An inversion procedure for oscillatory continuum spectra: Method and application to NaK

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An inversion procedure is developed for determining an attractive potential energy well from the structure of an oscillatory absorption or emission continuum originating in a single vibrational level of that well. It is successfully applied to synthetic data for the \( ^3\Pi_{1u} \rightarrow X(\Sigma^+ \text{g}) \) absorption continuum of \( \text{Br}_2 \) and to experimental data for \( d(\Pi_1) \rightarrow a(\Sigma^+ \text{g}) \) emission of NaK. The latter application succeeds in spite of the facts that (i) the repulsive wall of the final-state potential is also not known, and (ii) this final-state curve has an attractive well whose location causes the structured emission continuum to be truncated, making the vibrational assignment uncertain. This analysis yields potentials for the well of the \( d(\Pi_1) \) state and the repulsive wall of the \( a(\Sigma^+ \text{g}) \) state of NaK, together with the slope of the transition dipole function coupling these two states.

I. INTRODUCTION

A previous paper \(^1\) has described an inversion procedure for determining a repulsive final-state potential energy curve from an oscillatory absorption or emission continuum originating in a single vibrational level of a known initial-state potential. The present work presents and tests a complementary inversion procedure which determines the well of such an initial-state potential from a knowledge of this structured continuum and of the repulsive final-state potential energy curve. An illustrative application of the method to experimental data for NaK shows that it is also useful for cases in which the experimental data are incomplete and the vibrational assignment of the initial level is not certain. It is also shown that under some conditions, both the attractive initial-state potential and the repulsive final-state curve may be determined from a combination of such continuum data with discrete intensities and other spectroscopic information.

In the following, Sec. II describes the phenomenon of interest and reviews the uniform harmonic approximation for bound–continuum transition intensities on which the present method is based. \(^2\) The inversion procedure itself is presented in Sec. III. The new method is then tested in Sec. IV, first on synthetic data for a well-understood model problem, and then using experimental data for NaK as a model of a system for which incompleteness of the spectrum makes the vibrational assignment of the initial-state level uncertain. Finally, Sec. V describes a practical application of this approach to the \( d(\Pi_1) \rightarrow a(\Sigma^+ \text{g}) \) spectrum of NaK, a case in which neither the bound initial-state potential nor the repulsive final-state potential were accurately known. The summary and discussion presented in Sec. VI also argues that the quality of results obtained herein could not readily be obtained with the kind of trial-and-error spectral simulation and comparison approach often used for this type of analysis.

II. BOUND–CONTINUUM TRANSITION INTENSITIES AND THE UNIFORM HARMONIC APPROXIMATION

The phenomenon of interest here is schematically illustrated by Fig. 1. It consists of the absorption (or emission) of light of frequency \( \nu = |E - E_v| \) (in \( \text{cm}^{-1} \)) by a molecule which is initially in vibrational level \( v \) with energy \( E_v \) and inner and outer turning points \( a_v(\nu) \) and \( b_v(\nu) \) on an attractive potential energy curve \( V_1(R) \), causing a transition to the continuum level at energy \( E \) with turning point \( R_2(E) \) on the repulsive final-state potential \( V_2(R) \). \(^3\) The example considered in Fig. 1 is absorption from the \( \nu = 5 \) level of the \( X(\Sigma^+ \text{g}) \) state of \( \text{Br}_2 \) into the continuum associated with the repulsive \( ^3\Pi_{1u} \) state. However, the present discussion applies equally well to both absorption and emission.

A qualitative explanation of this phenomenon is provided by the simple reflection or delta-function approximation to the Franck–Condon principle for bound–continuum transitions. \(^4\) It predicts that the intensity of a transition at frequency \( \nu \) from vibrational level \( v \) with wave function \( \Psi_v(R) \) on potential energy curve \( V_1(R) \) into the continuum associated with final-state potential \( V_2(R) \) is

\[
I(\nu) = I[\nu(R_2)] \propto |\Psi_v(R_2)|^2,
\]

where \( \nu(R) = |V_2(R) - E_v| \) and \( R_2 = R_2(E) \) is as defined above. While Eq. (1) is only qualitatively correct, it does convey the information that the observed pattern of intensities generally represents a mapping of the squared initial-state wave function onto the energy axis. Since the radial Schrödinger equation may be rearranged as
FIG. 1. Schematic illustration of bound-continuum absorption from the $v = 3$ level of the $\chi (1 \Sigma_g^+)$ state of Br$_4$ into the $\Pi_{1g}$ state continuum. Left-hand segment: continuum absorption spectrum; right-hand segment: potential curves illustrating definitions of variables.

\[ V_1(R) = E_o + \frac{\hbar^2}{2\mu} \frac{1}{\Psi_{1,v}(R)} \frac{d^2 \Psi_{1,v}}{dR^2} \]  

(2)

It is clear that a knowledge of $\Psi_{1,v}(R)$ obtained from the pattern of such intensities implicitly defines the initial-state potential. This is the physical basis of the present method.

While Eq. (1) explains the qualitative behavior of most bound-continuum spectra, it has been amply documented that it is only qualitatively correct. An accurate inversion procedure must therefore be based on a more exact description of the transition intensities. The present approach is based on the uniform harmonic approximation of Hunt and Child, which has been shown to provide an extremely accurate description of bound-continuum spectra in the "Condon reflection" regime. The essential condition for this method to be applicable at a given final-state energy $E$ is that on the interval between the initial-state turning points $a_1(v)$ and $b_1(v)$, there exists only one momentum-conserving transition point $R_x$, as defined by the condition

\[ E - V_2(R_x) = E_o - V_1(R_x). \]  

(3)

If this condition is not satisfied, the transition intensity acquires a more complex interference structure, and neither the present inversion procedure nor the underlying theory are appropriate.

Hunt and Child’s uniform harmonic approximation shows that the transition amplitude coupling vibrational level $v$ to a continuum state at energy $E$ may be written as

\[ M_{\nu,E} = \int_0^\infty \Psi_{1,v}(R) M(R) \Psi_{2,E}(R) dR \]

\[ \approx M(R_x) \int_0^\infty \Psi_{1,v}(R) \Psi_{2,E}(R) dR \]

(4)

where $M(R)$ is the transition dipole function, $\phi_n(\xi)$ is the $n$th harmonic oscillator wave function

\[ \phi_n(\xi) = \left[ 2^n \sqrt{n!} \xi^{n+1/2} \right]^{-1/2} \exp(-\xi^2/2) \]  

(5)

and the argument $\xi(E)$ is implicitly defined by the equation

\[ \Delta(E) = \sqrt{2\mu/\hbar^2} \left\{ \int_{R_x}^{R_x(\xi)} [E - V_2(R)]^{1/2} dR ight\} \]

\[ + \int_{R_x}^{R_x(\xi)} [E_o - V_1(R)]^{1/2} dR \]

\[ = -\xi(2v + 1 - \xi^2)^{1/2}/2 \]

\[ + (v + 1)^{1/2} \cos^{-1} \left[ \xi/(2v + 1)^{1/2} \right], \]  

(6)

where $\mu$ is the reduced mass. The constant $\bar{\omega}$ appearing in Eq. (4) is the initial-state classical oscillation frequency for level $v$ (in radians per second),

\[ \bar{\omega} = (\partial E_o/\partial v)/\hbar \]

and the quantities $u_v$ and $\Delta F_v$ are defined by the properties of the two potential energy curves at the transition point $R_x$:

\[ u_v = \left\{ 2 [E - V_2(R_x)]/\mu \right\}^{1/2}, \]

(7)

\[ \Delta F_v = V_1(R_x) - V_2(R_x), \]  

(8)

where primes denote differentiation with respect to $R$.

Equation (4) predicts [in agreement with Eq. (1)] that the continuum absorption or emission spectrum originating in vibrational level $v$ has $(v + 1)$ maxima, one associated with each extremum of the harmonic oscillator wave function $\phi_n(\xi)$, separating zero-intensity minima, one associated with each of the nodes of $\phi_n(\xi)$. Since the $\xi$ values associated with the extrema and nodes of $\phi_n(\xi)$ are well known, the correct assignment of the observed intensity extrema to appropriate $\xi$ values uniquely defines the function $\xi(E)$. In the inversion problem, this "experimental" knowledge of $\xi(E)$ is combined with a knowledge of one of the potentials, $V_1(R)$ or $V_2(R)$, and used to determine the other.

