

NEAR-DISSOCIATION EXPANSIONS IN THE SPECTROSCOPIC DETERMINATION OF DIATOM DISSOCIATION ENERGIES: METHOD, AND APPLICATION TO BeAr⁺

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A simple method for determining improved diatomic molecule dissociation energies by imposing the theoretically-known limiting behaviour at dissociation on experimental vibrational data which *do not* include levels lying in the limiting near-dissociation region is described and demonstrated. Its application to BeAr⁺(X²Σ⁺) yields $\mathcal{D}_e = 4500 (\pm 50) \text{ cm}^{-1}$ and $\nu_D = 40.8 (\pm 0.5)$.

1. Introduction

It has long been known [1,2] that analysis of vibrational level spacings is generally the most accurate way of determining diatomic molecule dissociation energies. For more than forty years the accepted way of doing so was that suggested in 1926 by Birge and Sponer [3], who pointed out that the area under the correctly extrapolated $\Delta G_{v+1/2}$ versus v curve provides a good estimate of the binding energy of the highest observed level. Unfortunately, uncertainty regarding the shape of the extrapolated curve can introduce considerable error into the resulting dissociation energy. An illustration of this weakness is provided by the Birge-Sponer plot for the ground (X²Σ⁺) state of BeAr⁺, seen in fig. 1; the points represent the four vibrational spacings observed by Subbaram et al. [4] while the dashed curve was generated from their vibrational constants. The area of the shaded region corresponds to an uncertainty of 16–18% in the predicted dissociation energy (or 23–80% of the $v = 4$ binding energy), and in the absence of external constraints, other extrapolations lying well outside this shaded region would be equally plausible. It is therefore clear that the traditional approach can provide only a rough estimate of the dis-

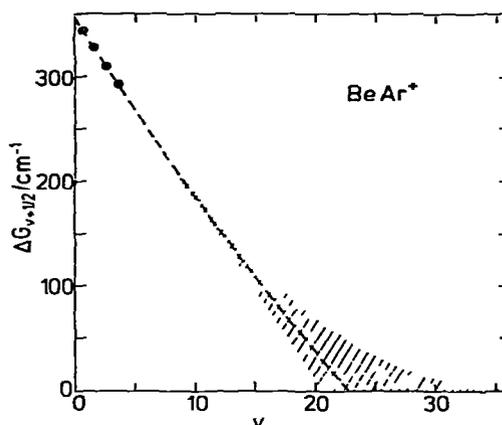


Fig. 1. Birge-Sponer plot for BeAr⁺(X²Σ⁺) with data (points) and vibrational constants defining the extrapolated (dashed) curve taken from ref. [4].

sociation energy for cases involving such long extrapolations.

A means of improving the accuracy of such extrapolations was introduced ten years ago when Le Roy and Bernstein [5,6]. (1) showed that the spacings of vibrational levels lying very near dissociation depend mainly on the asymptotically-dominant inverse-power contribution to the interatomic potential,

$$V(r) \approx \mathcal{D} - C_n/r^n, \quad (1)$$

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and (ii), for such levels derived the simple expression

$$dG(v)/dv = K_n [\mathcal{D} - G(v)]^{(n+2)/2n}, \quad (2)$$

and its integrated form (for $n \neq 2$)[‡]

$$G(v) = \mathcal{D} - X_0(n)(v_D - v)^{2n/(n-2)}. \quad (3)$$

For $n > 2$ the integration constant v_D corresponds to the non-integer effective vibrational index at the dissociation limit[‡], while $X_0(n)$ and $K_n = [2n/(n-2)] \times [X_0(n)]^{(n-2)/2n}$ are constants depending only on n , C_n and the diatom reduced mass μ ; in particular,

$$X_0(n) = \bar{X}_0(n)/[\mu^n(C_n)^2]^{1/(n-2)}, \quad (4)$$

where for energies in cm^{-1} , lengths in \AA and masses in amu the numerical constant $\bar{X}_0(n) = 7931.949, 9170.911, 13432.66, 36409.61$ and 0.01483008 for $n = 6, 5, 4, 3$ and 1 respectively. Another useful form of this result is that obtained by differentiating eq. (3):

$$dG(v)/dv = [2n/(n-2)]X_0(n)(v_D - v)^{(n+2)/(n-2)}. \quad (5)$$

For virtually any molecular state, the power n in eq. (1) is readily obtained from a knowledge of the electronic states of the atomic dissociation products and (sometimes also) the identity of the molecular electronic state [7]. Moreover, reasonably reliable values of the asymptotically-dominant potential coefficient C_n may be readily calculated for many species. Thus, the limiting near-dissociation behaviour of the distribution of vibrational levels for a given species is often accurately known even in the complete absence of experimental data. In spite of this, most utilization of eqs. (2)–(5) has involved their direct application to data for levels lying very near dissociation where they are expected to be quantitatively correct. For such cases (see, e.g. refs. [5–11]) this did prove to be an excellent way of determining accurate values of \mathcal{D} and C_n . However, the work of Tellinghuisen et al. [12] and Wilcomb and Bernstein [13] suggests that this knowledge of the correct functional behaviour at dissociation will probably be most important in cases where the available data *do not include* any levels lying in the limiting region where these equations are valid. These authors noted that since the approximation that $dG(v + \frac{1}{2})/dv \approx \Delta G_{v+1/2}$ allows eq. (2) to be rewritten as

