Direct determination of long-range inverse-power potential coefficients from spectroscopic data

Mark R. Davies, John C. Shelley, and Robert J. Le Roy

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3GI

(Received 8 October 1990; accepted 26 November 1990)

This paper presents and tests a method for determining the set of inverse-power coefficients defining the long-range potential tail of a given molecular state by least-squares fitting directly to the energies and inertial rotational constants \(B_j\)'s of vibrational levels lying very near dissociation. This approach is superior to the widely used procedure of determining potential points by some inversion procedure and fitting them to the inverse-power form, in that the fit is directly sensitive to the uncertainties in the experimental quantities, and that the parameter uncertainties due to interparameter correlation are greatly reduced. Moreover, the new method gives direct estimates of the number, energies, and other properties of unobserved levels lying above those being fitted. Improved results, including potential parameters up to \(C_{10}\), are presented for the \(B(3\Pi_{u}^+)\) state of \(I_2\).

I. INTRODUCTION

It has long been known that the long-range interaction potential between two atoms may be expressed as the sum of inverse-power terms,1,2

\[
V(R) = D - \sum_{m>n} C_m/R^m, \tag{1}
\]

where \(D\) is the energy at the molecular dissociation limit, the powers \(m\) are positive integers, and the electronic states of the atoms yielded on dissociation determine which terms contribute to this sum and sometimes also determines their sign.1-6 Over the years, a variety of theoretical methods have been developed for predicting the values of the inverse-power potential coefficients \(C_m\).1-3,7-9 However, most attention has been focused on lower-order terms corresponding to \(m<6\), and most methods are only valid for describing the interactions between ground-state atoms. At the same time, it has been surprisingly difficult to obtain reliable experimental values of these coefficients, so there exist few direct tests of the accuracy of theoretically predicted \(C_m\) values.

The purpose of the present paper is to present a method of determining reliable experimental values for the first few inverse-power coefficients \(\{C_m\}\) associated with a given molecular state. This procedure also yields extrapolated values for the energy at the dissociation limit \(D\), and for the number, the energies, and other properties of the vibrational levels lying closest to this asymptote, which are more accurate than those obtainable in any other way.

While many physical properties are affected by the values of the long-range potential coefficients,1,2,6,9,10 only four ways of determining such constants from experimental data have been proposed. These are (i) analysis of low-energy integral or absolute scattering cross sections,9,11 (ii) fits to the shape of the "limiting curve of dissociation" associated with the cutoff of the rotational series due to tunneling predissociation,12-15 (iii) fitting Eq. (1) to turning points determined by inversion of spectroscopic data,14,16-22 and (iv) direct fits to the patterns of the energies and other properties of vibrational levels lying very close to dissociation.23,24 However, while the analysis of low-energy scattering data [method (i)] seemed to yield values in reasonable accord with theory,10 by 1973 Bernstein and LaBudde concluded that "... it is not in general possible to extract \(C_n\) from such data." Thus, analyses of spectroscopic data [methods (ii)-(iv)] seem to offer the only direct way of determining experimental values of such coefficients.

The basis of method (ii) was Bernstein's demonstration that if the long-range potential consisted of a single term,

\[
V(R) \approx D - C_n/R^n, \tag{2}
\]

the shape of the limiting curve of dissociation25 at small values of the rotational quantum number became a simple function of \(n\) and \(C_n\).12 However, while it gave reasonable results for a limited number of systems,12-14 it has since been concluded that this approach is of limited practical utility because of the difficulty of obtaining adequate experimental data in the appropriate region.6,15

To date, method (iii) has been the only one of these procedures to yield experimental values for \(C_m\) coefficients corresponding to \(m>n\). It begins with an inversion of experimental vibrational rotational data, using either the semiclassical Rydberg-Klein-Rees (RKR) procedure26 or the iterative least-squares-fitting technique known as the "IPA method,"27 to obtain potential-energy turning points lying in the long-range region. The turning-point energies are then fitted by least squares to Eq. (1) to yield values for the coefficients \(\{C_m\}\) and the dissociation limit \(D\). However, while reasonably successful, this approach has serious shortcomings.

The most fundamental weakness of the turning-point fitting method has been the lack of a way of determining the
effect of the uncertainties in the experimental data on the turning points, and hence on the resulting knowledge of the potential coefficients. This difficulty is underlined by the fact that a given level of experimental uncertainty has the highest proportional effect on the (outer) turning points of levels near dissociation. For RKR turning points, this objection can, in principle, be removed by application of the very nice method for calculating turning-point uncertainties recently presented by Tellinghuisen. However, his procedure is not trivial to apply, and has not yet been used in a practical determination of \( C_m \) coefficients from turning points. Moreover, it does not address the question of the effect of model dependence, or sensitivity to the choice of the analytic functions used to represent the experimental data. This can be quite substantial, as Hertel and Beckel have shown that even small errors in the shape of the functions used to represent the spectroscopic data can give rise to massive errors in the turning points of levels lying near dissociation. All of these difficulties are compounded by the fact that the interparameter correlation associated with the fits of turning-point energies to Eq. (1) is extremely large. Thus, while turning-point fits have proved very useful, the inability to obtain realistic uncertainties for the resulting parameters values, and the high degree of interparameter correlation, have made the development of a better approach a matter of considerable importance.

The fourth of the methods listed above involves using direct fits to experimentally measured quantities to determine the parameters of interest. Its original form was based on an expression which relates the limiting near-dissociation behavior of the distribution of vibrational levels to the asymptotically dominant single-term potential of Eq. (2). It has proved remarkably successful. Indeed, some observers were troubled that it appeared to work better than it should, in that the pattern of level energies depended only on the single-term potential of Eq. (2) even when a significant fraction of the potential strength at their outer turning points was known to be due to higher-power terms in Eq. (1). This has since been shown to be due to a fortuitous cancellation of errors, an effect which is part of the strength of the present method. The original limiting near-dissociation theory approach has also been used to yield analogous limiting near-dissociation theory expressions for inertial and centrifugal distortion constants, and it has been extended to take account of the effects of additional terms in the long-range potential of Eq. (1). This latter generalization forms the basis of the present method.

The present paper presents and tests a method of determining the parameters of Eq. (1) from direct least-squares fits to experimental vibrational energies and inertial constants for levels near dissociation. In this approach, the statistical uncertainties of the resulting parameters directly reflect the uncertainties in the experimental data. Moreover, the effects of interparameter correlation are much smaller in this approach than in turning-point fits.

The following section begins by reviewing the semiclassical theory underlying the present method. This is followed by a presentation of the expressions relating the level energies and inertial rotational constants of levels near dissociation to the parameters of Eq. (1), and an outline of the strategy of the fitting procedure. Section III then presents an illustrative application of the method to the \( D(\Pi^m_u) \) state of \( I_2 \), which includes critical comparisons with the turning-point fitting approach.

II. THE METHOD

A. The underlying theory

The starting point for the present treatment is the familiar first-order phase-integral (or semiclassical, or JWKB) quantization condition for the vibrational eigenvalues of a particle of effective mass \( \mu \) subject to a potential-energy function \( U(R) \):

\[
v + \frac{1}{2} = \frac{\beta}{\pi} \int_{R_1}^{R_2} \frac{[E - U(R)]^{1/2}}{dR}. \tag{3}
\]

Here, \( \beta = (2\mu/\hbar^2)^{1/2} \), \( R_1 \) and \( R_2 \) are the inner and outer classical turning points defined by the condition that \( E = U(R_i) \) (for \( i = 1, 2 \)), and the eigenvalues are the energies \( E \) for which the right-hand side of this expression has precisely half-integer values.

Since we are interested in the levels of a diatomic molecule, the effective potential \( U(R) \) is, in general, the sum of the rotationless electronic potential energy \( V(R) \) plus the usual centrifugal term:

\[
U(R) = V(R) + J(J + 1)\hbar^2/2\mu R^2, \tag{4}
\]

where \( J \) is the rotational quantum number. In this context, \( E = E(v, J) \), and the inertial rotational constant associated with vibrational level \( v \) may be written as

\[
B_v = \left[ \frac{\partial E(v, J)}{\partial [J(J + 1)]} \right]_{v, J = 0} = -\left[ \frac{\partial [v + 1]}{\partial [J(J + 1)]} \right]_{v, J = 0} \cdot \frac{\partial E}{\partial v} \tag{5}
\]

Introducing the definition

\[
I_v = \int_{R_1}^{R_2} R^{-1} [E - V(R)]^{-1/2} dR, \tag{6}
\]

and applying the partial differentiation of Eq. (5) to the integral of Eq. (3) then allows the inertial rotational constant to be expressed as a ratio of two integrals:

\[
B_v = (1/\beta^2)I_v/I_0. \tag{7}
\]

Note that the integrals \( I_v \) depend on both \( E = E(v, J = 0) \) and on the parameters characterizing the rotationless potential \( V(R) \).

