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Heavy Rydberg behaviour in high vibrational levels of some ion-pair states of the halogens and inter-halogens

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We report the identification of heavy Rydberg resonances in the ion-pair spectra of I₂, Cl₂, ICl, and IBr. Extensive vibrational progressions are analysed in terms of the energy dependence of the quantum defect δ(E₀) rather than as Dunham expansions. This is shown to define the heavy Rydberg region, providing a more revealing fit to the data with fewer coefficients and leads just as easily to numbering data sets separated by gaps in the observed vibrational progressions. Interaction of heavy Rydberg states with electronic Rydberg states at avoided crossings on the inner wall of the ion-pair potential is shown to produce distinctive changes in the energy dependence of δ(E₀), with weak and strong interactions readily distinguished. Heavy Rydberg behaviour is found to extend well below near-dissociation states, down to vibrational levels ∼18 000-20 000 cm⁻¹ below dissociation. The rapid semi-classical calculation of δ(E₀) for heavy Rydberg states is emphasised and shows their absolute magnitude to be essentially the volume of phase space excluded from the vibrational motion by avoiding core-core penetration of the ions. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4921560]

I. INTRODUCTION

In their development of Birge-Sponer type extrapolations of high vibrational levels, LeRoy and Bernstein 1 specifically excluded potentials with long-range Coulomb behaviour from further consideration, and it was not until 15 yr later that Asaro and Dalgarno 2 treated the high vibrational levels of the lowest diabatic 3Σ− state of lithium fluoride as a Rydberg series using a model ion-pair (i.p.) potential. This approach was further developed by Pan and Mies 3 who presented fully quantal calculations for lithium iodide and confirmed that high vibrational levels in a model i.p. potential, close to the i.p. dissociation limit, formed a Rydberg series with large negative quantum defects. The change in vibrational motion of bound pairs of ions from nearly harmonic oscillation around their potential minimum to Rydberg-like behaviour in high vibrational levels continues to attract attention. 4−9 The description “heavy Rydberg” has been applied to the vibrational behaviour of i.p. states near dissociation, particularly to the H⁺H⁺ pair and to the pulsed field ionization 5 of H⁺F⁻. The higher members of extensive vibrational progressions in some of the lower i.p. states of Cl₂, ICl, IBr, and I₂ are recognised as having a spacing characteristic of motion in a potential that has a Coulombic outer branch rather than a shorter-range Morse potential 10 through the connection between the vibrational quantum number and the principal quantum number of a Rydberg progression when applied to vibrational levels rather than electronic levels. These progressions have been observed with bound energies E₀, measured from the i.p. dissociation limit, down to approximately ∼8000 cm⁻¹. Even nearer dissociation, in Cl₂ ~ 1000 cm⁻¹ below the 3rd i.p. dissociation limit, in

the gerade i.p. state of H₂ around −E₀ = 4000 cm⁻¹ and in the ungerade i.p. state 11,10 at −E₀ ~ 6000-2300 cm⁻¹, short sections of the i.p. vibrational progressions were fitted by the Rydberg formula in terms of an effective principal quantum number. In general, however, when the vibrational numbering is known, the fitting of vibrational progressions in i.p. states has been in terms of Dunham coefficients, typically up to 6th order or more in (v + 1/2). The alternative analysis, adopting the heavy Rydberg approach, is in terms of the bound energy of vibrational levels, E₀(v) rather than T₀, with the progression fitted by a Rydberg-type expansion in inverse powers of an effective principal quantum number n' (v) beginning with 1/n'². This type of expansion used in the past 11,12 beyond the leading 1/n'² term is not the conventional one of atomic spectroscopy 13 and in particular does not directly reveal the energy dependence of the quantum defect δ(E₀), which in unperturbed regions of motion in a dominantly Coulomb potential should be a smooth and slowly varying function of E₀. Instead, a fit of E₀ (v) in terms of higher inverse powers of v combined with, in effect, a constant quantum defect was used, with the exponents of v chosen empirically. The fitted coefficients are then extremely large and do not have any obvious physical interpretation. In this paper, we investigate the energy dependence of the quantum defect in both perturbed and unperturbed regions of several i.p. progressions. In the other cases, 6,7,9,10 where the Rydberg formula has been used, the i.p. vibrational numbering was not known and the absolute quantum defect could not be deduced, only one relative to an arbitrary starting point or the fractional part.

