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A Systematic Look at Weakly Bound Diatomics

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A little more than one hundred years ago, Johannes van der Waals proposed his celebrated equation of state for a real gas.[1] This equation incorporated two parameters to represent the macroscopic effects of intermolecular repulsions (molecular size) and intermolecular attractions. Comparisons among these parameters constituted one of the first systematic attempts to organize, interpret, and understand variations in weak intermolecular bonding from molecule to molecule.

What should one expect to learn from weak bonding? By ordinary chemical standards, such bonds are ridiculously weak. As a consequence, most of chemical thought is organized around an understanding of strong chemical forces. Terms such as covalent bond, donor-acceptor bond, hydrogen bond, charge delocalization, and the like, conjure specific models with a host of well understood consequences. Weakly bound molecules have historically not been thought of in these terms, but it is not at all obvious where one draws (or even if one should draw) the line separating molecules into categories based on bond energies.

Nevertheless, weakly bound molecules have a well defined set of bound quantum levels which can be analyzed by methods familiar to the realm of stable chemical compounds. Can such analyses expose the origins of weak bonding in greater detail? Can weak bonding be described <u>without</u> recourse to the terminology of chemical bonding, or are there clear examples of molecules for which this language is <u>essential</u>, despite the weakness of the interaction?

This article will begin with an introductory look at various families of weakly bound diatomics and the more important representatives of each. The next section will discuss a uniform method for describing and comparing the interatomic potential energy functions of these species. Finally, the implications of these functions and comparisons among them will be discussed. This is not intended to be an all-encompassing review of weakly bound diatomics;

consequently, an occasional reader may find a potentially important molecule left unmentioned. I apologize for this limitation in advance, and reiterate that the goal of the article is to illuminate families of interactions and the variations in bonding exhibited among them.

FAMILIES OF WEAKLY BOUND DIATOMICS

A cursory glance through the Periodic Table leads one to predict most of the weakly bound homonuclear diatomics. Certainly, the rare gas dimers, He_2 through Rn_2, are the best known examples. In fact, the interatomic potential function for Ar_2 is as well characterized[2] as that for many common stable diatomics. The next-best known family[3] is the Group II metal dimers: the alkaline earth diatomics, and Zn_2, Cd_2, and Hg_2. The ground state atoms have closed (s^2) configurations, and a formal analogy to rare gas dimers is predicted. However, as one proceeds atom by atom from the dimer to the bulk, these species revert to strongly bound metals due to the presence of low-lying sp or ds configurations. The possible role such configurations may have in the dimer bond will be discussed below.

Less obvious weakly bound homonuclear diatomics can be found scattered about the Periodic Table. Atomic Mn has a $3d^54s^2$ configuration in its ground state. The stability of the d^5 configuration in this first row transition element leads to an anomalously weak binding energy[4,5] for Mn_2: $D_e \sim 0.4 \pm 0.25$ eV (or[6] $\sim 3{,}500 \pm 2000$ cm^{-1}). Similarly, the stability of the $4f^76s^2$ configuration of Eu and the $4f^{14}6s^2$ configuration of Yb yields anomalously weak binding,[7] and the actinide dimers Pu_2, Am_2 and Bk_2 through No_2 are expected to be weakly bound due to the bonding ineffectiveness of the highly localized 5f electrons.[8]

Table I summarizes these diatomics. One can see that weak bonding can

result from a variety of atomic configurations, not necessarily limited to closed principal shell configurations. Moreover, binding energies are found throughout a two order of magnitude range. In general, these energies increase as one moves down a Periodic Group, in contrast to the behavior of chemically bound diatomics, for which the energies generally decrease.

A sufficiently large number of heteronuclear dimers have been studied to allow one to note certain trends. The majority of these dimers contain at least one rare gas, and the heteronuclear rare gas dimers are the prototypes. They provided the first arena in which simple combination rules could be tested (and found to be inaccurate).[9] Three other classes that are well studied are the rare gas-monohalides, the rare gas-alkali metal dimers, and certain molecular ions. The bonding in the monohalides, especially XeF, is of importance to one's basic understanding of the requirements for chemical bonding. Four of these (XeF, XeCl, KrF and ArF) are the active species in UV eximer lasers, the emission from which is to the weakly bound ground state. The rare gas-alkalis are also open shell dimers, dominated by the single alkali valence electron. NaAr[10] and NaNe[11] are the best characterized examples. These molecules have exceptionally weak bonds and long bond lengths. For instance, D_e = 41 cm^{-1} and R_e = 4.99 Å for NaAr. These values are striking, especially when compared to Ar_2 (D_e, = 100 cm^{-1}, R_e = 3.76 Å) or NeAr (D_e = 50 cm^{-1}, R_e = 3.43 Å).