Reference 1 was concerned with determination of the repulsive final-state potential $V_2(R)$ from a knowledge of the attractive initial-state potential $V_1(R)$, while the present paper presents a method for determining $V_1(R)$ from a knowledge of $V_2(R)$.

For the model problem of Fig. 1, the mapping of $M_{\nu,E}$ onto $\xi$ was illustrated by Fig. 3 of Ref. 1. That case was very straightforward, since there is no bound-bound contribution to the associated spectrum and all of the expected intensity extrema were clearly resolved. A more difficult case is illustrated by the present Fig. 2, which plots the positions of the intensity extrema in an NaK emission spectrum reported by Bredford and Engelke vs the values of $\xi$ appropriate to a $v = 13$ assignment for the emitting state. In this second example, the final-state potential has a shallow attractive well and the high frequency end of the emission spectrum becomes discrete, so the intensity extrema associated with the lowest final-state energies cannot be clearly resolved. As a result, the experimental points in Fig. 2 do not span a symmetric range of $\xi$ values, and the different possible extrapolations to the outer turning point $\xi = (2v + 1)^{1/2}$ indicate that

III. THE PRESENT INVERSION PROCEDURE

As in the inversion procedure of Ref. 1, the present method is based on the energy derivative of Eq. (6):

$$d\Delta/dE = \left(\mu/2\hbar^2\right)^{1/2} \int_{R_s(E)}^{R_u(E)} \left[ E - V_2(R) \right]^{-1/2} dR$$

$$= -(2\nu + 1 - \xi^{2})^{1/2} (d\xi/dE).$$

(10)

The $\xi(E)$ function is defined by associating the energies of the intensity extrema in the observed continuum spectrum with the (known) $\xi$ values at the extrema and nodes of the harmonic oscillator function $\phi_4(\xi)$ for the given initial-state vibrational assignment (e.g., see Fig. 2). For any chosen final-state energy $E$, the associated values of $\xi(E)$ and $d\xi/dE$ yield a value for $d\Delta/dE$. Since $V_s(R)$, and hence $R_s(E)$, are (assumed to be) known, the next step is simply to determine a value for $R_s(E)$ (the upper bound on the integral) which satisfies Eq. (10). This may be done using Newton-Raphson iteration or some analogous algorithm. Substituting the resulting $R_s(E)$ value into Eq. (3) then yields a point on the desired initial-state potential $V_1(R)$:

$$V_1[R_s(E)] = V_2[R_s(E)] + (E_o - E)$$

$$= V_2[R_s(E)] \pm \nu,$$

(11)

where the + and − signs on the right-hand side correspond to the cases of emission and absorption, respectively. This is the essence of the present inversion procedure.

A practical application of the above method would usually begin by determining the initial-state turning points $a_1(v)$ and $b_1(v)$ by extrapolating the experimentally determined $(E - E_o)$ vs $\xi$ data (see Fig. 2) to the phase values associated with the turning points, $\xi = (2\nu + 1)^{1/2}$. The corresponding values of $E$ are $E_o = V_2[a_1(v)]$ and $E_o = V_2[b_1(v)]$ (see Fig. 1). Since $a_1(v) = R_s(E_o)$ and $b_1(v) = R_s(E_o)$, interpolating for these energies on the known final-state potential $V_s(R)$ then yields the desired values of $a_1(v)$ and $b_1(v)$. Additional initial-state potential points in the range $a_1 < R < b_1$ may then be generated by applying Eqs. (10) and (11) at arbitrary energies in the range $E_o < E < E_o$.

In general, a structured absorption or emission continuum will be associated with nonzero values of the angular momentum quantum number $J$ for the initial and final states. The present method takes account of centrifugal distortion effects in the following way. First of all, the appropriate final-state centrifugal term is incorporated into the (known) effective potential $V_s(R)$ used in Eqs. (10) and (11). The values of $V_1(R)$ obtained from Eq. (11) [as well as the turning points $a_1(v)$ and $b_1(v)$ at energy $E_o$] will then contain the analogous centrifugal term associated with the initial-state rotational quantum number. The desired rotationless initial-state potential is then obtained by subtracting the appropriate centrifugal term from this inverted potential.

It is shown below that it is a straightforward matter to apply the above procedure to a complete set of intensity extrema associated with transitions onto a purely repulsive final-state potential. However, we also show that it may be readily applied to cases where a mainly repulsive final-state
TABLE I. Assignment of intensity extrema in the synthetic $^1\Pi_u \rightarrow X^1\Sigma^+_g$ $(v = 5)$ absorption spectrum of Br$_2$.

<table>
<thead>
<tr>
<th>Maxima</th>
<th>Minima</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi$</td>
<td>$E$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>--2.756 238</td>
<td>29 005</td>
</tr>
<tr>
<td>--1.475 241</td>
<td>25 802</td>
</tr>
<tr>
<td>--0.476 251</td>
<td>23 618</td>
</tr>
<tr>
<td>0.476 251</td>
<td>21 780</td>
</tr>
<tr>
<td>1.475 241</td>
<td>20 095</td>
</tr>
<tr>
<td>2.756 238</td>
<td>18 271</td>
</tr>
</tbody>
</table>

potent also has an attractive well, and some of the expected intensity extrema are not observed.

A couple of technical points concerning the application of the present method also deserve comment. Since the positions of the intensity extrema always have uncertainties associated with them, while the corresponding values of $\xi$ are exact, it is most appropriate to treat $\xi$ as the independent variable when fitting to phase information such as that shown in Table I or Fig. 2. The resulting function may then be inverted numerically to yield the required values of $\xi$ and $d\xi/dE$ associated with arbitrary values of $E$. This step introduces no significant complications.

Another point regarding the treatment of the intensity extrema-phase information concerns how such data should be weighted in the fits. In general, the uncertainties in the positions of intensity extrema increase with their widths, and the latter vary inversely as the spacing between adjacent extrema. In the least-squares fits to determine the desired smooth $E(\xi)$ function, the weight associated with each datum was therefore made proportional to the inverse square of the average spacing between adjacent extrema. For the 20 data shown in Fig. 2, this implies that the associated uncertainties decrease by a factor of 5.9 from the low- to the high-frequency end of the spectrum.

A final technical point concerns the relationship between the actual observed intensity maxima and the extrema of the harmonic oscillator function of Eq. (5). The strength of a bound-continuum transition is proportional to $\nu^p M_{\nu,R}^2$, where the power $p$ equals 1 for absorption and 3 for spontaneous emission. In general, therefore, both the frequency factor and the $R$ dependence of the transition dipole function will tend to shift the observed intensity maxima (though not the minima) away from the energies associated with the extrema of $\phi_0(\xi)$ [see Eq. (4)]. However, the magnitude of such displacements may readily be determined from simulations of the continuum spectrum which in turn include and omit these terms.\textsuperscript{11,12} An initial analysis which ignores these effects may therefore be used to determine trial potential energy and transition moment functions, and such simulations in turn used to determine the magnitude of such shifts for each of the peaks in the experimental spectrum. The resulting displacements may then be subtracted from the raw peak position energies, yielding values more directly attributable to the extrema of the $\phi_0(\xi)$ factor in Eq. (4).

Copies of a FORTRAN program which implements the present inversion procedure, together with a sample data set, may be obtained from the first author, on request.\textsuperscript{6,12}

IV. DEMONSTRATIONS OF THE METHOD

A. When the experimental data set is complete

As a first test, the above method was applied to synthetic data for the model problem schematically illustrated in Fig. 1, absorption from the $\nu = 5$ level of the $X^1\Sigma^+_g$ state of Br$_2$ into continuum levels of the $^1\Pi_{1u}$ state sharing the same dissociation limit. As in Ref. 1, the synthetic spectrum was generated by performing exact quantum mechanical photodissociation calculations using the (rotationless) potential energy curves of Ref. 6 and the assumed transition moment function: $M(R) = 1.11$

As is seen in Fig. 1, the spectrum for this Br$_2$ model problem has six intensity maxima interleaved with five intensity minima. Since this is the pattern expected for continuum absorption from a $\nu = 5$ vibrational level, these "experimental" intensity extrema were assigned to $\xi$ values associated with the extrema and nodes of the $\nu = 5$ harmonic oscillator wave function $\phi_5(\xi)$ (see Table I). After fitting these points to a polynomial, the present inversion procedure was applied to the resulting $E(\xi)$ function and the known final-state potential.\textsuperscript{6,13}

\[ V_2(R) = 7654 \exp[-4.6368(R - 2.3)] - 0.879(R - 2.3)^2 + 14311.38. \] (12)

For the case of a third-order polynomial representation of the phase information, Fig. 3 compares the resulting initial-state potential (points) with the "exact" potential used to generate the synthetic spectrum (solid curve). The agreement seen there is a very convincing illustration of the reliability of the present method.