Apart from minor corrections to the long-range behaviour arising from polarizability and dispersion forces, molecular i.p. potentials differ principally in the position and behaviour of the steeply rising repulsive branch, in particular, in the region of avoided crossings with electronic Rydberg states. For the
halogens and other i.p. states, where the electron affinity of one of the atoms is large, these crossings occur on the inner wall of the potential rather than on the outer branch as in \( \text{H}_2 \). For any i.p. potential, quantum defects for heavy systems are readily calculated to a good approximation in the adiabatic or diabatic limit by a simple semi-classical evaluation by quadrature of the volume of phase space excluded by the molecular potential from a pure Coulomb potential. We use this in some model calculations both to verify that the energy dependence of the quantum defects is consistent with the position of the inner wall of the i.p. potential and to show the effect of avoided crossings on the inner wall of i.p. potentials in the adiabatic limit that give rise to characteristic behaviour of \( \delta(E_b) \) once the perturbed region is entered. The aim of this paper is to see if an analysis of the observed high vibrational levels of i.p. states of the halogens in terms of the energy dependence of the quantum defect can both identify the region of heavy Rydberg behaviour and provide additional information on changes in the i.p. potential at avoided inner-wall crossings with electronic Rydberg states. A sufficient number of cases are included to suggest that the analysis can be applied generally to i.p. states of this type to define heavy Rydberg behaviour.

II. HEAVY-RYDBERG ANALYSIS

A. Preliminary analysis

The standard extension of the Rydberg formula for an electronic series \( T_n \) converging on an ionization limit \( T_\infty \) that is used in atomic spectroscopy to include core penetration is in terms of the effective principal quantum number \( n^* \) which replaces the principal quantum number \( n \),

\[
T_{nj} = T_\infty - R\gamma_\mu / n^*_j^2,
\]

where \( R\gamma_\mu \) is the Rydberg constant for the reduced mass \( \mu \) of the i.p. together with

\[
n^* = n - \delta n_J,
\]

and the \( n \) dependence of \( \delta \) as an expansion \(^{13} \) in inverse even powers of \( n - \delta_\infty \),

\[
\delta n_J = \delta_\infty J + \frac{\delta_1^J}{(n - \delta_\infty)^2} + \cdots,
\]

where \( \delta_\infty \) is then the quantum defect at electronic ionization in the atomic case or at the i.p. dissociation energy for molecular i.p. states. \( \delta_\infty \) is not known \textit{a priori} and to bring out the energy dependence of the quantum defect in a near-dissociation expansion (NDE), we adopt an equivalent expansion in the bound energy \( E_b \) of the vibrational levels,

\[
E_b (v) = T_v - T_\infty
\]

in the form

\[
\delta (E_b, J) = \delta (0, J) + \delta_1 E_b + \delta_2 E_b^2 + \cdots,
\]

where \( \delta(0, J) \) (\( = \delta_\infty J \) in Eq. (3)) is again the quantum defect at dissociation \( (E_b = 0) \), \( \delta(E_b, J) \) is now treated as a continuous function of \( E_b, J \) and \( \delta_1 = \delta_\gamma J / R\gamma_\mu \). For a heavy Rydberg description to be useful in a given energy region, the energy dependence of \( \delta \) should be well described by the leading linear term in Eq. (5). Perturbations in a heavy-Rydberg vibrational progression then show up as departures from the linear energy behaviour of \( \delta(E_b) \), marked by a rapid change in \( \delta_2 \). \( n^* \) is first calculated from the vibrational term values,

\[
n^* (v) = \sqrt{\frac{R\gamma_\mu}{T_v - T_{\nu J}}}.
\]

If the potential well were purely Coulombic, the quantum defect would be zero and

\[
n = v + J + 1.
\]

So, with a knowledge of \( n^* \) and \( v \), the quantum defect can be found,

\[
\delta (E_b, J) = v + J + 1 - n^*_J (v).
\]

If the vibrational numbering has not been established, then only the fractional part of \( \delta \) can be found.\(^2\) Pan and Mies\(^3\) showed that \( \delta(E_b, J) \) contains a linear and quadratic term in \( J \),

\[
\delta (E_b, J) = \delta (E_b, 0) + J - J (J + 1) B(E_b)/E_b.
\]

The last term in Eq. (9) tends to zero as \( E_b \to 0 \) because the rotational constant \( B(E_b) \) behaves asymptotically at high \( v \) as \( 1/r_{\text{out}} \), where \( r_{\text{out}} \) is the outer turning point of the motion and in the Coulomb region \( r_{\text{out}} \) increases as \( 1/E_b \). In the experimental vibrational progressions to be analyzed, the rotational branch structure at least of the higher members is usually not resolved, but the rotational constant of these high vibrational levels is so small that the effect of a small change in \( J \) on \( T_v \) is within the experimental bounds of a vibrational term value (typically \( 0.1 \sim 0.5 \) \( \text{cm}^{-1} \) at \( -E_b \sim 8000 \sim 10000 \) \( \text{cm}^{-1} \)). The linear term in \( J \) in Eq. (8) cancels when Eq. (9) is substituted into Eq. (8). Thus, we extract \( \delta(E_b, 0) \) from \( n^*(v) \) using

\[
\delta (E_b, 0) = v - n^* + 1
\]

and write the result simply as \( \delta(E_b) \).