In its normal form, the phase-integral quantization condition of Eq. (3) counts levels upward from the potential minimum, where \( v = -1/2 \). In the present context, however, we are interested in the pattern and properties of levels near dissociation, so it is more convenient to count down from dissociation. This is accomplished by noting that in the limit when \( E \to D \), for a rotationless \( (J = 0) \) molecule Eq. (3) becomes

\[
v_D + \frac{1}{2} = \frac{\beta}{\pi} \int_{R}^{\infty} [D - V(R)]^{1/2} dR, \tag{8}
\]
where \( v_D \) is the effective (noninteger) vibrational index at dissociation, and \( \sigma \) is the distance at which \( [D - V(R)] \) changes sign. Fixing \( J = 0 \) and subtracting Eq. (8) from Eq. (3) then yields the version of the phase-integral quantization condition used herein:

\[
\begin{align*}
\rho(E) &= \left[ \frac{\partial(u + \frac{1}{2})}{\partial E} \right]_{u=0} = (\beta/2\pi) I_0,
\end{align*}
\]

the validity of these assumptions for levels near dissociation was thoroughly demonstrated in the earlier work.\(^{6,22,24,31-33}\) Moreover, since the difference \( v_D - v \) may be expressed as the integral of the density of vibrational levels between energies \( E \) and \( D \), this validation also applies to the quantization condition of Eq. (9). These near-dissociation theory approximations will therefore be adopted here without further apology.

Setting \( R_1 - \sigma = 0 \) has the immediate effect of removing the third integral from Eq. (9).\(^{36}\) Substituting Eq. (1) into Eqs. (6) and (9) then transforms them into the basic working expressions underlying the present method:

\[
\begin{align}
I_1 &= \int_0^{R_2} R - \left[ \sum_{m \geq n} \left( C_m/R^m \right) - (D - E) \right]^{-1/2} dR, \\
I_2 &= \int_{R_1}^{R_2} \left[ \sum_{m \geq n} \left( C_m/R^m \right) \right]^{1/2} dR.
\end{align}
\]

Replacing \( V(R) \) by Eq. (1) also means that the outer turning point \( R_2(E) \) is defined by the equation

\[
E = E(v,J = 0) = D - \sum_{m \geq n} C_m/\left( R_2(E) \right)^m.
\]

In conclusion, for any given set of values of the parameters \( v_D, D, \) and \( \{C_m\} \), Eqs. (12), (7), and (11) define the semiclassical vibrational energies and \( B_v \) values of levels near dissociation.\(^{24}\) The vibrational eigenvalues are the energies \( E \) for which the right-hand side of Eq. (12) is precisely equal to a non-negative integer value of \( v \). Starting from any plausible initial trial value of \( E \), use of the energy derivative \( \partial E/\partial v = 2\pi/B_\sigma \) yielded by Eq. (10) facilitates rapid convergence on the exact eigenvalues. Substituting the \( I_1 \) and \( I_2 \) values associated with these energies into Eq. (7) then yields the associated \( B_v \) values. All of the integrals appearing in these expressions may be rapidly and accurately calculated using standard numerical methods such as those described in Appendix A.

B. The energies and \( B_v \) values for levels near dissociation

It is well known that the energies and other properties of vibrational levels lying near dissociation depend dominantly on the nature of the potential function near the outer turning points, \( R_2(E,v) \). Indeed, this fact is the common basis of both the present method and the turning-point fitting procedure for determining long-range potential coefficients. In the limiting region where \( v \rightarrow v_D \), simple analytic expressions which depend only on \( v, v_D, \) and on the parameters \( D, n, \) and \( C_n \) of the single-term potential of Eq. (2) have been derived for a variety of spectroscopic properties.\(^{6,22,23,31-33}\) Tests have shown that the limiting near-dissociation theory expression for the vibrational energies is quite accurate for levels close to dissociation. Moreover, while the analogous expressions for other properties are somewhat less quantitative there, their lower accuracy largely reflects a greater sensitivity to the higher inverse-power terms in Eq. (1). As one moves farther from dissociation, all of these properties become increasingly sensitive to these higher power terms. It is this sensitivity, and the fact that it is substantially greater for the \( B_v \) constants than for the vibrational energies,\(^{24}\) which makes direct fits of these expressions to experimental data such an effective way of determining long-range potential parameters.

The standard approximations of near-dissociation theory involve replacing the function \( V(R) \) by the expansion of Eq. (1), and setting both the inner turning point \( R_1 \) and \( \sigma \) equal to zero. For the integrals \( I_0 \) and \( I_2 \) which define both the \( B_v \) values and the density of vibrational levels,
C. The direct-fit procedure

The present method involves fitting experimental vibrational level energies and \( B_v \) values to semiclassical values of these quantities defined by Eqs. (7), (11), and (12). Since these properties are not linear functions of the parameters of the model, \( v_D, D \), and the \( \{ C_m \} \) constants, this requires the use of iterative nonlinear least-squares-fitting techniques. As in any such fitting procedure, in each cycle it is necessary to know the partial derivatives of each of the calculated quantities with respect to each of the parameters being fitted. In the present case, these derivatives are expressed in terms of integrals similar to those appearing in Eqs. (11) and (12) (see Appendix B), and are evaluated using the techniques described in Appendix A.

A serious concern in any nonlinear fitting procedure is whether the nonlinearity and interparameter correlation will prevent convergence to a unique result. In the present case, the different sensitivities of the two types of experimental observables to the various parameters helps avoid this problem. As was pointed out earlier, a convenient cancellation of errors causes the pattern of vibrational energies to be relatively insensitive to the higher-power (\( m > n \)) coefficients in Eq. (1).\(^{24}\) Thus, a preliminary fit to the vibrational energies alone, while neglecting all \( C_m \)'s for which \( m > n \), should yield reasonable initial trial values for \( v_D, D \), and \( C_s \); indeed, values obtained in this way are often surprisingly close to those yielded by the final multiparameter two-property fits (see below). In any case, they serve as excellent starting values for the subsequent fits to the full data set in which the additional \( C_m \) coefficient(s) are also varied. Realistic estimates of \( v_D, D \), and \( C_s \) required for initiating the nonlinear three-parameter fits to the vibrational energies alone may be obtained from approximate linearized fits to the vibrational level spacings.\(^{6,23,31}\)

In practice, the high correlation between certain parameters means that a succession of fits must be performed in which one (or more) additional parameter at a time is allowed to vary. As each additional \( C_m \) constant was released, it also proved desirable to initially hold \( v_D \) fixed, and only release it after an initial fit to the remaining variables had converged. These and other features of the present least-squares-fitting strategy are discussed in Ref. 37. An automated (near-) "black-box" computer program which implements the present method may be obtained from the authors on request.\(^{37}\)

Another problem encountered here (and in many other contexts) is that fits performed to different versions of the model (e.g., potential expansions with different numbers of terms) using data sets of different sizes can yield distinctly different parameter values and parameter uncertainties. The results presented below show that the statistics of fits using the present method will often clearly indicate both how many terms to include in the potential expansion, and the limits to the range of data which should be considered. However, as is often the case, there remain a number of separate "acceptable" fits, and the differences among the associated parameter values sometimes exceed the uncertainties suggested by the individual fits.