[‡] Analogous results for $n = 2$ and other special cases are discussed in ref. [6].

$$(\Delta G_{v+1/2})^{2n/(n+2)} = (K_n)^{2n/(n+2)} [\mathcal{D} - \bar{G}(v + \frac{1}{2})], \quad (6)$$

where $\bar{G}(v + \frac{1}{2}) = [G(v) + G(v + 1)]/2$, the intercept of an extrapolated plot of $(\Delta G_{v+1/2})^{2n/(n+2)}$ versus $\bar{G}(v + \frac{1}{2})$ which is constrained to have the theoretically-known limiting slope, $(K_n)^{2n/(n+2)}$, provides an improved estimate of \mathcal{D} . This approach effectively replaces a Birge–Sponer type extrapolation by an *interpolation* between the known limiting near-dissociation behaviour and the experimental data at low v . However, its graphical nature makes the uncertainties associated with it both relatively large and rather difficult to estimate. The present work therefore presents a simple procedure for making this type of “interpolation” more quantitative.

2. Method

One way of improving on eqs. (2)–(6), suggested in ref. [7], consists of the derivation and application of generalized versions of these equations which take account of one or more additional inverse-power contributions to the long-range potential of eq. (1). However, Stwalley [14] outlined some drawbacks of this approach, and tests have shown [15] that it does not explain the observed deviations from the (correctly-predicted) limiting behaviour. The present work therefore follows the lead of Beckel and co-workers [16] in using empirical correction functions whose parameters have no physical significance, to generalize eq. (3).

The traditional way [1,2] of representing a set of vibrational level energies utilizes an expansion in power of $(v + 1/2)$. The essence of the present approach is that this power series should be replaced by an empirical “near-dissociation expansion” which explicitly incorporates the correct limiting behaviour of eq. (3), and contains additional empirical parameters for taking account of the observed behaviour at low v . The two such expansions considered here are identified as an “ N_a -expansion”

$$G(v) = \mathcal{D} - X_0(n)(v_D - v)^{2n/(n-2)} \times [1 + a_1(v_D - v) + a_2(v_D - v)^2 + \dots], \quad (7)$$

and an “ N_b -expansion”

$$G(v) = \mathcal{D} - X_0(n)(v_D - v)^{2n/(n-2)} \times [1 + b_1(v_D - v) + b_2(v_D - v)^2 + \dots]^{2n/(n-2)}, \quad (8)$$

where the value of the parameter N_a or N_b indicates the number of correction terms included in the expansion [for $N_a = 0$ and $N_b = 0$, eqs. (7) and (8) reduce to eq. (3)]. Application of these expressions involves the use of nonlinear least-squares fits to determine values for the molecular parameters \mathcal{D} and v_D and for the expansion coefficients $\{a_i\}$ or $\{b_i\}$, while the remaining variables n and C_n [and hence $X_0(n)$] are held fixed at their theoretically-known values. This latter point is a crucial difference between the present work and that of Beckel and co-workers [16] who treated n and C_n as additional parameters to be determined from the fits. As will be seen below, holding these quantities fixed at their known values is essential if this approach is to yield reliable extrapolations.

As in any non-linear least-squares procedure, realistic initial trial values for the parameters are required before the fit can proceed. This presents little difficulty as plausible trial values of \mathcal{D} and v_D may be readily obtained from the graphs suggested by eq. (6) and the analogous rearrangement of eq. (5):

$$(\Delta G_{v+1/2})^{(n-2)/(n+2)} = \{[2n/(n-2)]X_0(n)\}^{(n-2)/(n+2)}(v_D - v - \frac{1}{2}). \quad (9)$$

Fits to linearized rearrangements of eqs. (7) and (8) may then be used to provide initial estimates of the $\{a_i\}$ or $\{b_i\}$ parameters. Alternatively, initial trial parameters for a given value of N_a or N_b may be chosen as the converged $(N_a - 1)$ or $(N_b - 1)$ parameters, plus $a(N_a) = 0$ or $b(N_b) = 0$, respectively. An annotated listing of a program which automatically generates the trial values and performs these non-linear fits, may be obtained from the first author (R.J.L.).