B. A semi-classical formula for \( \delta \)

For the general bound (negative) i.p. potential \( V(r) \) defined so that \( V(\infty) = 0 \), the semi-classical quantum defect at a bound (negative) energy \( E_b \) is given by the difference in phase space occupied by motion in the Coulombic potential and in the i.p. potential (see Pan and Mies for another use of the semi-classical approach in this context).

For \( J = 0 \),

\[
\delta (E_b, 0) = \frac{2}{\hbar} \int_{r_{\text{in}}}^{r_{\text{out}}} \sqrt{2\mu (-V (r) + E_b)} dr
\]

\[
- \int_{0}^{C/E_b} \sqrt{2\mu (C/r + E_b)} dr + 1/2,
\]

where \( \mu \) is the reduced mass, \( C = e^2/4\pi\epsilon_0 \), and \( C/E_b \) is the outer turning point in the pure Coulomb potential at \( E_b \). The limits \( r_{\text{in}}, r_{\text{out}} \) are the inner and outer turning points in the i.p. potential \( V(r) \) and in heavy Rydberg states, \( C/E_b \) is very close to \( r_{\text{out}} \). The final factor of \( 1/2 \) in Eq. (11) aligns the numbering of the i.p. vibrational levels with the principal quantum number from the first integral so that both start at 1. The second term in
The relative areas in $E_b/r$ space covered by the phase-space integrals in Eqs. (11) and (12). The core contribution to the quantum defect for $E_b$ comes from (a) bounded by $r=0$ and the inner turning point in $V(r)$ at $E_b$. The total Coulomb contribution is bounded by the red curve and $E_b$, the molecular contribution to the phase-space integral by the blue curve and $E_b$, region (b). Region (c) together with (a) are then regions in which the Coulomb and molecular contributions to the quantum defect do not cancel.

Eq. (11) can be split into the core exclusion contribution from $0 \leq r \leq r_{ni}(E_b)$ and the radial range $r_{ni}(E_b) \leq r < C/|E_b|$, the former being

$$\delta_{\text{core}}(E_b) = -\frac{2}{\hbar} \int_0^{r_{ni}} \sqrt{2\mu(C/r + E_b)} dr$$  \hspace{1cm} (12)$$

and over the remaining part of the radial integration in Eq. (11) from $r_{ni}$ to $r_{out}$, the two terms largely cancel. The ranges of integration are illustrated in Fig. 1 for a realistic i.p. potential, in which region (a) is the radial range of the core contribution in Eq. (12). Performing the integration in Eq. (12) for $E_b = 0$ gives

$$\delta_{\text{core}}(0) = -\frac{2}{\pi} \left( \frac{2r_{ni}\mu}{\alpha m_e} \right)^{1/2}$$  \hspace{1cm} (13)$$

where $a_0$ is the electronic Bohr radius and the ratio $\mu/m_e$ scales this in the heavy Rydberg case.

$|\delta(0)|$ obtained by extrapolation of experimental quantum defects will be greater than $|\delta_{\text{core}}(0)|$ because the Coulomb potential lies below $V(r)$ in the region $r_{ni} < r_c$ (the position of the minimum of the i.p. potential) that gives most of the remaining negative contribution to $\delta(0)$. Then substituting $|\delta(0)|$ for $|\delta_{\text{core}}(0)|$ in Eq. (13) will give an upper limit (since $\delta$ is negative) to the position of the inner zero of the i.p. potential.

In order to verify the accuracy of Eq. (11), we apply it to a model Rittner potential,

$$V(r) = \frac{A}{r} e^{-a r} - \frac{Z}{r}$$  \hspace{1cm} (14)$$

The vibrational term values were found by a quick search for eigenvalues of the wave equation using bisection (wave functions are not needed) and these were used to calculate $n^*$ and hence quantum defects from Eq. (10). A typical diatomic halogen i.p. state might have a well depth of 3.90 eV and an equilibrium separation of 3.45 Å, fitted by the parameter values $A = 1.448 \times 10^6$ eV Å, $a = 4.1283$ Å$^{-1}$, and $Z = 14.3997$ eV Å. This potential is plotted in Fig. 2(a) as the diabatic potential. For an oscillator with the reduced mass of $I_2$, the values of the quantum defects by the semi-classical and quantal methods agreed to better than 0.1. At $E_b = 0$, $\delta(0) = -721.1$, the core contribution is $-703.6$; at $E_b = 1$ eV, $\delta_{\text{core}} = -686.8$ and $\delta(1.0) = -701.8$; and at $E_b = -2$ eV, $\delta_{\text{core}} = -667.0$ and $\delta(2.0) = -680.7$. The core contribution is thus $>97\%$ of the total quantum defect over this energy range. This is illustrated in the schematic (Fig. 1) for motion in a realistic i.p. potential with a bound energy of $-15 \times 1000$ cm$^{-1}$, an inner turning point $r_{ni}(E_b) = 2.5$ Å, and $r_{out} = 7.5$ Å on the Coulomb branch of the molecular potential. Although not a phase space diagram, Fig. 1 conveys the dominance of $\delta_{\text{core}}$ to the quantum defect which arises from region (a) bounded by $r \leq r_{ni}(E_b)$ and the relative minor contribution of region (c), while in region (b), the two contributions largely cancel. When the value of $\delta(0)$ is substituted for $\delta_{\text{core}}$ in Eq. (13), $r_0 \leq 2.93$ Å is obtained, compared with the model potential value of 2.79 Å (see Fig. 2(a)).