On the scale of Fig. 3, inverted potentials based on second-, third-, and fourth-order polynomial fits to the phase information of Table I are indistinguishable. However, as a

![FIG. 3. For the model Br$_2$ absorption problem illustrated by Fig. 1, comparison of inverted potential points (■) with the smooth potential used to generate the synthetic spectrum (solid curve).](image-url)
TABLE II. For the synthetic Br$_2$ spectrum of Fig. 1 and Table I, results of tests of
dependence of $\xi$ on the energies of observed intensity extrema, energies are in
cm$^{-1}$ and lengths in Å.

<table>
<thead>
<tr>
<th>Order</th>
<th>$E_a$</th>
<th>$E_b$</th>
<th>$a_1(v)$</th>
<th>$b_1(v)$</th>
<th>$\Delta E_{rms}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>310.30</td>
<td>29086</td>
<td>16733</td>
<td>2.1541</td>
<td>2.5374</td>
</tr>
<tr>
<td>2</td>
<td>10.98</td>
<td>30498</td>
<td>17629</td>
<td>2.1332</td>
<td>2.4745</td>
</tr>
<tr>
<td>3</td>
<td>3.92</td>
<td>30565</td>
<td>17587</td>
<td>2.1233</td>
<td>2.4771</td>
</tr>
<tr>
<td>4</td>
<td>3.61</td>
<td>30546</td>
<td>17575</td>
<td>2.1235</td>
<td>2.4778</td>
</tr>
<tr>
<td>5</td>
<td>3.93</td>
<td>30540</td>
<td>17579</td>
<td>2.1236</td>
<td>2.4776</td>
</tr>
<tr>
<td>Exact values</td>
<td>30585</td>
<td>17602</td>
<td>2.1320</td>
<td>2.4762</td>
<td>0.0</td>
</tr>
</tbody>
</table>

potential is much steeper than $V_1(R)$ across the energetically
accessible interval, or (iii) there may simply be a loss of
intensity or resolution in the experimental spectrum.

An NaK spectrum reported by Breford and Engelke$^9$ is
an example of an incomplete structured emission continuum of type (i). While ten intensity maxima are clearly resolved in
the continuum region and at least three more peaks in the
discrete region, a piling up of the structure at the high fre-
quency end of the spectrum prevents an unambiguous vibra-
tional assignment of the emitting level. However, it is shown
here that this ambiguity does not prevent the determination of
an accurate initial-state potential from such data. This
NaK spectrum has been reassigned by Katô and Noda$^{10}$ as
emission from the $v = 13$ level of the $d^6(3\Pi_1)$ state into the
$a^2(\Sigma^+)$ state continuum. However, the appropriateness
of their reassignment and the accuracy of the assumed-known
final-state potential used in the present section are irrelevant
to the present discussion (these points are considered in
more detail in Sec. V). The object here is simply to demon-
strate that ignorance of the correct vibrational assignment
for the emitting level need not affect the accuracy of the (in-
complete) initial-state potential determined in such cases.

In Fig. 2, the positions of the first 20 intensity extrema in
this experimental NaK spectrum$^9$ are plotted vs the values of
$\xi$ appropriate to a $v = 13$ assignment for the emitting level.
The curves drawn there represent quadratic, cubic, and quartic
$E(\xi)$ polynomials determined by least-squares fits to
these data. Analogous plots for other plausible assignments
of the emitting level would be qualitatively very similar.
Figure 2 clearly demonstrates that incoherence of the data
set can give rise to significant uncertainty regarding the ex-
trapolation to determine $E_b$ (right-hand intercept), and
hence $b_1(v)$, even if the correct initial-state vibrational as-
signment is known. At the same time, however, the interpo-
lation over the available data and the extrapolation to deter-
mine $E_a$ (left-hand intercept), and hence $a_1(v)$, are clearly
quite insensitive to the order of the polynomial.

The $a^2(\Sigma^+)$ final state associated with this emission
continuum has a shallow ($\sim 209$ cm$^{-1}$) attractive well
at distances beyond 4.5 Å, which is responsible for the incoherence$^{15}$ of the experimental spectrum. However,
the observation of discrete emission into the bound levels of
this potential has allowed the construction of an RKR po-
tential for the well region$^{16,17}$ to which the repulsive final-
state potential of interest here is joined. In the present work,
this (assumed-known) potential repulsion was represented by
the simple exponential function

$$V_2(R) = A + Be^{-BR},$$

where $\beta = 1.67$ Å$^{-1}$ (for the examples described in the
present section), and the constants $A$ and $B$ are determined by
a fit to inner-wall RKR turning points.

For a case such as this, the incompleteness of the phase
information makes the initial-state vibrational assignment
uncertain. Together with the uncertainties regarding the ex-
trapolation (see Fig. 2), this means that the inversion pro-
dure alone will be unable to yield reliable initial-state potential
points extending all the way to the outer turning point $b_1(v)$.
In particular, unless the extrapolation is very short, the
end of the phase information (see Fig. 2) defines the

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**B. Application to an incomplete data set: The**
$d^6(3\Pi_1) \rightarrow a^2(\Sigma^+)$ **emission spectrum of NaK**

The above example shows that the present inversion procedure works well when the repulsive potential is mono-
tonic and all of the intensity extrema are clearly resolved and
included in the data set. In practice, however, a real experi-
mental data set may be incomplete$^{15}$ and the assignment of
the emitting level unclear for a variety of reasons, such as: (i)
if the final-state potential has a well, the pattern of intensity
extrema may be truncated or unresolved at final-state ener-
gies near the potential minimum, (ii) the full structure at
high final-state energies may be lost either because (in emis-
ion) $V_2(R)$ crosses the energy $E_a$ at a distance significantly
larger than $a_1(v)$, or because (in absorption) the final-state

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lowest final-state energy which should be used in Eq. (10). The $R_x$ value associated with this energy will then be an approximate upper bound to the range of reliable directly inverted initial-state turning points. Sometimes this range must be further truncated because of the simple requirement that the properties of the inverted potential be physically "reasonable." However, the details of such considerations have no bearing on the question of interest here, and their discussion is deferred to Sec. V B.

Using the "known" final-state potential specified above, the present inversion procedure was applied to the intensity extrema-phase information shown in Fig. 2, using a variety of initial-state vibrational assignments. The inverted initial-state potentials obtained when the emitting level was identified in turn as $v = 11, 12, 13, 14,$ and 15 are shown by Fig. 4 to be virtually coincident (solid curves). This figure clearly shows that over the region characterized by the phase information, exactly the same inverted potential is obtained, independent of the assumed vibrational assignment. At first glance, this result may seem somewhat surprising. However, Eq. (2) reminds us that the behavior of a wave function on a given interval defines exactly the same potential across that region, independent of how many additional nodes and extrema it may have at larger (or smaller) distances. The uniform harmonic approximation provides a unique mapping of the initial-state wave function onto the structured emission continuum (in the Condon reflection regime), and the stationary phase approximation underlying Eq. (4) means that these matrix elements will depend mainly on the wave functions in the immediate neighborhood of the transition point. Thus, the same considerations should carry over to the present inversion procedure, and the agreement seen in Fig. 4 is thus expected.

Although the potential obtained directly from the inversion procedure may have to be truncated for the reasons described above, a reasonable estimate of the outer turning point $b_i(v)$ may be obtained in the following manner. Different trial initial-state potentials are obtained on extrapolating beyond the (incomplete) directly inverted potential points to differential trial $b_i(v)$ values. As a matter of internal consistency, however, the calculated energy of vibrational level $v$ in the "correctly extrapolated" potential well must agree with the (known) $E_v$ value used in the inversion procedure. Using a standard potential eigenvalue program, calculations for a series of trial $b_i(v)$ values can be used to rapidly converge upon a unique value consistent with the assumed vibrational assignment. This approach was used to define the broken-curve extrapolations to the outer turning points (solid points) $b_i(v)$ consistent with the five initial-state vibrational assignments considered in Fig. 4.