The rare gas-alkaline earth cations, $BeAr^+$, $BeKr^+$, $BeXe^+$, and $CaAr^+$ are known from emission spectra.[12-15] These ions form an interesting contrast to the isovalent rare gas-alkalis, since these families differ by the presence or absence of a localized charge on the metal atom. The mixed rare gas ion, $HeNe^+$, is also known from emission spectra.[16] There are very few data on other mixed rare gas dimer cations,[17] but those between atoms of greatly

different ionization potential are expected to be weakly bound. Certain rare gas-alkali ions have been studied in scattering experiments at low enough energy to be sensitive to the well region of the potential.[18-20]

POTENTIAL ENERGY FUNCTIONS FOR WEAKLY BOUND DIATOMICS

The previous section described the variety of diatomics which can be expected, for one reason or another, to be weakly bound. To understand these molecules in greater detail than that afforded by a table of dissociation energies and bond lengths, an analysis of the full interatomic potential function[21] is called for.

If the reader would stop for a moment and picture in his or her mind the potential energy function for a favorite strongly bound diatomic graphed on the same scale as the potential function for a weakly bound diatomic, the imagined graph would probably look like the one shown in Fig. 1(a). In this figure, the potential functions for the ground states of H_2 and NaAr are drawn to scale. This example is admittedly a bit exaggerated, since the ratio of dissociation energies is nearly 1000 to 1 and the ratio of bond lengths is 0.74 to 5, but NaAr does have a potential well capable of supporting six vibrational levels.[14]

To emphasize the well region and to facilitate comparisons of the <u>relative</u> differences among many potential functions, it is instructive to plot these functions in a reduced coordinate system, scaling lengths by the equilibrium bond length, R_e, and energies by the dissociation energy, D_e. When Fig. 1(a) is replotted in these coordinates, Fig. 1(b) results. One is struck immediately by the relative narrowness of the NaAr potential.

This behavior is a rather general trait of weakly bound molecules. The fundamental parameter of such plots is the reduced curvature of the potential

at R_e. This quantity, denoted κ, is defined by

$$\kappa = \frac{R_e^2}{D_e}\left(\frac{d^2V(R)}{dR^2}\right)_{R_e} = \frac{R_e^2}{D_e} k_e. \tag{1}$$

In terms of spectroscopic constants,

$$\kappa = \frac{\omega_e^2}{2B_e D_e} \tag{2}$$

where ω_e is the equilibrium harmonic vibration constant and B_e is the equilibrium rotation constant. If one consults a standard compilation of diatomic spectroscopic constants[17] and computes κ values where sufficiently accurate data are available, a histogram, shown in Fig. 2, can be made and compared to κ values for weakly bound diatomics. Note first that, for chemically bound species, κ is confined to a tight range of values. Hydrides cluster at the low end of this range, and halogens cluster at the high end. The near constancy of κ, or, to a better approximation, the Periodic variations of κ, are at the heart of a number of empirical rules[22] relating force constants, bond lengths, and dissociation energies in various ways. Representative κ values for weakly bound molecules are generally large to enormous in comparison.

The next region of the potential worth scrutiny is the attractive tail. The behavior of the potential at very large R has been well understood for some time[23] in terms of a long range expansion of electrostatic, induction and dispersion forces. This is at once a blessing and a bane. Surely at very large interatomic distances these theories are correct, but at what distance do they begin to fail significantly? How long is "long range"? How can <u>equilibrium</u> measurements be related to a portion of the potential which is physically removed from the equilibrium region?

To answer these questions, one must have a method for obtaining interatomic potential functions from spectroscopic, scattering, or bulk property data, and,

ideally, the method should not be constrained to a priori expectations about the shape of the attractive tail of the potential. (One can, of course, use ab initio methods to calculate the potential directly, and several such calculations have appeared.[24]) The first step in any inversion method is to decide, in one way or another, on a functional form for the potential. Virtually every analytic function which has a steep repulsive wall, a single minimum, and a smooth rise to dissociation has been suggested as a model function. Many of these can be rejected on the basis of their inability to approximate even crudely the correct long range attraction. The simplest that remain are the Lennard-Jones (m,n) potentials,

$$V(R) = D_e\{1 + \frac{nm}{n-m}\,[\frac{1}{n}(\frac{R_e}{R})^n - \frac{1}{m}(\frac{R_e}{R})^m]\}, \tag{3}$$

the Morse potentials,

$$V(R) = D_e\{1 - \exp[-\beta(R-R_e)]\}^2, \tag{4}$$

and the (Exp-n) potentials,

$$V(R) = D_e\{1 + A\exp(-BR) - C_n/R^n\}. \tag{5}$$

Numerous variations exist, as do many types of piecewise analytic forms,[2] where several different functions are splined together to give a continuous, multiparameter function defined for all R. Multiparameter splined functions lack a certain uniqueness. One must make often arbitrary decisions as to where one function ends and the next begins. This is especially disadvantageous if one is concerned with the previously posed question, how long is "long range"?