In the present work, this problem was addressed by averaging over the results of the individual acceptable fits, weighting each result by the correlated uncertainty predicted by that fit. Thus, for parameter \( P \), with values \( \{ P_i \} \) and correlated uncertainties \( \{ \Delta P_i \} \) obtained from independent fits \( i \), for \( i = 1 \) to \( M \), the resulting averaged value is

\[
P = \left( \sum_{i=1}^{M} \frac{P_i}{(\Delta P_i)^2} \right) \left( \sum_{i=1}^{M} \frac{1}{(\Delta P_i)^2} \right)^{-1},
\]

while the corresponding averaged parameter uncertainty is

\[
\Delta P = \left( \sum_{i=1}^{M} \left( (P_i - \bar{P})^2 + (\Delta P_i)^2 \right) / (\Delta P_i)^2 \right)^{1/2} \times \left( \sum_{i=1}^{M} 1/(\Delta P_i)^2 \right)^{-1}.
\]

Equation (15) assumes that the parameter uncertainty associated with a given fit \( \Delta P \), and the differences between the parameter values associated with different fits are uncorrelated. This is certainly valid in principle, as the former largely reflects the interparameter correlation within the model, while the latter largely depends on the validity of the underlying physical assumptions. This type of "averaging over models" is used to generate the final recommended parameter values and parameter uncertainties reported below.

III. ILLUSTRATIVE APPLICATION TO THE \( B^3 \Pi_{\text{eq}} \) STATE OF \( I_2 \)

A. The input data

The \( B^3 \Pi_{\text{eq}} \) state of \( I_2 \) is an excellent candidate for this type of analysis because of the relatively high density of vibrational levels, and because of the availability of reliable spectroscopic data for levels lying near dissociation.\(^{38}\) The experimental vibrational energies and \( B_v \) values used as input to the present analysis, taken from Table V of Ref. 38, are listed here in Table I together with the statistical uncertainties used to weight them in the fits. A knowledge of these uncertainties is essential for two reasons. The first is simply

<table>
<thead>
<tr>
<th>( v )</th>
<th>Energy (cm(^{-1}))</th>
<th>( B_v ) (10(^{-4}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20 041.579 5 (0.0010)</td>
<td>2 836.33 (50.0)</td>
</tr>
<tr>
<td>79</td>
<td>20 040.728 9 (0.0050)</td>
<td>3 289.72 (20.0)</td>
</tr>
<tr>
<td>78</td>
<td>20 039.067 0 (0.0050)</td>
<td>3 746.36 (20.0)</td>
</tr>
<tr>
<td>77</td>
<td>20 038.170 8 (0.0050)</td>
<td>4 206.10 (20.0)</td>
</tr>
<tr>
<td>76</td>
<td>20 036.371 4 (0.0030)</td>
<td>4 668.83 (2.0)</td>
</tr>
<tr>
<td>75</td>
<td>20 034.160 7 (0.0030)</td>
<td>5 134.28 (2.0)</td>
</tr>
<tr>
<td>74</td>
<td>20 031.488 4 (0.0030)</td>
<td>5 602.03 (2.0)</td>
</tr>
<tr>
<td>73</td>
<td>20 028.302 7 (0.0030)</td>
<td>6 071.51 (2.0)</td>
</tr>
<tr>
<td>72</td>
<td>20 024.550 4 (0.0020)</td>
<td>6 542.65 (0.20)</td>
</tr>
<tr>
<td>71</td>
<td>20 020.177 4 (0.0020)</td>
<td>7 012.89 (0.20)</td>
</tr>
<tr>
<td>70</td>
<td>20 015.138 7 (0.0020)</td>
<td>7 483.78 (0.20)</td>
</tr>
<tr>
<td>69</td>
<td>20 009.348 8 (0.0020)</td>
<td>7 952.47 (0.20)</td>
</tr>
<tr>
<td>68</td>
<td>20 002.782 3 (0.0020)</td>
<td>8 419.76 (0.20)</td>
</tr>
<tr>
<td>67</td>
<td>19 995.373 7 (0.0020)</td>
<td>8 884.54 (0.20)</td>
</tr>
<tr>
<td>66</td>
<td>19 987.068 0 (0.0020)</td>
<td>9 346.25 (0.20)</td>
</tr>
<tr>
<td>65</td>
<td>19 977.810 8 (0.0020)</td>
<td>9 804.47 (0.20)</td>
</tr>
</tbody>
</table>
that when performing least-squares fits to different types of experimental observables which have very different magnitudes, such as these energies and \( B' \)'s, the relative uncertainties must be known if the combined fits are to have any significance. The second is that we wish the uncertainties in the parameters yielded by our fits to properly reflect the limits to our knowledge of the input quantities. As usual, the statistical weight associated with each datum used in a fit is proportional to the inverse square of its uncertainty. We note from Table I that these uncertainties become much larger for the highest vibrational levels. In contrast to turning-point fits (at least, as previously performed), the present method readily takes proper account of such differential uncertainties in the input data.

The highest level considered is \( v = 80 \), which lies only \( \sim 2 \text{ cm}^{-1} \) from the dissociation limit, while the lowest is bound by \( \sim 65 \text{ cm}^{-1} \). A number of empirical criteria have been proposed for defining the cutoff point beyond which long-range or near-dissociation theory methods should not be used.\cite{6,20} However, the 16 levels listed in Table I all lie within the "near-dissociation" region, regardless of which criterion is used.

Two competing considerations arise in any attempt to determine long-range potential coefficients from the properties of levels lying near dissociation. On the one hand, it is desirable to fit as many data as possible, so as to optimize the statistics of the fit. On the other hand, the physical assumptions underlying the present method (as well as turning-point fits) are most valid for the levels lying closest to the dissociation limit. An additional concern is that one must ensure that the data set is sensitive to the higher inverse-power potential coefficients, which become relatively more important for the deeper levels. In order to achieve a balance between these considerations, sequences of fits should be performed in which the range of levels considered is systematically varied. In each case, the data set should extend to the highest level for which information is available, with its range being defined by the choice of the deepest level whose properties are retained in the analysis. In the present work, the lowest level included in a given fit is denoted \( v_L \), so a given fit is based on the data for levels \( v = v_L \) to 80.

**B. Results from the direct-fit procedure**

In addition to choosing the range of the data to be used in the analysis, it is necessary to specify the number of in-

![Graph](https://example.com/graph.png)

**FIG. 1.** Fitted values for the \( B'(\Pi,v') \) state of I, dissociation limit \( D \) (upper segment) and the associated 95% confidence limit uncertainties \( u(D) \) (lower segment, and error bars on solid-square points in the upper segment) obtained from both the present direct-fit (solid points) and turning-point fit (open points) procedures, for potential models corresponding to \( m_{\text{max}} = 5 \) (diamond-shaped points), \( m_{\text{max}} = 6 \) (triangular points), \( m_{\text{max}} = 8 \) (circular points), and \( m_{\text{max}} = 10 \) (square points).
verse-power terms to be included in the potential model to which the data are being fitted. Each of our fits is therefore characterized by a value of $u_L$, which defines the range of the data used, and a value for $m_{\text{max}}$, the power of the highest inverse-power term included in the potential expansion. For the $B'(^1I_{1u})$ state of $I_2$, the leading contributions to the sum of Eq. (1) correspond to $m = 5, 6, 8, \text{ and } 10$. Thus, for $m_{\text{max}} = 5$ our direct-fit procedure has the three parameters $D, v_D, \text{ and } C_5$, while when $m_{\text{max}} = 10$ it has the six parameters $D, v_D, C_5, C_6, C_8, \text{ and } C_{10}$.

The present method was applied to the data in Table I using potential models in which $m_{\text{max}}$ ranged from 5 to 10, while $u_L$ ranged from 65 to the highest values which allowed the associated fit to have at least one degree of freedom. The resulting best-fit parameter values for each case are shown as solid points on Figs. 1–6, with results associated with the same value of $m_{\text{max}}$ being joined by solid lines. The predicted 95% confidence limit uncertainty in each parameter value is plotted on the same absolute scale in the lower half of each of these figures, with the uncertainties associated with the $m_{\text{max}} = 10$ fits also being shown as error bars in the corresponding upper figure segments.

The open points joined by dashed lines in Figs. 1 and 3–6 represent results obtained using the turning-point fitting approach. They will be discussed in the following section, and are included in these figures to facilitate later comparisons. The absence of open points and dashed lines from Fig. 2 simply reflects the fact that $v_D$ is not a parameter in the turning-point fits.

In general, the same qualitative behavior is reflected in each of Figs. 1–6. Note, however, that the $m_{\text{max}} = 5$ results are a special case, as they were obtained from fits to the vibrational energies alone, rather than from fits to both the energies and $B_e$'s. As a result, that case is considered separately, and the following remarks are initially concerned with the $m_{\text{max}} = 6, 8, \text{ and } 10$ fits to the combined vibrational energies and $B_e$ constants of the levels considered.