The only remaining problem is that of determining optimum values of \mathcal{D} and v_D and realistic estimates of their uncertainties from the results of fits to versions of eqs. (7) and (8) corresponding to different values of N_a or N_b . Each of these fits yields independent estimates of \mathcal{D} and v_D and of their uncertainties. The latter reflect a combination of the quality of fit and the amount of correlation associated with that particular model, and are typically much smaller than the differences between the results for the diverse values of N_a or N_b . Thus, model-dependence is the main source of the uncertainty in the final results. The recommended values of \mathcal{D} and v_D presented here were therefore defined as weighted averages of the values obtained

from the various fits, where each weight is proportional to the squared inverse of the parameter uncertainty yielded by that fit. An estimate of the uncertainty is then provided by the analogously-weighted root mean square deviation from the mean. As an additional refinement, one could delete from these averages results corresponding to fits whose standard errors are one or two orders of magnitude larger than the uncertainty in the data; however, the weighting described above makes this modification have little effect on the final values. A nice feature of this procedure is the fact that it obviates the need to define one particular fit as "best".

3. Application to the ground ($X^2\Sigma^+$) state of BeAr⁺

For the ground state of BeAr⁺, $n = 4$ and the theoretical $C_4 = 95340 \text{ cm}^{-1} \text{ \AA}^4$, calculated [7] from the Ar polarizability recommended by Teachout and Pack [17], yields $X_0(4) = 2.6053 \times 10^{-3} \text{ cm}^{-1}$. Holding these parameters fixed and with N_a and N_b in turn equal to 0, 1 and 2, eqs. (7) and (8) were fitted to the five vibrational energies reported by Subbaram et al. [4]. The resulting values of \mathcal{D}_e , v_D and of the standard error of the fit, σ , are summarized in fig. 2. The rapid

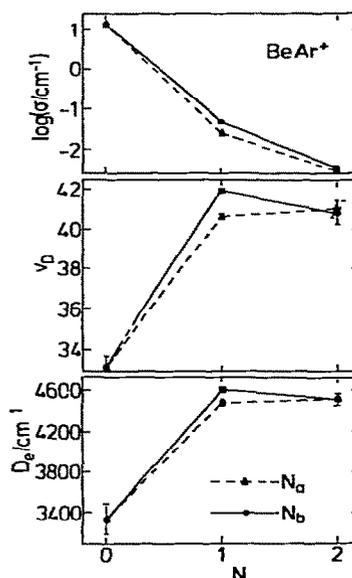


Fig. 2. Results of fitting eqs. (7) (triangular points, dashed lines) and (8) (round points, solid lines) to experimental data [4] for BeAr⁺($X^2\Sigma^+$).

decrease in σ and convergence of the fitted values of \mathcal{D}_e and ν_D attests to the significance of the present procedure. Averaging the fitted parameters in the manner outlined above then yields the present recommended results: $\mathcal{D}_e = 4499 (\pm 71) \text{ cm}^{-1}$ and $\nu_D = 40.78 (\pm 0.75)$. Alternately, following the "more refined" approach and deleting the obviously unrealistic $N_a = N_b = 0$ results from these averages yields the virtually identical \mathcal{D}_e and ν_D values $4501 (\pm 51) \text{ cm}^{-1}$ and $40.82 (\pm 0.47)$, respectively. This new dissociation energy is distinctly larger than previous estimates [4,18] based on the same data, $4112 (\pm 200)$ and $4157 (\pm 380) \text{ cm}^{-1}$, while the ν_D value indicates that this state has almost *twice* the number of vibrational levels predicted by the vibrational constants of ref. [4]. Moreover, changing the present assumed theoretical value of C_4 by $\pm 10\%$ changed these recommended \mathcal{D}_e and ν_D values by less than the quoted uncertainties.

While the present method requires performing non-linear least-squares fits to eqs. (7) and (8), it is useful to illustrate the results using graphs of the type suggested by eqs. (6) and (9). These graphs are shown in figs. 3 and 4; the points represent the experimental data, the solid curves were generated from the results of the present fits, and the dashed curves were generated from the vibrational constants (ω_e , $\omega_e x_e$ and $\omega_e y_e$) of ref. [4]. The intervals labelled SCJ and GHW in fig. 3 indicate the range of uncertainties of the dissociation energies of refs. [4] and [18], respectively. Note that in each plot, the slope of the $N_a = N_b = 0$ line and the slopes at their intercepts of the four solid curves, are exactly equal.