Once complete potential wells (up to energy $E_v$) have been determined using various plausible vibrational assignments, continuity and smoothness considerations may allow an unambiguous vibrational assignment to be made for the emitting level. For example, the relatively abrupt change in the shape of the $v = 11$ and 12 curves at the beginning of the extrapolation region in Fig. 4 suggests that the correct vibrational assignment in this case is most likely $v = 13.$ Similarly, the early (relative to the potential asymptote at $\sim 17000 \text{ cm}^{-1}$) inflection point on the $v = 14$ and 15 curves suggests that those values are too high. The implied $v = 13$ identity of the emitting vibrational level differs from the $v = 12$ assignment originally suggested in Ref. 9, but agrees with the reassignment proposed by Katô and Noda. In the present example, a definitive conclusion may not be reached from these considerations alone, since the (assumed-known) final-state potential has been, at this point, arbitrarily chosen. However, the five initial-state wave functions considered will have very different overlap integrals with the wave functions for the bound levels of the attractive well of the $a^3 \Sigma^-$-state potential, which lies at distances $R > 4.5 \text{ Å}.$ As will be shown below, the pattern of discrete intensities for transitions into these bound levels does unambiguously confirm this vibrational assignment.

In conclusion, therefore, the results shown in Fig. 4 demonstrate that uncertainty regarding the vibrational assignment of the discrete initial level giving rise to an incomplete structured continuum need not limit the accuracy of an inverted potential obtained using the present procedure. Moreover, for any assumed vibrational assignment, a realistic extrapolation of the inverted potential and a good estimate of the outer turning point $b_i(v)$ can readily be generated, and elementary smoothness criteria will often identify the correct initial-state vibrational assignment. Note, however, that this insensitivity to the initial-state vibrational assignment will hold only if the absolute numbering of the observed intensity extrema, counting from one end of the spectrum or the other, is certain. If this is not the case, considerably more uncertainty will arise.

V. ANALYSIS OF THE $d^{2}\Pi_{1/2} \rightarrow a^{3} \Sigma^-$ EMISSION SPECTRUM OF NaK

A. Overview of the problem and identification of the emitting level(s)

The structured emission continuum first seen by Bredford and Engelke arises following absorption of the 476.5

![Comparison of potentials for the d(11\text{H}_2) state of NaK obtained on inverting the data of Fig. 2 using the final-state repulsive potential of Eq. (13) with $B = 1.67 \text{ Å}^{-1},$ together with an assumed initial-state vibrational assignment $v$ ranging from 11 to 15 (near-coincident solid curves). The extrapolations shown as dashed curve segments were determined by the vibrational energy consistency requirement described in the text.](image)
nm Ar ion laser line by levels of the ground \(X'(\Sigma^+)^-\) state of NaK. The initial transitions into levels of the \(D'(\Pi)^+\) state were followed by fluorescence at frequencies near the exciting line, analysis of which yielded improved molecular constants for the ground state. However, a second spectrum observed at longer wavelengths was identified as simultaneous emission into bound and continuum levels of the shallow \(a(\Sigma^+)^-\) state potential which also dissociates to ground state atoms. Such transitions are of course forbidden from a \(1^1\Pi\) state, but spin–orbit interactions can mix the latter with a \(3\Pi_1\) state from which emission to the \(a(\Sigma^+)^-\) state is strongly allowed. Rotational analyses of the discrete portion of this spectrum, performed in the light of perturbation selection rules, confirmed the \(3\Pi\) nature of the emitting state.17,18 This allowed the upper state of this second spectrum to be identified as the previously unobserved \(d'(3\Pi)^+\) state which dissociates to Na\(\left(3P_3/2\right) + K\left(3S_1/2\right)\) atoms.

The rotational structure of the \(D'(3\Pi)^+ - X'(\Sigma^+)^-\) and \(d'(\Pi_1)^+ - a(\Sigma^+)^-\) spectra showed that fluorescence excited by 476.5 nm radiation is initiated by \(Q(14)\) and \(P(8)\) absorption into the \(v' J'\) = (12,14) and (12,7) levels of the \(D'(\Pi)\) state.17,18 It is the first of these transitions which is responsible for the structured emission continuum of interest here. Since angular momentum is conserved in the type of interstate perturbation giving rise to this spectrum, the centrifugal term associated with the structured emission continuum analyzed below also corresponds to \(J = 14\).

The positions and relative amplitudes of the intensity extrema in this emission continuum were carefully remeasured from an expanded version of the spectrum in Fig. 3 of Ref. 9 (kindly supplied by Dr. Breford19) and are listed in Table III. These values differ slightly from those used in Ref. 1. Following the approach described at the end of Sec. III, the shifts in peak position due to the frequency factor and the \(R\) dependence of the transition dipole function were determined to be 6, 2, 1, and 1 cm\(^{-1}\) for the first four (lowest frequency) maxima, and zero for the remainder. These corrections were therefore subtracted from the "raw" peak positions of Table III to obtain the input data for the intensity extrema-phase fits which define the \(E(\xi)\) function required by the present inversion procedure.

As was indicated above, neither the bound initial-state curve nor the repulsive final-state potential associated with this fluorescence spectrum is accurately known. The identification of the final state as the weakly bound \(a(\Sigma^+)^-\) state is almost certainly correct, but its repulsive wall has not been independently determined. Moreover, there has been some uncertainty regarding the vibrational assignment of the emitting level.10 In their original discussion, Breford and Engelske assumed that the \(d'(3\Pi_1)^+\) state potential was essentially identical to that for the \(d'(3\Pi)\) state excited by the initial absorption step, and hence that the triplet emission effectively originated in \(d'(3\Pi_i)^+\) state level \(v' = 12\). However, Refs. 1 and 10 independently showed that the \(v' = 12\) wave function of this (known) \(D'(3\Pi)^+\) state potential cannot be the source of the observed spectrum.

The discussion of Sec. IV B supports the suggestion of Katō and Noda10 that the emitting level is actually \(v' = 13\), rather than \(v' = 12\). Moreover, while the results shown correspond to the particular case of \(\beta = 1.67\) Å\(^{-1}\), the conclusion regarding the \(v = 13\) assignment was found to remain valid for a range of assumed final-state potentials. However, that approach is still qualitative. The problem addressed here is therefore that of providing more definitive confirmation for this assignment and determining both the otherwise unknown \(d'(3\Pi_i)^+\) initial-state potential and the repulsive part of the \(a(\Sigma^+)^-\) final-state curve, together with the \(R\)-dependent transition dipole function coupling the two.

As mentioned earlier, the relative intensities of discrete lines at the high frequency end of the \(d'(3\Pi_i)^+ - a(\Sigma^+)^-\) emission spectrum are also required for the present analysis. The intensities used here are for \(P(8)\) emission into \(a(\Sigma^+)^-\) state levels \(v = 0–14\) from the same \(d'(3\Pi_i)^+\) state vibrational level giving rise to the structured emission continuum. These results, kindly provided by Professor Katō,10,20 are listed in the first column of Table IV.

### Table III: Frequencies and relative amplitudes of the intensity extrema in the oscillatory \(d'(3\Pi_i)^+ - a(\Sigma^+)^-\) emission continuum of NaK reported by Breford and Engelske.

<table>
<thead>
<tr>
<th>(v) (cm(^{-1}))</th>
<th>Amplitude</th>
<th>(v) (cm(^{-1}))</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.267</td>
<td>36</td>
<td>15.350</td>
<td>78</td>
</tr>
<tr>
<td>14.468</td>
<td>0</td>
<td>15.405</td>
<td>0</td>
</tr>
<tr>
<td>14.614</td>
<td>40</td>
<td>15.462</td>
<td>85</td>
</tr>
<tr>
<td>14.748</td>
<td>0</td>
<td>15.520</td>
<td>0</td>
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<td>120</td>
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<td>14.956</td>
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<td>0</td>
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<tr>
<td>15.046</td>
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<td>15.660</td>
<td>150</td>
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<tr>
<td>15.209</td>
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<td>15.755</td>
<td>165</td>
</tr>
<tr>
<td>15.286</td>
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<td>15.790</td>
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### Table IV: Comparison of experiment (Refs. 10 and 21) with predicted relative intensities for \(P(8)\) emission from \(d'(3\Pi_i)^+\) state level \(v' = 13\) into levels \(v = 0–14\) of the \(a(\Sigma^+)^-\) state of NaK, as calculated from some proposed potentials.