In principle, we would expect the best results to be those associated with the highest values of both $u_L$ and $m_{\text{max}}$. The reason for the latter is of course the fact that the potential model becomes more realistic with increasing $m_{\text{max}}$. Thus, up to the point at which introduction of additional potential
terms amplifies the interparameter correlation excessively or causes the fits to become unstable, fits associated with the larger values of $m_{\text{max}}$ are preferred. In the present case, the fits became unstable when $m_{\text{max}}$ was increased beyond 10 \[ by adding an m = 12 \text{ term to Eq. (1).} \] This shows that the $C_{10}$ constant is the highest inverse-power coefficient to which the existing data are sensitive.

Regarding choice of the optimum value of $m_{\text{max}}$, we first note (from Figs. 1–6) that as $v_L$ increases, parameter values associated with different values of $m_{\text{max}}$ are approaching the same limits, which we take to be the “true” values of the various parameters (see below). The onset of significant deviations from these limiting values with decreasing $v_L$ then indicates the lower limit to the region in which that particular model potential can adequately explain the experimental energies and $B_L$ values. The range of $v_L$ over which the parameter values obtained remain near these limits is clearly broadest for $m_{\text{max}} = 10$ (solid square points in Figs. 1–6). In contrast, parameters values yielded by the $m_{\text{max}} = 6$ fits (solid triangular points) have relatively large uncertainties and vary drastically with $v_L$, and those fits become unstable when $v_L$ drops below 74. This confirms that the combined data set (energies and $B_L$'s) is indeed quite sensitive to the absence of the higher inverse-power terms from the $m_{\text{max}} = 6$ model potential. Moreover, except for the very highest $v_L$ values, where statistical effects muddy the picture slightly (see below), the uncertainties in the fitted parameter values are always much smaller for $m_{\text{max}} = 10$ (solid square points) than for $m_{\text{max}} = 8$ (solid circular points). Thus, the $m_{\text{max}} = 10$ model appears to provide the best physical description of this system.

The reason for preferring results associated with the larger values of $v_L$ is the fact that as more of the deeper levels are included in the fits, both the model potential and the physical approximations underlying the method become increasingly inappropriate. This is the reason that the fitted parameter values deviate from their common high-$v_L$ limits and the parameter uncertainties grow at low $v_L$. For the $m_{\text{max}} = 10$ fits (solid squares in Figs. 1–6), the region in which the fitted parameter values are approximately insensitive to $v_L$ ends at $v_L = 71$, which is also where the low-$v_L$ growth of the parameter uncertainties begins. It is very reas-
suring to have the statistics of the fit provide such a clear indication of when the method should no longer be used; this does not occur for the turning-point fits.

In general, all parameter uncertainties yielded by fits of this type will have the qualitative behavior seen for the \( m_{\text{max}} = 10 \) results (solid square points) in the lower segments of Figs. 1–6. At sufficiently small \( u_L \) they grow because the model no longer adequately describes the data for the deeper levels, while at sufficiently large \( u_L \) they grow because of the increasing importance of interparameter correlation, an effect magnified for the very smallest data sets by the number of degrees of freedom in the fits becoming very small. For \( m_{\text{max}} = 6 \) and 8, the balance point between these tendencies lies off scale at high \( u_L \), as those model potentials are unable to fully account for the experimental data. For the better turning-point fits (open square and circular points; see below), the balance point is off scale to low \( u_L \), and lies in the region where the unsuitability of the potential model causes the fitted parameter values to shift systematically with \( u_L \). For the present \( m_{\text{max}} = 10 \) fits, however, this balance point lies at \( u_L = 71 \), in the middle of the region where the model is expected to be physically appropriate.

Although their predicted parameter uncertainties are the smallest obtained for any case, it would be unwise to simply accept the \( u_L = 71 \) results as optimal, both because they are associated with the lower edge of the range of acceptable (i.e., approximately insensitive to \( u_L \)) fits, and because parameter values associated with some of the higher \( u_L \) values differ from one another by more than these predicted uncertainties. Rather, this situation calls for use of the “averaging-over-models” procedure described at the end of Sec. II C. Our final recommended values and uncertainties for \( u_D \) and the potential parameters for this system were therefore obtained by substituting the values obtained from \( m_{\text{max}} = 10 \) fits corresponding to \( u_L > 71 \) into Eqs. (14) and (15). These results are presented in Table II, together with the results of previous analyses of experimental data\(^\text{21,39}\) and theoretical estimates of the \( C_m \) coefficients (to be discussed later). While the uncertainties associated with these recommended values may still be somewhat small, the present

![FIG. 4. Fitted values for the potential coefficient \( C_6 \) and its 95% confidence limit uncertainties \( u(C_6) \), as in Fig. 1.](image-url)
methodology does offer a systematic way of taking account of most sources of error and generating estimated uncertainties which are realistic.

As a further indication of the nature of the uncertainty in the parameter values yielded by the present method, Table III presents the correlation matrix for the $m_{\text{max}} = 10$ fit to the 18-member data set for $v_L = 72$. We note that while the correlation among the $v_D$, $C_5$, and $C_6$ parameters is fairly high, most of the other parameters are relatively weakly correlated with one another. This situation differs significantly from that for turning-point fits (see below).

It has been shown elsewhere that the $B_v$ constants are much more sensitive to the higher-power ($m > n$) terms in Eq. (1) than are the vibrational energies themselves. For this reason, one might expect that $m_{\text{max}} = 5$ fits to both the energies and $B_v$'s would be much less meaningful than $m_{\text{max}} = 5$ fits to the vibrational energies alone. This proved to be the case; indeed, even when two inverse-power terms were included in the potential expansion (case $m_{\text{max}} = 6$, solid triangles in Figs. 1-4), our combined fits to energies and $B_v$'s became unstable when more than a few of the very highest levels are considered. As a result, the direct-fit $m_{\text{max}} = 5$ results reported herein (solid diamonds in Figs. 1-3) were obtained by fitting to the vibrational energies alone.

As has been discussed elsewhere, the surprisingly good quality of the $D$, $v_D$, and $C_5$ values obtained from $m_{\text{max}} = 5$ fits to the vibrational energies alone arises from a fortuitous, but not accidental, cancellation of errors. It occurs because whenever the second inverse-power term in Eq. (1) has a power $m = n + 1$, the leading correction to the one-term expression for the level energies is identically zero. For this reason, $m_{\text{max}} > n = 5$ fits to the vibrational energies alone were made unstable by excessive interparameter correlation, so that determination of more than the longest-range inverse-power potential coefficient requires combined fits to both the energies and $B_v$'s. Note, however, that while this is likely to be true for all cases in which the powers of two leading terms in Eq. (1) differ by one, it may not be so in other situations.

![FIG. 5. Fitted values for the potential coefficient $C_5$, and its 95% confidence limit uncertainties $u(C_5)$, as in Fig. 1.](image-url)
Davies, Shelley, and Le Roy: Inverse-power potential coefficients

**TABLE II.** Comparison of the present recommended parameter values for the $B^{(1}1_{1/2})$ state of $\mathcal{J}$, with those obtained from turning-point (Ref. 21) and limiting near-dissociation theory fits (Ref. 39) and with available theoretical $C_{\infty}$ constants; parameter uncertainties are given in parentheses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recommended*</th>
<th>Ref. 21b</th>
<th>Ref. 39c</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (cm$^{-1}$)</td>
<td>20 043.22 (0.01)</td>
<td>20 043.190 (0.001)</td>
<td>20 043.16 (0.02)</td>
<td>...</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>87.52 (0.04)</td>
<td>...</td>
<td>87.32 (0.04)</td>
<td>...</td>
</tr>
<tr>
<td>$C_3$ ($10^8$ cm$^{-1}$ Å$^2$)</td>
<td>3.14 (0.06)</td>
<td>3.16 (0.03)</td>
<td>2.88 (0.03)</td>
<td>3.39 to 4.54e</td>
</tr>
<tr>
<td>$C_4$ ($10^8$ cm$^{-1}$ Å$^4$)</td>
<td>1.48 (0.07)</td>
<td>1.51 (0.04)</td>
<td>...</td>
<td>1.77 or 1.85f</td>
</tr>
<tr>
<td>$C_5$ ($10^8$ cm$^{-1}$ Å$^5$)</td>
<td>3.05 (0.10)</td>
<td>2.48 (0.14)</td>
<td>...</td>
<td>1.69f</td>
</tr>
<tr>
<td>$C_{\infty}$ ($10^8$ cm$^{-1}$ Å$^{10}$)</td>
<td>1.11 (0.17)*</td>
<td>&lt;4.2 (0.3)</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

*Obtained using Eq. (14) and (15) to average over results obtained using the present direct-fit procedure with $m_{\text{max}} = 10$ and $\psi_L = 71–77$.

bObtained in Ref. 21 from fits to the turning points for levels $v = 69–77$; note, however, that neglect of interparameter correlation made their uncertainties anomalously small compared to those yielded by the turning-point fits performed here (see footnote 43).

cObtained from limiting near-dissociation theory fits to the vibrational energies alone (Ref. 39).

dCalculated from Eq. (16) using expectation values $\langle r^4 \rangle$ from Refs. 44–46.