Pan and Mies$^3$ calculated $\delta(E_b)$ for LiI using a diabatic model i.p. potential that included long-range polarization and dispersion terms. They found an extended linear portion of $\delta(E_b)$ that extrapolates at $E_b = 0$ to a value close to their calculated value of $\delta(0) = -177.5$. This value, when used as
an approximation to $\delta_{\text{core}}(0)$ in Eq. (13), gave $r_0 = 1.70$ Å compared with the actual value for their potential of 1.56 Å. The actual value of $r_0$ when used in Eq. (13) gives $\delta_{\text{core}}(0) = -170$, which is 96% of $\delta(0)$—a ratio very similar to that for the model potential without polarization, Eq. (14), used above.

Two general points emerge from these model calculations. First, over a wide range of bound energies, at least down to 2 eV, $\delta(E_b)$ exhibits nearly linear behaviour, and second, extrapolation of this linear behaviour to $E_b = 0$ produces a realistic value of $r_0$. We will see if these properties can be used to identify heavy Rydberg behaviour in i.p. states where vibrational progressions have been experimentally numbered in the 1–2 eV region below dissociation, but there is one additional factor that will affect all molecular i.p. quantum defects as $E_b$ approaches zero.

### C. The effect of avoided crossings on $\delta$

An avoided crossing in an i.p. potential can occur on the outer Coulombic branch, leading to predissociation to neutral products, and on the inner wall leading in some cases to double minima and shelf-states. The effect on the quantum defect is qualitatively the same in both cases because both soften the potential below the crossing and hence open up additional phase space for the vibrational motion. This produces a localised change in the energy dependence of $\delta(E_b)$ for vibrational levels around the crossing. In the alkali halides, the crossing is on the outer branch and in the halogens, the more strongly avoided crossings are on the repulsive branch. For LiF, Asaro and Dalgarno\(^7\) calculated the quantum defect by solving the radial wave equation for a model i.p. potential in which a modified Rittner potential was crossed on the outer branch by a weakly repulsive state that correlated with the correct atom-pair dissociation limit. They presented their results for the diabatic potential as a $\delta(E_b)$ vs. $v$ plot. This type of plot illustrates the rapid change in gradient from low-$v$ harmonic oscillator behaviour as the vibrational levels enter a region where the outer turning points lie on an almost unaltered Coulomb potential, but unlike the plot against $E_b$ does not tend to nearly linear behaviour in the diabatic Coulombic region as $v$ increases.

An avoided crossing at an energy $V_X$ on the inner wall of an i.p. potential with a bound electronic Rydberg state, typically near $r_e$ of the latter state, has two limiting effects on $\delta(E_b)$ in the region of each crossing. If the crossing is weakly avoided, the nuclear motion at energies immediately above and below $V_X$ is essentially diabatic and the inner turning point continues to be on the inner wall of the diabatic i.p. potential as $|E_b|$ decreases. At the energy of each vibrational level of the interloper state, the effect of the perturbation is then to cause the characteristic increased separation of the interacting vibronic levels that have come into near resonance and a slight compression of the vibrational levels of the i.p. state between successive vibrational levels of the interloper state. This leads to a distinctive local twisting of the gradient of $\delta(E_b)$ between each resonance,\(^6\) but the median gradient through successive perturbations is unchanged from that of the linear behaviour of the lower vibrational levels below $V_X$.

The anomalous behaviour near a crossing is magnified in $\delta(E_b)$ vs. $v$ plots compared with $T_v$ vs. $v$ plots because the dominant Coulomb behaviour has been stripped out.

If the crossing is strongly avoided, intruder states are strongly mixed and cannot be uniquely identified and removed from the vibrational numbering. The nuclear motion as $E_b$ approaches $V_X$ then follows the adiabatic potential and the inner turning point then falls more rapidly with decreasing $|E_b|$ than it would have done on the steeper diabatic inner wall. More phase space is opened up, causing the gradient of $\delta(E_b)$ to decrease and even to change sign as in several examples to be presented in Sec. III. From Eq. (10),

$$\frac{d\delta}{dE_b} = \frac{dv}{dE_b} - \frac{dn^*}{dE_b},$$

so the gradient of $\delta(E_b)$ will change sign if the energy density of vibrational levels in the real potential becomes greater than those in a Coulombic potential at $E_b$.