Fig. 3 is the type of plot used by Tellinghuisen et al. [12] and Wilcomb and Bernstein [13] for extrapolating to determine dissociation energies, while fig. 4 is the near-dissociation theory's analog of the Birge-Sponer plot of fig. 1. The contrast between the uncertainty of the fig. 1 extrapolation and the close agreement among the results of fits to different versions of eqs. (7) and (8), imposed by the requirement that they all have the same limiting behaviour, is quite striking. Moreover, the similarity of the four curves for $(N_a, N_b) \neq (0, 0)$, seen in figs. 3 and 4, indicates that there will be little disagreement about the predicted energies of the unobserved levels. These figures also illustrate the fact that without the value of the limiting slope provided by knowledge of the C_4 constant (i.e. with C_4 treated as a free parameter in the fits), it would be impossible

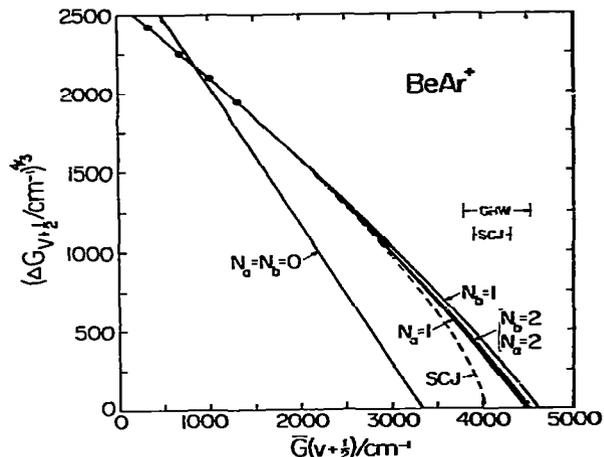


Fig. 3. Plot suggested by eq. (6) for $\text{BeAr}^+ (X^2\Sigma^+)$, comparing present extrapolations (solid curves) with that implied by the vibrational constants of ref. [4] (dashed curve); SCJ is ref. [4] and GHW ref. [18].

for the present approach to yield reliable estimates of \mathcal{D} and ν_D . At the same time, knowledge of this potential constant need not be extremely precise, as demonstrated by the small effect of the 10% changes in the C_4 used in the present analysis.

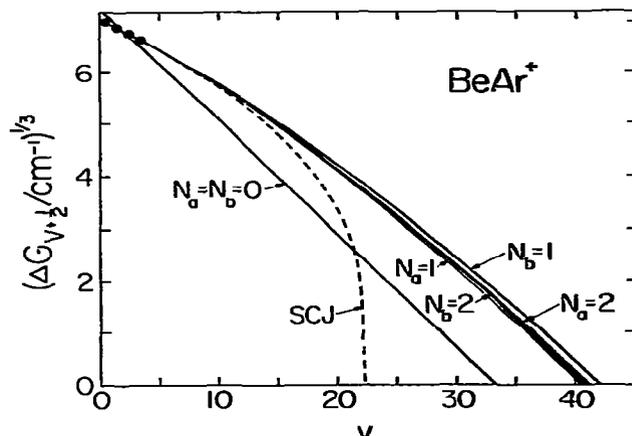


Fig. 4. Plot suggested by eq. (9) for $\text{BeAr}^+ (X^2\Sigma^+)$, as in fig. 3.

4. Discussion

The main source of error in the present method is the model-dependence of the fitted parameter values, i.e. their dependence on the functional form used for expanding about the limiting behaviour of eq. (3). To obtain highly reliable results would require an average of estimates obtained from as wide a variety of such functions as possible. In this regard, an obvious generalization of eqs. (7) and (8), suggested by the work of Beckel and co-workers [16], is the replacement of each of the present polynomial correction functions by a Padé approximant (a ratio of polynomials). However, preliminary results indicate that this generalization has little effect on the recommended \mathcal{D}_e and ν_D values for BeAr^+ .

For every system for which the availability of data near dissociation has allowed eqs. (2)–(5) to be tested, their validity has been confirmed. Thus, with the exception of situations complicated by curve crossings or potential maxima, the *best possible estimate* of the dissociation energy and of the number and energies of unobserved levels should be provided by the type of approach proposed here. In such analyses, n should always be held fixed at its theoretically-known value, and unless the experimental data include several levels lying in the limiting region, so should C_n .

Just as near-dissociation expressions analogous to eq. (3) have been derived for rotational and centrifugal distortion constants [19,20] and for many other molecular properties [21,22], so expansions analogous to eqs. (7) and (8) may be used for these properties as well. In this regard, an RKR potential calculated from such near-dissociation expansion expressions for $G(v)$ and the rotational constant B_v should yield potential curve extrapolations as reliable as or better than those obtainable in any other way. The drastic change in the total number of bound BeAr^+ levels implied by the present results indicates that use of these expansions will also have important implications with regard to the calculation of thermodynamic properties. This further emphasises the importance of the further development and systematic application of theoretical methods for calculating the long-range potential constants C_n .

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