*eValues taken from Refs. 47 and 17, respectively.

fValue from Ref. 17.

As discussed in Sec. IV, our final estimate of the $C_{\infty}$ uncertainty is somewhat larger than this.
Because of the cancellation of errors mentioned above, the relatively small parameter uncertainties associated with the \( m_{\text{max}} = 5 \) fits (to the energies alone) are not realistic. On the other hand, the results in Figs. 1–3 show that in the absence of \( B_{v} \) data for this type of system, one could be reasonably confident that fits to an \( m_{\text{max}} = 5 \) model would yield quite reasonable estimates of the three parameters. In contrast, for turning-point fits, use of an \( m_{\text{max}} = 5 \) model yields totally unreasonable results with enormous uncertainties. For the sake of comparison, the third column of Table II presents the results of the \( m_{\text{max}} = 5 \) or limiting near-dissociation theory fit to the vibrational energies alone reported in Ref. 39.

An important feature of the present approach is the ease with which it yields estimates of the energies and other properties of additional levels lying above the highest one observed. To this end, Eqs. (7), (11), and (12) were combined with the recommended parameter values of Table II and used to generate the estimates of the energies and \( B_{v} \)'s for levels \( v = 81–87 \) given in Table IV. Of course, these predictions are based on a mechanical model for this state which neglects the effect of the perturbations which are expected to arise for the levels lying closest to dissociation.39 However, this offers the possibility of using comparisons of these “mechanical” predictions with future experimental results for these levels to determine the nature of the perturbations in question.

### C. Comparisons with turning-point fits

This section presents detailed comparisons of the above results with those yielded by fits to turning points for the same sets of vibrational levels. While the coefficients obtained are exactly the same as those reported in Ref. 21, the turning-point fits were repeated here to facilitate the examination of parameter uncertainties and interparameter correlation. The turning points used here were generated by the RKR method using the molecular constants of Ref. 38, with the inner wall being smoothed (and the outer wall corrected) above \( v = 55 \). However, the resulting parameter values were identical to all digits reported with those obtained in Ref. 21 from fits to turning points generated using the IPA method. Thus, any differences between the IPA and RKR potentials for this system have no effect on the long-range potential coefficients yielded by fits to such turning points.41

As in all previously reported turning-point fits, the potential energies at the specified turning points were fitted to the model potential [here Eq. (13)], with all points being weighted equally. Thus, although the turning points are determined by the vibrational energies and \( B_{v} \)'s, the substantial differences in the uncertainties of those quantities for different vibrational levels are completely ignored.41

The results described here were obtained from fits to the outer turning points associated with integer values of \( v \) for levels ranging from \( v_L = 65 \) to \( 80 \). As in the preceding section, the range of the data used in each fit is characterized by \( v_L \), the identity of the lowest level whose turning point is considered, and all data sets extend to the turning point for the highest observed level, \( v = 80 \). Thus, the results associated with a given value of \( v_L \) are based on \( 80 - v_L + 1 \) outer turning points. A key difference between the two methods is therefore the fact that for each level considered, the present direct-fit procedure utilizes two independent data (an energy plus a \( B_v \) value) rather than one (the outer turning point).

One implication of the above difference is that to achieve a given number of degrees of freedom, a turning-point fit will have to include data for a substantially wider range of vibrational levels than would the present direct-fit procedure. In a molecular state for which few observed vibrational levels lie close to dissociation, this may tend to require the use of turning points lying outside the long-range region, or alternately, only permit fits in which the very small number of degrees of freedom grossly exaggerates the effect of interparameter correlation. In a recent work, Gerstenkorn and Luc attempted to circumvent this difficulty by simply generating an arbitrarily large number of turning points at fractional \( v \) values within a given range, and treating them as independent data.22 As might be expected, this had the effect of dramatically reducing the interparameter correlation contributions to the parameter uncertainties, since this factor scales as \((N_f)^{-1/2}\), where \( N_f \) is the number of degrees of freedom of the fit. However, this stratagem is fundamentally invalid, as the additional “data” are really interpolated rather than independent values of the “observable” being fitted to, since they were generated from the same molecular constants used to define the turning points at integer \( v \).

The results of the present fits of turning-point energies to Eq. (13) are presented as open points (joined by dashed lines) in Figs. 1 and 3–6. As with the present direct-fit results, squares, circles, and triangles represent results corresponding to \( m_{\text{max}} = 10, 8, \) and 6, respectively. To further

### TABLE III. Correlation matrix for an \( m_{\text{max}} = 10 \) direct fit to the vibrational energies and \( B_v \)'s for levels \( v = 72-80 \) of the \( B(\Pi_{u},z) \) state of \( I_2 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( D )</th>
<th>( v_L )</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
<th>( C_{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D )</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( v_L )</td>
<td>0.987</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_1 )</td>
<td>0.979</td>
<td>0.998</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_2 )</td>
<td>0.973</td>
<td>-0.996</td>
<td>-0.999</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_3 )</td>
<td>0.759</td>
<td>0.796</td>
<td>0.794</td>
<td>-0.798</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{10} )</td>
<td>0.001</td>
<td>0.086</td>
<td>0.033</td>
<td>-0.049</td>
<td>-0.250</td>
<td>1.000</td>
<td></td>
</tr>
</tbody>
</table>
be approaching a common asymptote with increasing $u_L$, initially the same as for our direct-fit method. For example, the behaved than the present direct fits, in that the values of $m_{\text{max}} = 8$ and 10 cases lie segments of Figs. 1 and 3-5). This again suggests that the effective to the choice of $u_L$ (see the open points in the upper figures). As such, the differences between the two approaches, Table V compares our direct-fit and turning-point fit results for the case $m_{\text{max}} = 10$ and $v_L = 72$, while the correlation matrices for these two fits are compared in Tables III and VI.

Some features of the turning-point fit results are essentially the same as for our direct-fit method. For example, the results corresponding to different values of $m_{\text{max}}$ appear to be approaching a common asymptote with increasing $v_L$, and those for the larger $m_{\text{max}}$ values are again the least sensitive to the choice of $u_L$ (see the open points in the upper segments of Figs. 1 and 3-5). This again suggests that the "best" results are those associated with large $m_{\text{max}}$ and large $v_L$. In some regards, the turning-point fits even appear better behaved than the present direct fits, in that the values of some parameters vary more gradually and more smoothly with $v_L$, and the results for the $m_{\text{max}} = 8$ and 10 cases lie relatively close together. However, the smoother dependence on $v_L$ merely reflects the additional layer of averaging in the fits to determine the molecular constants which in turn yielded the turning points being fitted to. Furthermore, while some parameter values may deviate from the limiting high-$v_L$ values more slowly than was the case for the turning-point fits, this trend is sometimes (e.g., for $D$, $C_8$, and $C_{10}$) monotonic, with no "plateau" region to identify a recommended asymptotic value.

Even more unsettling behavior is exhibited by the parameter uncertainties shown in the lower segments of Figs. 1 and 3-6. In particular, while larger values of $m_{\text{max}}$ are expected to yield "better" results, the parameter uncertainties grow dramatically as $m_{\text{max}}$ increases from 8 to 10 (and for high $v_L$, also for $m_{\text{max}}$ increasing from 6 to 8). Moreover, these uncertainties grow rapidly and monotonically with increasing $v_L$ over the range considered, and for $m_{\text{max}} = 10$ they become virtually the same size as the $C_m$ constants themselves for even moderately large values of $v_L$. These observations are illustrated by the contrast between the parameter uncertainties for the present direct-fit and turning-point fit results shown in Table V.