The rapid change in gradient of the quantum defect with $E_b$ calculated for a model adiabatic potential created by the avoided crossing at 2.96 Å of a Morse upper state potential and a Rittner potential for the lower state with $H_{12} = 0.1$ eV, illustrated in Fig. 2(a) exhibits a point of inflection at $E_b$ close to $\sim 10000$ cm$^{-1}$ (1.2 eV). The diabatic potential parameters are representative of an electronic Rydberg state and the $E$ or $D$ state of $I_2$, and the derived quantum defect plot using Eq. (10) is in Fig. 2(c). For the adiabatic potential, $\delta(0) = -702$, compared with $-729$ for the diabatic potential. Substituting the diabatic $\delta(0)$ value into Eq. (13) gives $r_0 = 3.08$ Å compared with the actual value of 2.96 Å for the model diabatic potential. The vibrational term value plot for the adiabatic potential in Fig. 2(b) shows no abrupt change in gradient around the position of the avoided crossing ($v \sim 500$), but the quantum defect shows a rapid decrease in gradient at the avoided crossing. Fig. 2(c).

Linear extrapolation of $\delta(E_b)$ to lower $|E_b|$ from an unperturbed region exhibiting linear or near-linear behaviour gives the quantum defect expected if the inner turning points continued on the wall of the diabatic potential. The difference between an extrapolated $\delta(E_b)$ and the observed values at $E_b$ is then the (fractional) number of vibrational levels introduced by the softening of the inner wall of the potential at that energy. As $E_b$ continues towards zero, the velocity at the crossing increases and eventually the motion becomes diabatic, with the inner turning points again on the inner wall of the i.p. state. The vibrational numbering in the i.p. state could then be resumed as though the motion had continued to be on the diabatic potential through the interaction region by subtracting the appropriate number of vibrational quanta, as done by Asaro and Dalgarno.\(^2\)

### III. SOME I.P. STATES OF $I_2$

#### A. The $D(0^+)$ state

The Cordes band system of $I_2$, arising from $D(0^+_u) \leftarrow X(0^+_g)$, has been recorded by Hoy and Lipson\(^14\) using fluorescence excitation for $v = 140–342$, by Bartels et al.\(^15\) for $113 \leq v \leq 201$, and the lower levels up to $v = 124$ by Ishiwata.
and Tanaka. The vibrational numbering in the composite progression, which is interrupted at higher \( v \) by gaps due to predissociation or homogeneous perturbations from electronic Rydberg intruder states, was obtained by the conventional procedure of fitting \( T_v \) by a polynomial in \( v + \frac{1}{2} \), with the numbering of missing levels adjusted to obtain a smooth fit and requiring up to ten Dunham coefficients for large ranges of vibrational term values. The complete \( \delta(E_b) \) plot with the numbering of Hoy and Lipson is shown in Fig. 3(a) and shows an abrupt change in gradient at \( E_b \sim -14\,000 \) cm\(^{-1}\), which marks the onset of a perturbed region and a major avoided crossing. The corresponding \( T_v \) plot in the high-\( v \) region from 264 to 345, Fig. 3(b), does not show any abrupt change in gradient and a local cubic fit is compatible with numbering of Hoy and Lipson. The gradient of the linear portion of the plot in Fig. 3(a) is \(-1.604 \times 10^{-3} \) cm\(^{-1}\), which extrapolates to a zero-energy quantum defect, \( \delta(0) \approx -678 \), giving \( r_0 \approx 2.59 \) Å from Eq. (13). An enlargement of the quantum defect plot in the perturbed region is shown in Fig. 3(c), together with a cubic extrapolation of \( \delta(E_b) \) from the more deeply bound region—\( E_b \sim 14\,000-16\,000 \) cm\(^{-1}\), in which the onset of curvature is visible. The two higher groups of vibrational levels show reversals of gradient in the \( E_b \) plot due to compression between consecutive vibrational levels of electronic Rydberg states, that of the first block requiring a vibrational spacing of \(-250 \) cm\(^{-1}\) for the intruder state. However, there are no \([3/2]6p; 0_u^+\) in the required position to account for the compression of the first block, but \([3/2]6p; 1_u; v = 3, \) and \( v = 4 \) are in the right position and we suggest that this group, which also has anomalous fluorescence,\(^{27} \) is assigned to a \( 1_u \) i.p. state in the first cluster. In contrast, the compression of the second, higher, group occurs between \( v = 1 \) (\( T_v = 59\,237 \) cm\(^{-1}\)) and \( v = 2 \), \( T_v = 59\,449 \) cm\(^{-1}\) of the \([3/2]6p; 0_u^+\) Rydberg state. In order to bring this group more in to line with the extrapolation of the unperturbed levels requires \( v = 330 \) to be re-numbered as 331, thus raising the quantum defect of all the members of the group by one. The resulting \( \delta(E_b) \) plot is used in Fig. 3(c), but such re-numbering is, to some extent, arbitrary. At the highest observed \( E_b \), \(-12\,708 \) cm\(^{-1}\), the value of \( \delta(E_b) \) obtained by linear extrapolation from the region \(-E_b = 15\,000-18\,000 \) cm\(^{-1}\) is \(-657.7 \) compared with the value of \(-653.8 \) calculated from \( n^2 \) and using the numbering of Lipson and Hoy. Thus, approximately four vibrational levels have been added at this energy by switching to the adiabatic potential.