<table>
<thead>
<tr>
<th>(v)</th>
<th>(\beta(\text{Å}^{-1}))</th>
<th>Experiment</th>
<th>1.52</th>
<th>1.68</th>
<th>1.80</th>
<th>2.27</th>
<th>KN*</th>
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<tr>
<td>0</td>
<td>10.0</td>
<td>9.66</td>
<td>9.87</td>
<td>9.93</td>
<td>10.17</td>
<td>10.05</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.6</td>
<td>3.65</td>
<td>3.09</td>
<td>2.98</td>
<td>1.78</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.1</td>
<td>4.84</td>
<td>5.03</td>
<td>5.05</td>
<td>5.24</td>
<td>5.15</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.23</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>2.70</td>
<td>2.40</td>
<td>2.35</td>
<td>1.65</td>
<td>1.87</td>
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<tr>
<td>5</td>
<td>2.7</td>
<td>2.92</td>
<td>2.97</td>
<td>2.95</td>
<td>2.95</td>
<td>2.98</td>
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<tr>
<td>6</td>
<td>0.8</td>
<td>0.65</td>
<td>0.79</td>
<td>0.79</td>
<td>1.11</td>
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<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>0.91</td>
<td>0.79</td>
<td>0.79</td>
<td>0.54</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.6</td>
<td>1.50</td>
<td>1.43</td>
<td>1.41</td>
<td>1.24</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.3</td>
<td>1.34</td>
<td>1.33</td>
<td>1.31</td>
<td>1.30</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
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<td>0.86</td>
<td>0.84</td>
<td>0.91</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
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<td>0.41</td>
<td>0.48</td>
<td>0.71</td>
<td></td>
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<tr>
<td>13</td>
<td>0.3</td>
<td>0.13</td>
<td>0.15</td>
<td>0.15</td>
<td>0.20</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.0</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
<td>0.24</td>
<td></td>
</tr>
</tbody>
</table>

*Potentials of Ref. 10.
Another type of experimental data used below is the observation that excitation of a variety of other $D^1(\Pi)$-state levels also gives rise to triplet fluorescence. In particular, Eisel et al. found that singlet and triplet fluorescence was excited at 488.0 nm by an $R(22)$ transition from $X$-state level ($v' = 1, J' = 22$) into the $D^1(\Pi)$-state level ($v' = 7, J' = 23$), and Ross et al. identified 11 other $D^1(\Pi)$-state levels whose excitation also gives rise to triplet emission. Such fluorescence can only occur if the initially excited $D^1(\Pi)_\text{a}$ state is mixed with a nearly degenerate $d^2 \Sigma^+_g$ state level with the same rotational quantum number. It will be shown below that the observation of such near coincidences is a powerful tool for discriminating among various possible potentials.

B. Application of the inversion procedure

Figure 2 shows that "reasonable" fits to the phase information of Table III are obtained for polynomials of order $\geq 2$. In particular, for a $\nu' = 13$ initial-state vibrational assignment, the standard errors of weighted least-squares fits to these data of order 2, 3, and 4 are 5.1, 3.7, and 3.4 cm$^{-1}$, respectively, and similar results were obtained for other vibrational assignments. Throughout the present work, the $E(\xi)$ functional behavior was represented by a third-order polynomial fitted to the data set obtained on combining the energies in Table III (shifted as described above) with an appropriate set of $\xi$ values. Use of the analogous fourth-order polynomials instead does not change the results significantly.

Throughout our discussion of this system, the zero of energy is set at the $a^3\Sigma^+$ state dissociation limit, and centrifugal terms were removed from all potentials shown or tabulated. For the latter reason, the highest turning points listed for the inverted potentials presented below correspond to energies somewhat lower than that of the emitting level. For the $J' = 14$ initial-state assignment associated with the structured continuum, the energy of the emitting level, $E_\text{a} = 15.788.0$ cm$^{-1}$, was determined by subtracting the ground-state dissociation energy. From the absolute upper state energy of 21 062.91 cm$^{-1}$ listed in Ref. 21.

An essential constraint on the present analysis is provided by the RRK potential for the attractive well of the $a^3\Sigma^+$ state determined from the discrete part of this emission spectrum. The present work used an RRK curve calculated from the (corrected) molecular constants of Ref. 16. In view of irregularities in the slopes of the turning points on the upper part of its inner wall, those for $R < 4.6460$ Å were deleted from consideration. The overall final-state potential therefore consists of a cubic spline function through the RRK turning points for the well region, joined to an analytic function at shorter distances. The latter was usually represented by Eq. (13), where for any assumed value of $\beta$ the constants $A$ and $B$ were determined by requiring this function to pass through the $(\nu'' = 5$ and 6) inner-wall turning points at 4.6894 and 4.6460 Å.

With the $a^3\Sigma^+$ state repulsive wall constrained in this way, choice of a trial value for the exponent parameter $\beta$ completes the definition of an assumed final-state potential.

For four such trial $\beta$ values, the lower segment of Fig. 5 shows the final-state potentials obtained in this way; the solid points seen there are the RRK turning points used to define all of these functions of the region $R > 4.6460$ Å. For each of these curves, application of the present inversion procedure while assuming a $\nu'' = 13$ assignment for the emitting level yields the unique initial-state potential seen in the upper segment of Fig. 5. As in Fig. 4, the latter are shown as broken curves in the extrapolation region where they were determined by the $E_\text{a}$ consistency requirement.

It was pointed out in Sec. IV B that the cutoff of the phase data seen in Fig. 2 means that the directly inverted potential may not be reliable all the way to the outer turning point $b_1(\nu)$, and that other considerations may further truncate the range over which this curve is reliable. In the present work, the "reasonableness" of an inverted potential was tested by examining the behavior of its derivatives. In particular, as $R$ increased from $a_1(\nu)$ through the minimum and partway up the outer wall, the second derivative was found to decrease monotonically, appearing to indicate that the potential was smoothly approaching an inflection point in the expected manner. However, at distances $R \approx 4.6-5.0$ Å (depending on the value of $\beta$), this trend abruptly reversed and the curvature began to increase rapidly. While such be-
behavior can occur legitimately when diabatic electronic states mix, it could also be due to small systematic error in the positions of the observed intensity extrema. Since Ross et al.\textsuperscript{10} noted such errors in the positions of discrete lines reported by Breden and Engelke,\textsuperscript{17} the latter seems more likely. We therefore truncated our inverted potential at the onset of this change in character, and used the vibrational energy consistency constraint of Sec. IV B to define the potential the rest of the way out to $b_i(v)$ (broken curves in Figs. 4 and 5).

C. Potential energy curves for the $d^(3\Pi_i)$ and $a^(3\Sigma^+)$ states of NaK

It is important to understand how the results of the present analysis will be affected by the fact that all of the levels serving as upper states for the observed triplet emission are perturbed. Within a perturbation theory description, the first-order wave function of the emitting level is a linear combination of a wave function for a level associated with the diabatic (unperturbed) $D^(3\Pi_i)$-state potential and one associated with the diabatic $d^(3\Pi_i)$-state curve. At the same time, the actual energy of this upper state $E_u$ will differ from both the diabatic $d^(3\Pi_i)$-state eigenvalue associated with the portion of the wave function reflected in the triplet emission, and from the diabatic energy of the $D^(3\Pi_i)$-state level coupled to the ground $X'(3\Sigma^+)$ state by the initial absorption step. This means that the $d^(3\Pi_i)$-state potential yielded by the inversion procedure will be displaced (vertically) from the true diabatic $d^(3\Pi_i)$-state curve by the difference between the energy of the actual emitting level and that of the diabatic $d^(3\Pi_i)$-state level. However, within this first-order description, the perturbation should not distort the triplet component of the upper state wave function. This in turn means that it should not distort the observed oscillatory continuum spectrum or the pattern of discrete intensities associated with a given upper state level. Thus, although it gives rise to a vertical displacement of up to a few cm$^{-1}$, the shape of the $d^(3\Pi_i)$-state potential obtained from the present analysis should be unaffected by the singlet–triplet perturbations which give rise to the observed spectra.