The reason for the size and unpleasant behavior of the parameter uncertainties yielded by the turning-point fits is the fact that they are much more strongly affected by interparameter correlation effects than are those yielded by the present direct fits to energies and $B_{\text{eff}}$. This was predicted in Ref. 24 on the basis of qualitative considerations of how the higher-order potential terms affect the "observables" being fitted in the two cases. It is clearly confirmed here by a comparison of the correlation matrices of Tables III and VI. The latter shows that in the turning-point fits, all of the potential coefficients are very highly correlated, one with another, while Table III shows that within the present direct-fit procedure, only the $C_8$ and $C_{10}$ coefficients are highly correlated.

For small $v_L$, the parameter uncertainties yielded by the turning-point fits are much smaller than those yielded by the corresponding direct fits. However, these apparently improved uncertainties occur for $v_L$ values where the corresponding fitted parameter values are beginning to change rapidly. Thus, the behavior of the predicted parameter uncertainties provides no indication of the suitability of any particular turning-point fit. For the present direct-fit procedure, the opposite is true, and the predicted parameter uncertainties both are more realistic, and provide a clear indication of which case will yield the best parameter values and uncertainties obtainable for the given system. Thus, even overlooking their neglect of the uncertainties in the underlying experimental data, the effects of interparameter correlation make it much more difficult to determine meaningful estimates of the desired parameters from turning-point fits than from the present direct-fit procedure.

### D. Comparisons with theoretical $C_m$ coefficients

The $C_i/R^4$ term in a long-range intermolecular potential arises as a first-order interaction energy between atoms which have permanent quadrupole moments. On taking account of angular momentum considerations, the theory shows that for the $B'(1\Pi_u^o)$ state of $I_2$,

$$C_3 \text{(theory)} = 0.96 \left\langle \langle r^{2}_{sp} \rangle \right\rangle^2,$$

where $\langle r^{2}_{sp} \rangle$ is the expectation value of the squared radius of the electrons in the atomic valence shell, and all quantities are in atomic units. A theoretical estimate of this potential constant is therefore readily obtained by substituting values of $\langle r^{2}_{sp} \rangle$ generated from electronic structure calculations into Eq. (16). Unfortunately, the calculated values of $\langle r^{2}_{sp} \rangle$, and hence of the resulting theoretical $C_3$ values shown in the last column of Table II, differ significantly amongst themselves. Moreover, even the smallest of these

---

**Table V.** Parameters and predicted uncertainties for the $B'(1\Pi_u^o)$ state of $I_2$, obtained from $m_{\text{max}} = 10$ fits to data corresponding to $v_L = 72$, using the present direct-fit and turning-point fit procedures.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Direct fit</th>
<th>Turning point</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (cm$^{-1}$)</td>
<td>20 043.219 (0.008)</td>
<td>20 043.19 (0.03)</td>
</tr>
<tr>
<td>$v_L$</td>
<td>87.53 (0.03)</td>
<td>…</td>
</tr>
<tr>
<td>$C_5$ (10$^3$ cm$^{-1}$ Å$^3$)</td>
<td>3.17 (0.06)</td>
<td>3.17 (0.85)</td>
</tr>
<tr>
<td>$C_6$ (10$^4$ cm$^{-1}$ Å$^4$)</td>
<td>1.45 (0.06)</td>
<td>1.49 (1.26)</td>
</tr>
<tr>
<td>$C_7$ (10$^5$ cm$^{-1}$ Å$^5$)</td>
<td>1.08 (0.09)</td>
<td>2.66 (5.55)</td>
</tr>
<tr>
<td>$C_8$ (10$^7$ cm$^{-1}$ Å$^6$)</td>
<td>1.10 (0.07)</td>
<td>4.01 (11.4)</td>
</tr>
</tbody>
</table>

*Present method.

Values as in Ref. 21, with (correlated) uncertainties obtained here.

**Table VI.** Correlation matrix for an $m_{\text{max}} = 10$ fit to the turning points of levels $v = 72$–80 of the $B'(1\Pi_u^o)$ state $I_2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$D$</th>
<th>$C_5$</th>
<th>$C_6$</th>
<th>$C_7$</th>
<th>$C_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_5$</td>
<td>0.987</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6$</td>
<td>-0.982</td>
<td>-0.999</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>0.970</td>
<td>0.996</td>
<td>-0.998</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>-0.958</td>
<td>-0.991</td>
<td>0.994</td>
<td>-0.999</td>
<td>1.000</td>
</tr>
</tbody>
</table>
values differ from our recommended value (column 1) by much more than our current predicted uncertainty.

While theoretical values of $^{17,47}$ $C_n$ and of $^{17} C_n$ are much more difficult to generate, we note that the values given in the last column of Table II are at least similar to our recommended experimental values. However, the differences are again much larger than the predicted uncertainties in the present recommended values (column 1). Thus, it appears that the present approach is already providing experimental $C_m$ coefficients with which to test theory.

IV. DISCUSSION AND CONCLUSIONS

Two main types of questions may be raised about the reliability of the present method. The first concerns the validity of the first-order or one-term semiclassical quantization condition of Eqs. (3) or (9), on which the method is based. This condition represents an approximate solution to the effective one-dimensional or radial Schrödinger equation, and comprises the leading term in an asymptotic series representation for this quantity.48 However, it has been shown that the higher-order terms in this approximation decrease rapidly in magnitude, and that this leading term is an extremely good approximation in most practical cases.49-51 Moreover, since it is also the basis of the RKR inversion procedure, any weakness in it would also affect RKR turning points used in a turning-point fit analysis.

In spite of the above arguments, it is appropriate to examine this question in more detail. This may be done using the results of Ref. 49, where it was shown that for levels near dissociation, the leading correction to the first-order eigenvalues yielded by Eqs. (3) or (9) could be written as

$$
\delta E^{1}_{\text{nd}} = - \left[ (n^2/(C_n)^2)^{1/2} \right] R_0 (v_0 - v)^{4/(n-2)}
$$

where $n$ and $C_n$ are the power and coefficient of the leading term in the potential expansion of Eq. (1), $\mu$ is the reduced mass, and $\bar{R}(n)$ a numerical constant depending only on $n$ and physical constants. For the present $n = 5$ case, $\bar{R}(n) = 589.1$, and hence $R(n) = 1.3 \times 10^{-4}$ cm$^{-1}$. This implies that omission of higher-order contributions to the quantization condition gives rise to an error of $-0.005$ cm$^{-1}$ for $v = 72$ and $0.002$ cm$^{-1}$ for $v = 80$, and hence to a discrepancy of only 0.02% in the spacing between these levels. It seems clear that this difference will not significantly affect the results of the present analysis, or of analogous studies for most heavy systems.

In spite of the assurance provided by the present application of Eq. (17), the effects of error in the first-order quantization condition may not always be negligible. This is because of the inverse dependence of $R(n)$ on $\mu$ and $C_n$, and because the numerical factor $\bar{R}(n)$ increases to 1781.6 and 20 074.7 for $n = 4$ and 3, respectively (though it drops to 318.9 for $n = 6$). On the other hand, systems with small reduced mass where this type of error would tend to be largest are also cases in which the relatively low density of levels would make it least likely that data for a significant number of levels lying very near dissociation would be available. Moreover, the quadrature techniques introduced in Refs. 49 and 52 will allow the present method to be extended to incorporate higher-order terms into the quantization condition, and hence completely remove this possible source of error. This is a promising direction for future work.

A second type of question regarding the present method concerns the form and truncation of the expansion [Eq. (1)] used to represent the long-range potential. In the present work, the potential was expressed as a linear sum which was simply truncated after the last term considered, $m = m_{\text{max}}$, an approach which implicitly assumes that all higher-order terms are identically zero. However, Ref. 20 showed that the results of turning-point fits could depend significantly on implicit assumptions regarding potential terms which were not explicitly included.