B. The \( E(0_u^+) \) state

The \( E(0_u^+) \) state vibrational progression has been completely assigned\(^{18,19} \) up to \( T_v \sim 61\,700 \) cm\(^{-1}\), \( v = 422 \). An additional set of \( T_v \) values was originally assigned to the \( \beta \) state and subsequently re-assigned\(^{20,21} \) to the \( E \) state with a consequent change in numbering now starting at \( v = 518 \). The vibrational term value plot is shown in Fig. 4(a). Up to ten Dunham coefficients are required to fit such an extended vibrational progression. Small perturbations adjacent to each electronic Rydberg level occur, typical of weakly avoided crossings, but these are not large enough to prejudice the proposed numbering of the start of the added data set at \( v = 519 \), \( T_v = 63\,380 \) cm\(^{-1}\). We will see if the energy dependence of the quantum defect supports this vibrational assignment.

The plot of \( \delta(E_b) \) vs. \( E_b \) in Fig. 4(b) shows that the region of linear dependence is well established in the region \(-\delta(E_b) \sim 10\,000-16\,000 \) cm\(^{-1}\). In order for the group of highest vibrational levels, \(-E_b \sim 9000-8000 \) cm\(^{-1}\) to line up with the lower energy plot, \( v = 519 \) must be lowered to 518 to bring the start of the highest cluster of points into line with the linear extrapolation of the lower data set. After this adjustment, the highest set of \( \delta \) values still shows short sections with a negative gradient that is the results of including intruder levels in the sequentially numbered vibrational term values as was done in the original paper. Five such inflections in \( \delta(E_b) \) can be identified and at each removing, one vibrational level with a largely electronic Rydberg character \( (v = 528, 545, 564, 581, 601 \) in the numbering of Ref. 21) brings the median line of the \( \delta(E_b) \) vs. \( E_b \) plot into line with that of the lower data set as shown in Fig. 4(c). The gradient of \( \delta(E_b) \) in the linear portion between \(-11\,000 \) and \(-17\,000 \) cm\(^{-1}\) is \( 2.50 \times 10^{-3} \) cm\(^{-1}\) which extrapolates to \( \delta(0) \approx -707 \) for diabatic behaviour. Taking this as an approximation to \( \delta(0) \) in Eq. (13) gives a value for the hard core radius \( r_0 \approx 2.8 \) Å. Applying the suggested reduction of 4% to \( \delta(0) \) brings \( r_0 \) down to 2.56 Å, consistent with extrapolation of the lower energy section of the inner
FIG. 4. (a) The vibrational term value plot for $I_2(E)$ up to $v = 597$; a 6th order Dunham fit is shown in red. (b) The quantum defect over the same vibrational range with all $v > 523$ in the original numbering lowered by 5. (c) $\delta(E_b)$ for $v = 275 - 592$ after removing five interloper vibronic states.

wall of the $E$ state potential known from a Rydberg-Klein-Rees (RKR) analysis$^{21}$ and other 1st tier $I_2$ i.p. states.

C. The $D'(2g)$ state

The higher vibrational term value plot from data in Lawley et al.$^{21}$ is shown in Fig. 5(a) and the quantum defect plot in Fig. 5(b). The quantum defect plot in the energy range $v = 267 - 345$ shows two distinct regions with a marked change in gradient at around $E_b \sim -13\,500\,\text{cm}^{-1}$ ($T_v \sim 58\,700\,\text{cm}^{-1}$), consecutive numbering. (b) The quantum defect in the same energy region, consecutive numbering of all vibrational levels as in (a). (c) Vibrational numbering up to $v = 310$ ($T_v = 58\,652\,\text{cm}^{-1}$) as in (b), but with four higher vibrational levels attributed to the 5d electronic Rydberg state removed.