It is clear from Fig. 5 that the present approach can yield an infinite family of pairs of possible upper- and lower-state potentials for this system. In particular, for any plausible assumed final-state potential, the inversion procedure yields a unique initial-state curve defined by the fact that it provides an accurate description of the oscillatory emission continuum. While the continuum alone provides no way of distinguishing among these possibilities, Katō and Noda\textsuperscript{10} suggested that requiring simultaneous agreement with the measured relative intensities of transitions in the discrete part of this spectrum may do so. This should be possible because the RKR curve defining the well of the $a^(3\Sigma^+)$-state potential is independently determined, while the $d^(3\Pi_i)$-state well yielded by the inversion procedure shifts continuously with the assumed value of $\beta$ (see Fig. 5). The intensities (though not the positions) of the discrete transitions into the levels of the shallow $a^(3\Sigma^+)$-state well should therefore vary markedly with the choice of $\beta$, allowing comparisons with experiment to determine an optimum pair of initial- and final-state potentials.

Following the above approach, a diatomic intensity factor program\textsuperscript{14} was used to calculate the intensities of the $P(8)$ emission from the (fixed energy) $d^(3\Pi_i)$-state level $v' = 13$, $J' = 7$ into levels $v'' = 0–14$ of the (fixed) $a^(3\Sigma^+)$-state potential well, for assumed final-state and (inverted) initial-state potentials associated with a range of trial values of the exponent parameter $\beta$ of Eq. (13). The root mean square error remaining after scaling these intensities to optimize agreement with experiment is plotted vs $\beta$ in the lower segment of Fig. 6, while the (scaled) intensities associated with a few particular $\beta$ values are listed in columns 3–6 of Table IV. Unfortunately, while this plot indicates a distinct preference for $\beta$ values near 1.9 Å$^{-1}$, it is inconclusive, both because of the incipient second minimum for $\beta > 5$ Å$^{-1}$, and because a considerable range of $\beta$ values give fits which are "reasonable" relative to the expected experimental uncertainty. The magnitude of the latter is demonstrated by the fact that Katō and Noda\textsuperscript{10} were content with potentials which yield relative intensities whose root mean square error is twice as large as the optimum agreement found here [see Fig. 6(A) and Table IV]. It is therefore clear that we need additional means for discriminating among the possible potentials for this system.

One such independent test is suggested by the observa-
that a variety of other $D(\Pi) - X(\Sigma^+)$ transitions also give rise to triplet emission. Such emission can be initiated by excitation of a $D(\Pi)$-state level only if its energy is very close to that of a $d(\Pi_1)$-state level with the same total angular momentum, with which it is mixed by the spin-orbit coupling Hamiltonian. While the levels of both potentials will be perturbed by this interaction, a “good” (uncoupled) $d(\Pi_1)$-state potential must have a bound level with the same angular momentum lying close to each of the $D(\Pi)$-state levels whose excitation gives rise to triplet fluorescence. Ross et al.\textsuperscript{21} identify a total of 14 $D(\Pi)$-state levels whose excitation yields triplet fluorescence. However, five of them lie at energies significantly above that of the level giving rise to the structured continuum of interest and depend on the $d(\Pi_1)$-state potential beyond the range on which it may be determined from this spectrum. They were therefore omitted from consideration. The energies and rotational assignments for the remaining nine levels are listed in the first two columns of Table V.

For inverted initial-state potentials $V_i(R)$ associated with the range of $\beta$ values considered in Fig. 6(A), the radial Schrödinger equation was solved to locate the $d(\Pi_1)$-state level with the same angular momentum lying closest to each of (observed) emitting levels listed in the first two columns of Table V. The sets of $d(\Pi_1)$-state levels obtained in this way were then shifted vertically so as to minimize the root mean square discrepancy with the (observed) energies of the emitting levels. This step takes account of the fact that the $J' = 14$ level at 15 788.0 cm$^{-1}$ giving rise to the continuum whose inversion yielded the potential in question, is also perturbed, and hence that the potential yielded by the inversion procedure should be shifted to remove the effect of this perturbation.

For each $\beta$ value, the maximum discrepancy, $\max(|\Delta E_{i,j}|)$, found for the nine pairs of corresponding $D$- and $d$-state levels is plotted in the upper segment of Fig. 6. For the potentials associated with the four local minima lying nearest to the minimum of the curve seen in Fig. 6(A), the actual discrepancies $\Delta E_{i,j}$ and the associated $d(\Pi_1)$-state vibrational assignments are listed in Table V, together with analogous results for the potential of Katô and Noda.\textsuperscript{10} Since the coupling which gives rise to the singlet–triplet mixing perturbs the strongly coupled levels of both states, one does not expect a comparison such as this to yield exact agreement. However, the marked preference for certain $\beta$ values in Table V reveals the $d(\Pi_1)$-state potential to be more accurate than any attempt to reproduce it by the $D(\Pi)$-state potential. This is particularly evident for $\beta = 1.80$ Å$^{-1}$, where the agreement is much closer than for $\beta = 1.52$ Å$^{-1}$.
values confirms that this is a useful criterion for discriminating among the possible potentials. For each case, the \( \Delta E_{\nu, J'} \) value obtained for the \( J' = 14 \) level giving rise to the emission continuum, after shifting to minimize the rms energy discrepancy (see above), is an estimate of the energy shift required to yield the corresponding diabatic \( d(\Pi_I) \)-state potential for that case.

The results in Fig. 6 and Tables IV and V suggest that the optimum initial- and final-state potentials for this system are those associated with either \( \beta = 1.68 \) or \( \beta = 1.80 \text{ Å}^{-1} \). The "deperturbed" or diabatic potential for these two cases, obtained after adding the energy shifts \( \Delta E_{\nu, J', 1} \) as shown by solid curves in Fig. 7, while sets of points defining these alternative "best estimates" of the (rotationless) \( d(\Pi_I) \) initial-state potential are presented in Table VI, and calculated values of their molecular constants are listed in Table VII. Unfortunately, the existence of these two sets of recommended potentials means that our conclusions are not as definitive as one would like; it is also possible that the potentials corresponding to one of the neighboring minima on the max\( [\Delta E_{\nu, J'}] \) curve (at \( \beta = 1.52 \) or \( 2.27 \text{ Å}^{-1} \)) might be "correct." However, it seems most likely that the truth will correspond to one or the other of these pairs of potentials, and not some intermediate situation.

Although the properties considered above cannot distinguish which of the two sets of preferred potentials (for \( \beta = 1.68 \) or \( 1.80 \text{ Å}^{-1} \)) is correct, the similarity between them means that the present analysis is still fairly definitive. Moreover, the results presented in Tables IV, V, and VII suggest a variety of ways of resolving this ambiguity. For example, Table V shows that for these two cases, the fluorescence arising upon excitation of the \( J' = 23 \) emitting level at 15 444 cm\(^{-1}\) or the \( J' = 30 \) level at 15 616 cm\(^{-1}\) are associated with different \( d(\Pi_I) \)-state vibrational assignments. The patterns of the discrete intensities in these fluorescence series should therefore be quite different for these two cases, an expectation confirmed by the predicted relative intensities for \( R(22) \) and \( R(29) \) emission series seen in Table VIII. Another way of distinguishing between the various cases is suggested by the very different sets of molecular constants shown in Table VII. However, it may be difficult to observe these levels directly.

It is appropriate to recall that the above analysis was performed using a \( \nu' = 13 \) assignment for the initial-state level giving rise to the oscillatory emission continuum. As a test of this point, the procedure described above was repeat-

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**TABLE VII.** Molecular constants (in cm\(^{-1}\)) for the two alternate potentials for \( d(\Pi_I) \)-state NaK (see Table VI) yielded by the present analysis.

<table>
<thead>
<tr>
<th>( \nu' )</th>
<th>( T_{\nu' \beta} )</th>
<th>( B_{\nu' \beta} )</th>
<th>( T_{\nu' \beta} )</th>
<th>( B_{\nu' \beta} )</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>15 776</td>
<td>0.0583</td>
<td>15 768</td>
<td>0.0571</td>
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**TABLE VIII.** Predicted relative intensities of dispersed \( d(\Pi_I) \)–\( d(\Sigma^+ \Pi) \) fluorescence initiated by excitation of the \( J' = 23 \) and \( 30 \) \( D(\Pi_I) \)-state levels at \( E_\nu = 15 444 \) and 15 616 cm\(^{-1}\), respectively. The results for each series are expressed relative to an arbitrary maximum value of 100.