For $B$ state of $I_2$, terms omitted from our model for the long-range potential include the next contribution to the second-order dispersion energy, $C_{12}/R^{12}$, the leading contribution to the third-order interaction energy, $C_{12}/R^{11}$, and a repulsive exponential exchange term.7,21,53 The effect of omitting these terms from a turning-point fit analysis was examined in some detail in Ref. 21, and many features of that discussion also apply here. In particular, it was shown there that the $C_{12}$ and the exchange term are of opposite sign and tend to qualitatively cancel one another, and that high interparameter correlation prevented the determination of distinct values of $C_{11}$ and/or $C_{12}$. Those observations concur with the present result that insensitivity to the additional variables and interparameter correlation made the present direct fits become unstable whenever $m_{\text{max}}$ was set larger than 10. This means that little can be done to determine the magnitude of these higher-order interactions, and that their effect is implicitly incorporated into the values of the coefficients we have determined. This effect will be largest for our highest-power term, so the real physical uncertainty in the $C_{10}$ value determined here is substantially larger than that obtained by the procedure described in Sec. III B. Indeed, this model dependence may well be the largest source of uncertainty in all of our parameter values. This question will be examined further in future work.

On reviewing the comparisons between the direct-fit and turning-point fit procedures, it is interesting to note that in spite of the problems described in Sec. III C, the turning-point fits for high $m_{\text{max}}$ and $v_L$ yield parameter values very similar to those obtained from the present direct fits. Thus, it appears that when carefully done, turning-point fits can yield parameters which are more accurate that their correlated43 statistical uncertainties might suggest. This should not be too surprising, since the turning points are implicitly defined by the same data used as input to the direct fits. However, the interparameter correlation underlying those uncertainty estimates cannot be ignored, and any effort to realistically account for the differential uncertainties in the underlying experimental data will only make things worse. Thus, since no parameter can be said to be known to better than its uncertainty, turning-point fits yield much more poorly defined parameter values than do the type of direct fits to energies and $B_n$'s introduced here.

It is also important to note that the present direct-fit method yields an estimate of the value and uncertainty of the
parameter $v_D$, a quantity which cannot be readily obtained from an analysis of turning points. This parameter has clear physical significance, as (when truncated to an integer) it indicates how many additional vibrational levels lie above the highest one used in the analysis. On substituting it and the associated potential parameters into Eqs. (7), (11), and (12), one can generate reliable estimates of the energies and $B_0$ constants of all such unobserved levels.

For the $B(^3\Sigma_u^+)$ state of $I_2$, the present analysis yields improved estimates of the dissociation limit $D = 20.043.22(\pm 0.01)$ cm$^{-1}$, of the parameter $v_D = 87.52(\pm 0.04)$, and of the first four long-range potential coefficients: $C_5 = 3.14(\pm 0.06) \times 10^5$ cm$^{-1}$ A$^5$, $C_6 = 1.48(\pm 0.07) \times 10^6$ cm$^{-1}$ A$^6$, $C_8 = 3.05(\pm 0.10) \times 10^7$ cm$^{-1}$ A$^8$, and $C_{10} = 1.11(\pm 1.1) \times 10^8$ cm$^{-1}$ A$^{10}$. For $C_5$ and $C_6$, the present recommended values differ from those of Ref. 21 by less than the (more realistic) present predicted uncertainties, while for $D$ the difference is only slightly outside of that limit. However, the fact that the present method gives much more meaningful parameter uncertainties means that we are now much better off. On the other hand, since the $C_{10}$ coefficient subsumes most of the model dependence due to omission of additional terms from the potential, our final best estimate of its uncertainty (see above) is distinctly larger than that presented in Table II.

In closing, we note that the $B(^3\Pi_u^+)$ state of $I_2$ is actually a very atypical system, in that it has been exhaustively studied and the data analysis has been done with unusually great care.23,38 This may partly explain the unexpectedly good agreement of the turning-point fit results with the recommended parameter values obtained here. However, application of the present approach to a variety of other systems should hopefully yield a database of reliable experimental $C_m$ coefficients to spur the development of better theoretical methods for calculating such coefficients, especially for excited electronic states.

ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work. This paper is respectfully and affectionately dedicated to the memory of the late Joseph O. Hirschfelder, who contributed so much to our knowledge of intermolecular forces, and whose Theoretical Chemistry Institute provided such a stimulating personal and professional environment for young scientists.

APPENDIX A: NUMERICAL METHODS

In preparation for numerically evaluating the integrals of Eq. (11) and (12), it is convenient to first use the definition of the turning point, Eq. (13), to express $D - E$ in terms of $R_2$. Introduction of the dimensionless variables $x = R_2 / R_2$ and $y = 1 / x$ then yields

$$I_i = (R_2)^{(1-n)} \int_0^1 \left[ \sum_{m=n}^{m_{\text{max}}} C_m R_2^{-m}(x^{-m} - 1) \right]^{1/2} x^{-1} dx,$$

and

$$v - v_D - (\beta / \pi) R_2 \left[ \int_0^1 \left\{ \sum_{m=n}^{m_{\text{max}}} C_m R_2^{-m}(x^{-m} - 1) \right\}^{1/2} dx - \int_0^1 \left( \sum_{m=n}^{m_{\text{max}}} C_m R_2^{-m}(y^{-m} - 1) \right)^{1/2} y^{-1} dy \right].$$

These same changes of variables convert the integrals appearing in the expressions for the partial derivatives given in Appendix B into analogous definite integrals over the dimensionless variables $x$ or $y$.

The integrands of most of the above integrals have square-root singularities of the form $(1 - x)^{1/2}$ or $(1 - y)^{1/2}$ at one or both limits. Although these singularities are integrable, care must be taken to choose an appropriate integration scheme for each case. In the program used in the present work, all of the integrals encountered are evaluated using Gauss-Legendre quadrature procedures. Integrand with no singularities are integrated using this scheme with a weight function of $1$, while those which have square-root singularities when $x = 1^-$ and $y = 1^-$ are evaluated using Gauss-Legendre quadrature procedures. Integrands with no singularities are integrated using this scheme with a weight function of $1$, while those which have square-root singularities when $x = 1^-$ and $y = 1^-$ are evaluated using Gauss-Legendre quadrature procedures. The alternative scheme used here is to perform all integrations with the same fixed numbers of points and weights $N$ (e.g., $N = 16$), and to achieve the desired accuracy by repeatedly subdividing the interval and summing the component integrals, until convergence is achieved. However, this would require either storing an arbitrarily large number of quadrature points and weights, or the time-consuming computation of those points and weights as each integral is being evaluated.

The alternative scheme used here is to perform all integrations with the same fixed numbers of points and weights $N$ (e.g., $N = 16$), and to achieve the desired accuracy by repeatedly subdividing the interval and summing the component integrals, until convergence is achieved. The error formulas in Ref. 34 show that for an $N$-point quadrature scheme, the total error decreases by a factor of $2^{-2N}$ each time the interval is halved, and the integration on each of the half-intervals performed using the same number of points $(N\pi)$ previously used for the whole interval. This procedure is repeated until the difference between the values of the complete integral yielded by two adjacent cycles either becomes zero (to machine accuracy) or increases from its value for the preceding test. The latter only occurs when numerical roundoff effects at the threshold of machine precision become the dominant source of error, which provides a clear indication that the optimum numerical accuracy has been achieved.

The alternative scheme used here is to perform all integrations with the same fixed numbers of points and weights $N$ (e.g., $N = 16$), and to achieve the desired accuracy by repeatedly subdividing the interval and summing the component integrals, until convergence is achieved. The error formulas in Ref. 34 show that for an $N$-point quadrature scheme, the total error decreases by a factor of $2^{-2N}$ each time the interval is halved, and the integration on each of the half-intervals performed using the same number of points $(N\pi)$ previously used for the whole interval. This procedure is repeated until the difference between the values of the complete integral yielded by two adjacent cycles either becomes zero (to machine accuracy) or increases from its value for the preceding test. The latter only occurs when numerical roundoff effects at the threshold of machine precision become the dominant source of error, which provides a clear indication that the optimum numerical accuracy has been achieved.
Once this is done, values of $I_0$, $I_2$, and the other integrals appearing in Eq. (A2) and the expressions for the various partial derivatives presented in Appendix B may be readily evaluated using the quadrature techniques described above.

The final numerical problem to be addressed here concerns the determination of the vibrational eigenvalues of a given model potential. This may be accomplished using a simple steepest descent technique. In particular, for any given trial energy $E$, evaluation of the integrals in Eqs. (12) or (A2) yields the corresponding value of the effective vibrational index $\nu$. At the same time, Eq. (10) provides an expression for the rate of change of $\nu$ with energy. Thus, an estimate of the energy change $\Delta E$ which will cause Eqs. (2) or (A1) to yield a desired integer value of $\nu$ is readily obtained as $\Delta E = (2\pi/\beta) \Delta \nu / I_0$, where $\Delta \nu$ is the requisite change in $\nu$. Iterative application of this procedure leads to rapid convergence on the desired eigenvalues.