IV. THE $\beta(1g)$ STATE OF $\text{Cl}_2$

Higher i.p. vibrational levels of the $\beta$ state of $\text{Cl}_2$, correlating with $\text{Cl}^+ (^{1}P_2)$, were accessed by two-photon excitation via a repulsive intermediate state by Al-Kahali et al.$^{22,23}$ which allows direct access to the i.p. levels rather than via doorway states. Lower levels from $v = 0$ were reported by Ishiwata et al.$^{24}$ The term value plot is shown in Fig. 6(a) and has no marked anomalies. Removing electronic Rydberg states identified as intruder states from the vibrational interaction from lower vibrational levels. In order to bring the quantum defect for i.p. vibrational levels between $v = 312$ and 345 into line with the linear dependence shown by lower levels requires four vibrational levels to be assigned to electronic Rydberg interloper states and removed from the i.p. numbering. These are $v = 312, 320, 330, 341$, all previously identified$^{21}$ as having high electronic Rydberg character, and the result is shown in Fig. 5(c).
The observed vibrational term values of ICl supports the assignments of Hasegawa et al.,23 and this has been done in Fig. 6(c). The highest group of δ-values, beginning at \( E_b \approx -16 200 \text{ cm}^{-1} \), lies 1.7 below their position expected from a linear extrapolation from the unperturbed region as a result of the softening of the inner wall of the i.p. potential which has in effect added almost two vibrational levels when \(|E_b| \) has fallen to 16 000 cm\(^{-1}\). The gradient of \( \delta(E_b) \) in the linear region is \(-4.09 \times 10^{-4} \text{ cm}^{-1} \), which extrapolates to \( \delta(0) \approx -313 \). Using this value of \( \delta(0) \) in Eq. (13) gives \( r_0 \approx 2.01 \text{ Å} \). This value is compatible with the extrapolation of the inner wall of the known part of the i.p. potential or ab initio calculations by Hao et al.,25 for the ungerade i.p. states or Kokh et al.,26 the calculations of the latter for the \( \beta \) state extend to 80 000 cm\(^{-1}\) at \( r = 2.17 \text{ Å} \) and point to \( r_0 \approx 1.9 \text{–} 2.0 \text{ Å} \) at the dissociation limit \( T_{\infty} = 96 094 \text{ cm}^{-1} \).

V. THE \( E(0^+) \) STATES OF ICl AND IBr

The VUV fluorescence excitation spectrum of ICl11 shows a long closely spaced vibrational progression in the \( E(0^+) \) i.p. state and resonance enhanced multiphoton ionization (REMPI) spectra27 extend the range to \( v = 0 \text{–} 387 \), ending at \( T_v = 64 000 \text{ cm}^{-1} \), 8500 cm\(^{-1}\) below dissociation. An equally long progression has been published12 for the lowest 0\(^+\) i.p. state of IBr up to 10 800 cm\(^{-1}\) below dissociation. The uncertainty in \( T_v \) at the highest vibrational levels in the REMPI spectrum of ICl is \( \pm 2 \text{ cm}^{-1} \), but this only leads to an uncertainty in \( \delta \) of \( \pm 0.1 \). The \( T_v \) vs. \( v \) plot for ICl is shown in Fig. 7(a)

![Graph](image1.png)

**FIG. 6.** (a) The \( T_v \) vs. \( v \) plot for Cl\( _2 \beta(1\_\beta) \) from \( v = 0 \) to \( v = 166 \). (b) The quantum defect as a function of \( E_b \) over the same vibrational range. (c) \( \delta(E_b) \) in the region of the strongly avoided crossing with \([1/2]3d;1_g \) at approximately \(-17 000 \text{ cm}^{-1} (T_v \sim 79 000 \text{ cm}^{-1})\).

![Graph](image2.png)

**FIG. 7.** (a) The observed vibrational term values of ICl \( E(0^+) \) from \( v = 96 \) as a function of the vibrational quantum number. (b) The quantum defect over the same energy range.
and shows no obvious anomalies. The gradient of the \( \delta(E_b) \) vs. \( E_b \) plot in Fig. 7(b) shows a rapid change at \( E_b \sim -10\,000 \text{ cm}^{-1} \) \((v \sim 245)\) and an unperturbed linear region \(12\,000 \leq |E_b| \leq 22\,000 \text{ cm}^{-1}\) with a gradient of \(-1.04 \times 10^3 \text{ cm}^{-1}\) which extrapolates to give \( \delta(0) = -432 \). This corresponds to a value for the inner zero of the i.p. potential \( r_0 \sim 2.37 \text{ Å}\). At the lowest value of \( E_b \) recorded, \(-8500 \text{ cm}^{-1}\), the difference between the quantum defect deduced from the original numbering and the value expected by extrapolation from the unperturbed region indicates that approximately three additional vibrational quanta have been created by the widening of the potential at an avoided crossing. The first 0\(^{+}\) electronic Rydberg state with singlet character that is crossed by the inner wall of the i.p. state is the \([3/2]6p;0^{+}\) which causes the quantum defect plot to begin to depart from linear behaviour around \( E_b = -12\,000 \text{ cm}^{-1}\). The REMPI spectrum shows a rapid decrease in intensity at around \( T_e \sim 63\,500 \text{ cm}^{-1} \) \((E_b \sim -10\,000 \text{ cm}^{-1})\), marked by the sudden change in gradient of the quantum defect plot.

