function  $G(v)$ . Thus,  $v_D$  is correctly found by setting the derivative of  $G$  with respect to  $v$  equal to zero, and solving for  $v = v_D$ :

$$\frac{dG(v)}{dv} = \omega_e - 2\omega_e x_e(v + 1/2) = 0 \quad (20)$$

This gives for  $v_D$  the value in eq 19, precisely equal to the abscissa intercept on a Birge–Sponer plot of  $\Delta G$  vs.  $v + 1/2$ .

### Application of Birge–Sponer Extrapolation to Real Data

To apply the method to actual spectroscopic data, a least-squares line should be fit to a plot of the measured  $\Delta G$  vs.  $v + 1/2$ . If “hot” bands are seen (so that  $\Delta G$  data come from several vibronic progressions, originating in different vibrational levels of the ground electronic state and going to vibrational levels of the same excited electronic state) then all the data should be used in the same Birge–Sponer plot to find the parameters of the upper state. For good results, it is important to calibrate the wavelength scale of the spectrophotometer. For  $I_2$ , the band head positions (i.e., the data measured in the usual undergraduate experiment) are very good approximations to the positions of the band origins (6, 15).

Students in the advanced laboratory course at Barnard College apply linear Birge–Sponer extrapolation to band head data from the three overlapping vibrational progressions they see in the visible absorption spectrum arising from the  $B \leftarrow X$  electronic transition of  $I_2$ . Over the past 15 years typical student data has yielded results for the B state in the ranges ( $\text{cm}^{-1}$ ) shown in the table from measurements on the following transitions.

- $v' = 12 - 61 \leftarrow v'' = 0$
- $v' = 13 - 28 \leftarrow v'' = 1$
- $v' = 6 - 19 \leftarrow v'' = 2$

McNaught warns against too facile comparison of student results with literature values (6). Older values may have been revised or reinterpreted. Newer data analyses use fitting methods more sophisticated than Birge–Sponer plots, so not all parameters are comparable. Student results also depend on instrument calibration, resolution, and extent of data. We believe the most useful reference values for comparison are those shown in the table.

Accurate high resolution spectroscopy shows that values of  $D_e$  estimated by simple linear Birge–Sponer extrapolation are systematically incorrect. The discrepancy arises principally from the departure of successive term differences from linearity at high  $v$ , approaching the dissociation limit. The Morse potential does not adequately represent the long-range attractive forces between the two atoms of a diatomic molecule at large separations. For the excited B state of  $I_2$ , however, this inadequacy becomes apparent only at very high values of  $v'$ . These are usually difficult or impossible to observe because these transitions have such low intensities.

### Correct Extrapolation as $v$ Approaches the Dissociation Limit

More accurate methods for large  $v$  that take into account the actual long-range potentials are discussed in Steinfeld

## Typical Student Data Compared to Literature Values

Student Data	
$\omega_e$	127–135
$\omega_e x_e$	0.94–1.05
$D_0/hc$	4171–4422
$D_e/hc$	4236–4490
Literature Values	
$\omega_e$	132.1 $\text{cm}^{-1}$
$\omega_e x_e$	1.05 $\text{cm}^{-1}$
	(fit of band head data to a Morse potential (6))
$D_e/hc$	4391 $\text{cm}^{-1}$
	(estimate of actual well depth (3))

(15). In an elegant application to  $I_2$ , Le Roy and Bernstein (19) used an extrapolation appropriate to a potential  $V(R) = D_e - CR^{-5}$  at large internuclear separation  $R$ . This is the correct potential between the  $J = 1/2$  and  $J = 3/2$  atoms into which  $I_2$  in the B state dissociates. The fit to the  $I_2$  data at very high values of  $v'$  is excellent. Thus, this extrapolation provides an accurate determination of the energy at the dissociation limit, which lies just above  $v'_{\text{max}} = 87$ . (Linear Birge–Sponer extrapolation using  $\Delta G$  up to  $v' = 50$  underestimates the dissociation limit of this state by 140  $\text{cm}^{-1}$  (20).) An even more elaborate analysis, applying a power series in  $R^{-m}$ , of the long-range potential curves of the excited B electronic states in the series  $I_2$ ,  $\text{Br}_2$ , and  $\text{Cl}_2$  was given by Le Roy (21).

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