Once the vibrational eigenvalues have been determined, the rotational constants $B_i$ and the partial derivatives of Appendix B may be calculated and used to perform one cycle of fit. The resulting improved parameter values are then used to calculate a “new” outer turning point and thus “new” vibrational energies and rotational constants. This procedure is continued until the effect of further changes in the parameters is negligible.

APPENDIX B: INTEGRAL EXPRESSIONS FOR PARTIAL DERIVATIVES REQUIRED BY THE FITS

Expressions for the partial derivatives required for the least-squares-fitting procedure are readily generated from Eqs. (7) and (11)–(13). With use of the transformations outlined in Appendix A, the derivatives of the vibrational energies with respect to the various parameters of the model may be expressed as

\[
\frac{\partial E}{\partial D} \bigg|_{v,D,(c_m)} = 1, \tag{B1}
\]

\[
\frac{\partial E}{\partial \nu} \bigg|_{v,D,(c_m)} = -2\pi/\beta I_0, \tag{B2}
\]

\[
\frac{\partial E}{\partial C_k} \bigg|_{v,D,(c_m),m_{+k}} = \frac{R_0^{\frac{1}{2}}}{I_0^{\frac{1}{2}}} \left( \int_0^1 \left[ \sum_{m=n}^{m_{+k}} C_m R_2^{m} x^{-m} \right]^{-1/2} dx \right)
- \left[ \sum_{m=n}^{m_{+k}} C_m R_2^{m} (x^{-m} - 1) \right]^{-1/2} x^{-k} dx
+ \int_0^1 \left[ \sum_{m=n}^{m_{+k}} C_m R_2^{m} x^{-m} \right]^{-1/2} j^{-k-2} dy. \tag{B3}
\]

The partial derivatives of the $B_i$'s are generated from the partial derivatives of the $I_i$ integrals using the familiar quotient rule result:

\[
\frac{\partial B_i}{\partial \nu} = \left[ I_0 \left( \frac{\partial I_0}{\partial \nu} \right) - I_2 \left( \frac{\partial I_2}{\partial \nu} \right) \right] / \beta^2 I_0. \tag{B4}
\]

However, we note from Eq. (A1) that $I_1$ depends explicitly only on $R_2$ and the $C_m$'s, while $R_2$ depends [see Eq. (13)] on $E, D$, and the $C_m$'s, and $E$ in turn depends on all of $v, v_D, D$, and the $C_m$'s. Moreover, the partial derivatives of interest are associated with the properties of particular vibrational levels, and hence must be evaluated at constant $\nu$ rather than at constant $E$. Thus, their determination will clearly involve extensive use of the chain rule.

As a starting point, consideration of Eqs. (13) shows that

\[
\left( \frac{\partial R_2}{\partial E} \right) \bigg|_{(c_m)} = \left( \sum_{m=n}^{m_{+k}} mC_m R_2^{m+1} \right)^{-1}
= - \left( \frac{\partial R_2}{\partial E} \right) \bigg|_{(c_m)} = R_0^\frac{1}{2} \left( \frac{\partial R_2}{\partial E} \right) \bigg|_{(c_m),m_{+k}} \tag{B5}
\]

Combining this result with Eq. (B1) then shows that $\left( \frac{\partial I_1}{\partial E} \right) \bigg|_{v,D,(c_m)} = 0$, and hence that

\[
\frac{\partial B_2}{\partial E} \bigg|_{v,D,(c_m)} = 0. \tag{B6}
\]

For the remaining parameters, the chain rule shows that

\[
\frac{\partial I_1}{\partial C_k} \bigg|_{v,D,(c_m),m_{+k}} = \left( \frac{\partial I_1}{\partial C_k} \right) \bigg|_{(c_m)} + \left( \frac{\partial I_1}{\partial R_2} \right) \bigg|_{(c_m)} \times \left( \frac{\partial R_2}{\partial C_k} \right) \bigg|_{(c_m)} \times \left( \frac{\partial E}{\partial C_k} \right) \bigg|_{v,D,(c_m),m_{+k}} \tag{B7}
\]

and

\[
\frac{\partial I_1}{\partial \nu} \bigg|_{v,D,(c_m),m_{+k}} = \left( \frac{\partial I_1}{\partial \nu} \right) \bigg|_{(c_m)} + \left( \frac{\partial I_1}{\partial R_2} \right) \bigg|_{(c_m)} \times \left( \frac{\partial R_2}{\partial \nu} \right) \bigg|_{v,D,(c_m),m_{+k}} \times \left( \frac{\partial E}{\partial \nu} \right) \bigg|_{v,D,(c_m),m_{+k}}. \tag{B8}
\]

The partial derivatives of $E$ are given by Eqs. (B1)–(B3), while those of $R_2$ are obtained from Eq. (B5). Expressions for the two remaining terms are then obtained by differentiating Eq. (A1):

\[
\left( \frac{\partial I_1}{\partial R_2} \right) \bigg|_{(c_m)} = \frac{(1 - h)I_1 - R_0^{\frac{1}{2}}}{R_2} \times \left( \frac{1}{2} \right)
\times \left( \int_0^1 \left[ \sum_{m=n}^{m_{+k}} mC_m R_2^{m} (x^{-m} - 1) \right]^{-3/2} dx \times \left( \int_0^1 \left[ \sum_{m=n}^{m_{+k}} mC_m R_2^{m} (x^{-m} - 1) \right] \right) dx \right). \tag{B9}
\]

and

\[
\left( \frac{\partial I_1}{\partial C_k} \right) \bigg|_{R_2,(c_m),m_{+k}} = - \frac{1}{2R_0^{\frac{1}{2}} \left( \frac{1}{2} \right)} \times \left( \frac{1}{2} \right)
\times \left( \int_0^1 \left[ \sum_{m=n}^{m_{+k}} mC_m R_2^{m} (x^{-m} - 1) \right]^{-3/2} dx \times (x^{-k} - 1) x^{-l} dx \right). \tag{B10}
\]

\[
\]

Downloaded 03 Nov 2003 to 128.97.80.195. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp
This completes the specification of the partial derivatives required for the fitting procedure.

The integrals that must be evaluated are therefore those appearing in Eqs. (A1), (A2), (B3), (B9), and (B10). The integrands appearing in (A1), (B9), and (B10) all have the same qualitative behavior; they have a simple square-root singularity at the upper bound, while at the lower bound they are well behaved if $m_{\text{max}}$ is an even integer but have a square-root singularity if it is odd.\(^\text{(1)}\) In the latter case, we note that if we divide the range in two, the integrands on the resulting subintervals both have a square-root singularity at one end of the range and are well behaved at the other, and hence may be evaluated using the same quadrature procedure.

To evaluate the first integral in Eqs. (A2) and (B3), it convenient to first divide the range of integration in half. The resulting integrands on the range \([0, 1/2]\) are well behaved at the upper bound but have a square-root singularity at the lower bound if $m_{\text{max}}$ is an odd number. On the subinterval from \([1/2, 1]\) the first term in the integrand is well behaved everywhere, while the second is well behaved at the lower limit but has a square-root singularity at the upper limit. Finally, the last integral \((\text{over } v)\) in Eqs. (A2) and (B3) is well behaved at the upper limit, but has a square-root singularity at the lower bound if the leading inverse power $n$ is odd. Thus, since all of the integrands encountered here are either well behaved everywhere or have a square-root singularity at one end of the range, they may be accurately and efficiently evaluated using the quadrature procedures described in Appendix A.


A concise summary of the rules determining which terms contribute in a given case is given in Sec. 2 of Ref. 6, while the underlying theory is found in Refs. 1 and 2, and references therein.


\(^14\)W. C. Stwalley, Paper D12 at the 25th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1970 (unpublished); L. Gott-


\(^16\)W. C. Stwalley, Paper D12 at the 25th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1970 (unpublished); L. Gott-
values of $\nu_L$.

49 The neglect of interparameter correlation effects is the reason that the uncertainties reported in Ref. 21 (see column 2 of Table II) are almost 2 orders of magnitude smaller than the correlated uncertainties obtained here for turning-point fits which yield exactly the same parameter values.


50 The one situation in which the magnitudes of these terms do not decrease rapidly with increasing order is the pathological case of energies extreme-