<table>
<thead>
<tr>
<th>( \nu' )</th>
<th>( R(22) )</th>
<th>( R(29) )</th>
<th>( R(22) )</th>
<th>( R(29) )</th>
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ed using, in turn, \( \nu' = 12 \) and 14 assignments for the emitting level. However, the standard errors of the resulting fits to the discrete intensities were typically an order of magnitude larger than those for the best cases seen in Fig. 6(A). This provides quantitative confirmation of the Katô and Noda assignment of this level as \( \nu' = 13 \).

As a test of the sensitivity of our conclusions to uncertainty regarding the absolute energy of the \( J' = 14 \) level giving rise to the oscillatory continuum spectrum, the analysis summarized in Fig. 6 was repeated using an emitting level energy arbitrarily placed at 15 794.0 cm\(^{-1} \) (rather than 15 788.0 cm\(^{-1} \)). In the resulting analog of Fig. 6(A), the minimum at \(-\beta = 1.9 \text{ Å}^{-1}\) is shifted to the left by approximately 0.5 Å\(^{-1}\). However, the positions of the minima on the associated analog of Fig. 6(B) are essentially unchanged! Thus, the conclusion that the “truth” most likely correspond to the pair of \( \chi (3 \Pi_{1/2}) \) - and (repulsive) \( \alpha (3 \Sigma^+ ) \)-state potentials corresponding to one of \( \beta = 1.68 \text{ Å}^{-1} \) or \( \beta = 1.80 \text{ Å}^{-1} \) would be unaffected by even a 6 cm\(^{-1} \) error in the assumed value of \( E_0 \).

As a check on the consistency of the present procedure, Figs. 8 and 9 compare the structured emission continuum implied by the present recommended potentials with experiment. (Note that in these tests, the results for the \( \beta = 1.68 \) and 1.80 Å\(^{-1}\) cases are essentially identical.) The solid curve in Fig. 8 is a plot of the continuum spectrum generated from the present recommended potentials, while the vertical bars indicate the positions and (for the maxima) the intensities of the corresponding experimental intensity extrema (see Table III). Another view of these results is provided by Fig. 9, where the errors in the extrema positions in our synthetic spectra (round points joined by solid lines) are plotted vs the peak positions. The vertical bars drawn on this second plot are a measure of the experimental uncertainties implied by the scatter in the fit to the phase information to determine the \( E(\xi) \) dependence (see Fig. 2).

D. The transition dipole function

As described in Ref. 1, Eq. (4) shows that within the uniform harmonic approximation, the transition dipole function may be determined in a pointwise fashion for the \( R_s \) values associated with the final-state energies \( E'_{\text{max}} \) for which the predicted spectrum has intensity maxima. In particular,

\[
M \left[ R_s (E'_{\text{max}}) \right] = M_0 \left[ I_{\text{obs}} (v'_{\text{max}}) / I_{\text{calc}} (v'_{\text{max}}) \right]^{1/2},
\]

(14)

where \( v'_{\text{max}} = |E_{v',J'} - E'_{\text{max}}| \) is the position of the \( i \)th intensity maximum, \( I_{\text{obs}} (v'_{\text{max}}) \) the observed intensity there, \( I_{\text{calc}} (v'_{\text{max}}) \) the corresponding intensity maximum calculated from the assumed potentials using a constant transition moment function of \( M(R) = 1 \), and \( M_0 \) is a scaling factor introduced because the experimental intensities used here were reported in arbitrary units.

The solid points in Fig. 10 were obtained by substituting the values of the observed and calculated intensity maxima into Eq. (14) and scaling the result by a constant factor \( M_0 = 2.83 \) (a.u.), whose value was chosen so as to facilitate comparisons with the \textit{ab initio} transition dipole function of Ratcliff et al.\textsuperscript{26} (dashed curve in Fig. 10). This plot clearly illustrates one of the nice features of the uniform harmonic approximation of Eq. (4), the fact that the range on which information about the transition dipole is obtained is clearly delineated. The solid line in Fig. 10 is the linear function

\[
M(R) = M_0 [1 + 0.0762 (R - 4)]
\]

(15)

(for \( R \) in Å) determined from a least-squares fit to these intensity maxima.

In the present work, the analysis of Sec. V C was first performed using the transition dipole function and peak shifts recommended in Ref. 1. The potentials obtained were then used to determine an improved \( M(R) \) function in the manner described above, and improved estimates of its effect

\[\text{FIG. 8. Comparison of the predicted } \nu' = 13, J' = 14 \text{ state continuum emission spectrum implied by the present recommended (} \beta = 1.68 \text{ or } 1.80 \text{ Å}^{-1} \text{)} \text{ potentials, with that obtained using the recommended potentials of Katô and Noda (Ref. 10) (dashed curve). The vertical bars indicate the positions (and for the maxima, the relative intensities) of the experimental intensity extrema.}\]

\[\text{FIG. 9. Illustration of the (dis)agreement with experiment regarding the positions of the intensity extrema of the oscillatory NaK emission continua generated from the present recommended potentials (} \Delta \text{ points joined by solid lines), and those implied by the potentials of Katô and Noda (Ref. 10) (} \Delta \text{ points joined by dashed lines).}\]
on the continuum peak positions determined from synthetic spectra (see Sec. V A). This cycle was then repeated until convergence was achieved.

E. Comparisons and discussion

Katô and Noda\textsuperscript{10} were the first to realize that the observed\textsuperscript{9} continuum emission into the \(a(3\Sigma^+)^{-}\) state of NaK did not originate in a wave function equivalent to that for the \(v' = 12\) level of the \(D(4\Pi)^{-}\) state, and that the vibrational assignment of the emitting level was probably actually \(v' = 13\). They modeled the data using a Morse potential to represent the \(D(4\Pi)^{-}\) state well. Fixing its \(v' = 13\) inner turning point at the \(v' = 12\) inner turning of the \((\text{known})\) RKR potential for the \(D(4\Pi)^{-}\) state to which it was coupled, they empirically varied the Morse function parameters and the extrapolated \(a(3\Sigma^+)^{-}\) final-state curve until reasonable agreement was obtained with both the relative discrete intensities and the positions of the intensity extrema in the continuum region. The potentials they obtained are shown as dashed curves in Fig. 7.

While the Katô–Noda analysis was a very perceptive first approach to this problem, their recommended potentials do not explain the discrete spectra as well as do those yielded by the more systematic methodology used here [see Table IV and Fig. 6(A)]. Figures 8 and 9 show that the continuum spectrum generated from their potentials (dashed curves and triangular points) is also in distinctly worse agreement with experiment that yielded by the present recommended potentials. Moreover, the last column of Table V shows that the singlet–triplet level energy discrepancies implied by their upper-state potential are significantly larger than those for the potentials recommended here. Thus, these comparisons confirm that the present recom-

mended potentials for this system are considerably more accurate than those available heretofore. This result also attests to the advantages of the present inversion procedure-based analysis over the more empirical approaches available previously.

In independent work, theoretical potentials based on \textit{ab initio} calculations of various types have been reported for this system.\textsuperscript{24,25} The best of these are the potentials of Stevens \textit{et al.},\textsuperscript{25} which are plotted in Fig. 7 as round points joined by straight lines. However, their results show only qualitative agreement with our experimental curves; in particular, they find that the near coincidence with the \(v' = 12\) \(D(4\Pi)^{-}\)-state level which gives rise to the observed emission continuum implies that the emitting level is\textsuperscript{25} \(v' = 18\) rather than \(v' = 13\), and the associated \(d(4\Pi)^{-}\)–\(a(3\Sigma^+)^{-}\) line intensities do not agree with experiment.\textsuperscript{21} Thus, while a plausible guide in the absence of other information, the potentials of Stevens \textit{et al.}\textsuperscript{25} have significant shortcomings which illustrate the difficulty of performing accurate calculations for the excited states of these systems. This is further emphasized by the fact that while the \(a(3\Sigma^+)^{-}\)-state potential of Jeung \textit{et al.}\textsuperscript{24} is realistic, their \(d(4\Pi)^{-}\)-state curve is too shallow and is actually off scale on the upper half of Fig. 7.

In contrast with the relatively poor agreement found for the \textit{ab initio} potentials, Fig. 10 shows that the shape of the theoretical transition moment function of Ratcliff \textit{et al.}\textsuperscript{26} agrees remarkably well with the experimental functional behavior determined here. In contrast with these results, Katô and Noda\textsuperscript{10} reported a transition dipole function which is flat for \(R > 4\) Å and linear for \(R < 4\) Å, but with a slope in the latter region which is an order of magnitude larger than that determined for Eq. (15). However, neither the manner in which their function was determined nor its expected region of validity was clearly specified. In contrast, the present analysis clearly defines the region over which the experimental data can provide information. In conclusion, therefore, the theoretical transition dipole of Ratcliff \textit{et al.}\textsuperscript{26} is the recommended function for this system.