The corresponding pair of graphs for the \( E(0^+) \) state of IBr using data from Lipson and Hoy\(^\text{15}\) is shown in Figs. 8(a) and 8(b). A major avoided crossing with an electronic Rydberg state, identified by the onset in curvature in the \( \delta(E_b) \) plot, occurs at \( E_b \sim -12\,000 \text{ cm}^{-1} \) \((v \sim 340, T_e \sim 59\,800 \text{ cm}^{-1})\). This is close to the excitation energy at which there is a marked decrease in the VUV absorption\(^\text{28,29}\) and is in the region occupied by the \([3/2]6p;0^{+}\) electronic Rydberg states. The vibrational levels are only perturbed by up to 0.5 \text{ cm}^{-1} by weak local interactions in the bound energy region around \(-14\,000 \text{ cm}^{-1}\). The onset of curvature of the \( \delta(E_b) \) plot as \( E_b \rightarrow 0 \) begins at around \(-13\,000 \text{ cm}^{-1}\) as a major avoided crossing is approached. The gradient of \( \delta(E_b) \), where linear behaviour is established, \(~E_b \sim 13\,000–20\,000 \text{ cm}^{-1}\) is \( \delta_1 \sim -1.465 \times 10^3 \text{ cm}^{-1} \). This extrapolates to \( \delta(0) \approx -592 \), giving an upper limit to the radial position of the inner zero of the potential of 2.53 Å. This is consistent with an extrapolation of the inner wall of the potential established from a RKR analysis\(^\text{29}\) of rovibrational levels down to \( E_b \sim -16\,000 \text{ cm}^{-1}\).

**VI. CONCLUSION**

The quantum defects of vibrational progressions in a range of i.p. states of the halogens and inter-halogens show a linear dependence on the binding energy \( E_b \) from \(-20\,000 \text{ cm}^{-1}\) below dissociation up to the onset of strong interactions with electronic Rydberg states. This linear behaviour is also exhibited by realistic model i.p. potentials. Avoided crossings on the inner wall of the i.p. potential then produce two types of disturbance to the smooth behaviour of \( \delta(E_b) \): (i) a rapid decrease in the gradient of \( \delta(E_b) \), sometimes turning negative, as a strongly avoided crossing is approached and (ii) with weaker, local interactions, the median gradient is un-interrupted but passes through short sequences of negative gradient due to the compression of the i.p. vibrational levels between successive intruder levels. The behaviour of \( \delta(E_b) \) at major avoided crossings is much more pronounced than in \( T_e \) vs. \( v \) plots because Coulomb behaviour, which comes to dominate the \( v \) dependence of \( T_e \), has been removed. The number of extra vibrational levels that have been created by the widening of the potential at \( E_b \) can be estimated by comparing \( \delta(E_b) \) with the linearly extrapolated value at that energy.

Quantum defect plots of the \( D \) state of I\(_2\), the \( \beta \) state of Cl\(_2\), and the \( E \) states of ICl and IBr all show the result of a major avoided crossing, but the \( D' \) state of I\(_2\) does not. Changes in gradient of \( \delta(E_b) \) for the \( E \) and \( D' \) states of I\(_2\) can be interpreted as due to including intruder electronic Rydberg states in the sequential vibrational numbering; when these are removed, there is no evidence of a major avoided crossing. Using a model adiabatic potential produced by the avoided crossing of a generic i.p. potential and a Morse function for the electronic Rydberg state, the change in gradient of \( \delta(E_b) \) is illustrated using numerical evaluation of the difference in the volume of phase space between the model potential and the reference Coulomb potential available to vibration as a function of \( E_b \) in the diabatic case. Extrapolation of the linear portion of the \( \delta(E_b) \) vs. \( E_b \) plot from a region below any major interaction to \( E_b = 0 \) gives a good approximation to the quantum defect at zero binding energy if the inner turning points of the heavy i.p. states were to follow the diabatic potential. This simple semiclassical approach shows that \( \delta(0) \) is very largely (typically >95%) determined by \( r_0 \), the radial position of the inner turning point of the motion at \( E_b = 0 \) (i.e., at the inner zero of the diabatic i.p. potential) and this dominant contribution continues to deeper bound levels. The values derived for \( r_0 \) for all...
the i.p. states analysed here, although approximate, are entirely consistent with extrapolations of the known portions of the inner wall of i.p. potentials below any avoided crossings. This supports the use of the analysis of i.p. vibrational progressions in terms of $\delta(E_b)$ in identifying the energy region of heavy Rydberg behaviour. Major interactions that lead to softening of the inner wall of the potential and which are not immediately apparent from a term-value plot are readily located.