All of the calculations presented above used Eq. (13) to represent the short-range repulsive part of the final-state potential. However, similar conclusions were reached using the alternate functional form:

\[
V_2(R) = A + B(R_0 - R)e^{-BR},
\]

(16)

where the distance \(R_0\) was set equal to the innermost RKR turning point used, and \(A\) and \(B\) were again determined by requiring Eq. (16) to pass through the two innermost RKR turning points. In this case, the analog of Fig. 6(A) shows very similar behavior, and the corresponding pairs of potentials are quite similar. Thus, the conclusions reached here regarding the optimum potentials for this system are also at least approximately model independent.

VI. CONCLUSIONS

An inversion procedure for determining an attractive potential energy well from the structure of an oscillatory absorption or emission continuum originating in a single vibrational level of that well, has been derived and tested. It was shown to be stable and reliable for a case in which the final-state potential is purely repulsive and all intensity ex-
trema are clearly resolved, as well as for a case in which the final-state potential has an attractive well and the experimental spectrum is "incomplete." It was also shown that the accuracy of a potential determined in this way need not be affected by uncertainty regarding the vibrational assignment of the emitting level.

In an application of the new method to an emission continuum of NaK, improved potentials have been determined for both the well of the previously little-known $d(\Pi_1)$ state and the short-range repulsive wall of the weakly bound $a(\Sigma^+)$ state, together with a linear representation of the transition moment function coupling these states. The present inversion procedure yields a unique pointwise initial-state potential well for any given repulsive final-state potential. As the final-state potential well was not previously known for this case, an infinite range of possible potentials could have been generated from the continuum data alone. However, Katô and Noda's measurements of relative discrete intensities in the $d(\Pi_1) \rightarrow a(\Sigma^+)$ spectrum, and the observations by Ross et al. of a range of $D'(\Pi_1) \rightarrow d'(\Pi_1)$ level near-degeneracies, made it possible to discriminate among those possibilities. Some residual uncertainty remains, as it was not possible to distinguish between two alternate sets of recommended potentials, while the interstate perturbation which gives rise to the observed continuum introduces an unknown additive energy term of up to a few cm$^{-1}$. However, the two set of possible curves are quite similar to one another, and both the differences between them and the magnitude of the unknown perturbative shift are much smaller than the differences between them and other proposed potentials for this system. Moreover, it has been shown (Table VIII) that measurement of the relative intensities of lines in other discrete $d(\Pi_1) \rightarrow a(\Sigma^+)$ fluorescence series will readily discriminate between these two cases.

This successful analysis of the NaK $d(\Pi_1) \rightarrow a(\Sigma^+)$ spectrum, a case in which the oscillatory continuum spectrum was incomplete and the repulsive final-state potential not known, is a very convincing demonstration of the power of the present method. In contrast to most other work in this area, both this approach and the companion procedure of Ref. 1 are essentially model independent, yielding numerical potentials with any desired density of points. Moreover, tests of its accuracy have shown that relative to the uncertainties associated with continuum intensity measurements, the uniform harmonic approximation on which these procedures are based, may be considered to be virtually exact. Of course the underlying theory, and hence also the present method, becomes invalid outside the "Condon reflection" regime, at energies where the final-state turning point $R_f(E)$ does not lie between the two initial-state turning points, or the stationary phase condition of Eq. (3) is satisfied at more than one point on this interval. However, this does not prevent the method being used at other energies in the same spectrum where these conditions are satisfied.

Tellinghuisen has argued that results yielded by inversion procedures of this sort could equally well be obtained using trial-and-error simulations of the continuum spectrum. However, the differences between our results and those of Katô and Noda cast doubt on the validity of that suggestion. In general, the deficiencies of the trial-and-error approach will be particularly marked for cases in which an attractive initial-state potential well (or both it and the repulsive final-state curve) is being determined, because of the number of parameters required to accurately describe the shape of an attractive well. An important advantage of a direct inversion procedure is the absence of the kind of bias implicitly introduced by the form chosen for the trial potential function(s). It is this feature which allowed Ref. 1 to conclude that the original Breford and Engelke initial-state wave function assignment was incorrect from the continuum data alone, while Katô and Noda needed the discrete intensities to reach this result.

The present work clearly illustrates the (underexploited) utility of continuum spectra for determining potential energy curves and transition moment functions. More particularly, since accurate continuum intensities are easier to measure than accurate integrated line strengths, bound-continuum spectra are a much more promising source of accurate transition dipole functions than are discrete spectra. In view of the accelerating growth of elegant laser techniques for producing such data, and the availability of reliable methods of analyzing it, it appears that the determination of potentials and transition dipole functions from continuum spectra is a field poised for rapid growth.

ACKNOWLEDGMENTS

We are pleased to acknowledge the efforts of Mr. R. VanFleet in implementing a preliminary version of the present inversion procedure. We would also like to thank Professor H. Katô for helpful comments and supplementary information, and Dr. E. J. Breford and Dr. A. J. Ross for providing us with unpublished details of their work. We are also most pleased to acknowledge the very extensive comments of Dr. Warren M. Kosman whose conscientious refereeing led to significant improvements in the presentation of our results. This research was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

2P. M. Hunt and M. S. Child, Chem. Phys. Lett. 88, 202 (1978). Note that the right-hand side of Eq. (4) should be multiplied by the factor $-1$, and Eq. (5) should contain the additional factor $(\pi/2M(r_c))$ (this point was incorrectly presented in footnote 15 of Ref. 1).
3In contrast to Refs. 1 and 2, the present paper adopts the convention of labeling the initial state as "1" and the final state as "2." Note too that the mapping which determined $\xi$ was defined in Ref. 2 in terms of the shaded area in its Fig. 1(a), while in the present work (Ref. 1) it is defined in terms of the complementary unshaded area on that figure. This has the effect of reversing the sign convention for $\xi$, so that positive values are now associated with larger distances and negative values with smaller distances, but has no effect on the calculated intensities.
7Note that at the harmonic oscillator classical turning points
$\xi = \pm \left( 2n + 1 \right)^{1/2}$, the zero of the factor $\left[ 2n + 1 - \xi (E) \right]^{1/4}$ is canceled by that in the radial velocity factor $\sqrt{u}$, so the intensity implied by Eq. (4) remains nonzero.

A subroutine for generating the characteristic harmonic oscillator phase values is included in the authors' computer program implementing the present inversion procedure, available as: University of Waterloo Chemical Physics Research Report CP-327 (1988).


A FORTRAN program for performing bound-continuum transition intensity calculations may be obtained from the first author (R.J.L.) on request: University of Waterloo Chemical Physics Research Report CP-329 (1988) (Ref. 12).

Requests for this program will receive particularly prompt response if sent by electronic mail to LEROY@WATDCS on Bitnet and accompanied by an accessible electronic mail return address.

In this example, the energy of the (absorbing) initial-state level is defined as the zero of energy.

Standard programs for solving the radial Schrödinger equation and calculating radial matrix elements for bound and quasidebound levels of arbitrary (known) potentials are widely available; see, for example, R. J. LeRoy, University of Waterloo Chemical Physics Research Report CP-230R (1986) (Ref. 12).

Here, "incomplete" simply means that not all of the structure of the initial-state wave function is observed in the experimental spectrum.


E. J. Breford (private communication, 1980).

H. Katô (private communication, 1983).


A. J. Ross (private communication, 1988) pointed out that the value for $a_{0,0}$ printed in Ref. 16 should actually read: $-0.1532 38 \times 10^{-7}$ cm$^{-1}$. She also confirmed that the published turning points are not quite correct, and should be recalculated.

Note that because of the singlet-triplet perturbation effects discussed in the text, the $d(\Pi, \Sigma)$-state potentials properties seen in Tables VI and VII and Fig. 7 include the deperturbing energy shift ($\Delta E_{\nu, \nu'} = 13, \Sigma' - \Pi$, see Table V). However, in using these potentials to predict a continuum spectrum originating in one of the perturbed upper states, the "diabatic" potential should be shifted by subtraction of the corresponding $\Delta E_{\nu, \nu'}$ shift value.