If the data consist of spectroscopic term values, the well-established RKR method[25] may be used to compute the inner and outer classical turning points of the rotationless level of each observed vibrational level. Extrapolation of these data to unobserved vibrational levels generally requires some assumption about the potential function's R dependence. The result is a tabulated potential function which is difficult to interpret by itself or to compare to other molecules. The RKR points can be fit to any suitable analytic function, of course, but it would seem advantageous to begin an analysis with such a function if one wishes to establish comparisons.

We have therefore chosen to use an analytic potential function which has the capabilities of avoiding piecewise analyticity while answering many questions concerning the shape of the potential well not only near R_e but also at large R. This function, first suggested by Thakkar[26] in 1975, is a straightforward extension of the familiar expansion introduced by Dunham[27] in 1932. Dunham considered an expansion about the point $R=R_e$ in terms of the variable $(R-R_e)/R_e$. This expansion cannot converge for $R>2R_e$, and it is therefore of little use for our purposes.

The Thakkar function avoids this problem. It is written

$$V(R) = e_o\lambda^2[1 + \sum_{n=1}^{\infty} e_n\lambda^n] \tag{6}$$

where

$$\lambda = \mathrm{sgn}(p)[1 - (R_e/R)^p] \tag{7}$$

and $\mathrm{sgn}(p) = +1$, $p>0$, or -1, $p<0$. If $p \equiv -1$, the Dunham potential results. If $e_n=0$, $n = 1, 2, 3, \ldots$, the Lennard-Jones (p, 2p) potential results (with $e_o=D_e$; compare Eq.(3) with $n = 2m$). In general, p is simply a non-zero parameter which we are free to vary, along with the e_n's. Thakkar argued that

one could choose p by a criterion which is optimum in several ways. This criterion may be written[28] in terms of the second and third derivatives of V(R) at R_e by choosing p such that

$$p = -\frac{\ell_e R_e}{3k_e} - 1 \tag{8}$$

(where ℓ_e is the third derivative). In terms of the first Dunham potential coefficient, a_1, p may be written as

$$p = -a_1 - 1, \tag{9}$$

or in terms of equilibrium spectroscopic constants,

$$p = \alpha_e \omega_e / 6B_e^2. \tag{10}$$

In Eq.(10), α_e is the vibration-rotation interaction constant, relating[29] the rotational constant for level v to the equilibrium rotational constant <u>via</u>

$$B_v = B_e - \alpha_e(v + 1/2). \tag{11}$$

This choice of p causes the leading term of Eq.(6) to reproduce both k_e and ℓ_e exactly. It also forces the first correction parameter, e_1, to be zero, and it is the correct expression for p when the true potential is just a simple Lennard-Jones type. Thus, the Thakkar potential with this choice for p is essentially an expansion in a series of Lennard-Jones functions.

Note that p has considerable physical significance. The potential function approaches dissociation as a polynomial lead by R^{-p}. This behavior holds the promise that Eq.(6) can approximate the anticipated long range behavior of a weakly bound species. However, as Eq.(8) shows, p is directly calculated from the <u>equilibrium</u> properties of the potential function.

We have obtained the Thakkar potential constants for a variety of weakly bound molecules.[2,3,10,12,24] Throughout the well region, the Thakkar function is superior to the Dunham function or the Simons-Parr-Finlan function[30] (which is just a Thakkar potential with $p \equiv +1$), and is roughly as good as the Huffaker-Morse potential[31] (except at long range, where a Morse functionality is usually poor) or an RKR potential.[25]

One fault of the Thakkar function is occasional non-physical behavior at the repulsive wall. Certain sets of parameters which otherwise reproduce the equilibrium and long range regions of the potential sometimes cause the repulsive wall to appear (or disappear, to be more accurate), as shown by the dashed curve in Fig. 3. Here, the Thakker function for $BeAr^+$ $X^2\Sigma^+$ is compared to a model potential[12,15] devised for this family of molecules, the (Exp-Z4) potential

$$V(R) = A \exp(-BR) - Z^2e^2\alpha/2R^4 \qquad (12)$$

where α is the polarizability of Ar, e is the elementary charge, and A, B, and Z are variable parameters. Z is interpreted as the effective nuclear charge on Be^+ to account for partial overlap and deshielding by the 2s electron of Be^+. For this molecular state, Z = 1.29, and the model potential is virtually identical to the Thakkar function, except at the repulsive wall.

The potential function for $BeAr^+$ was derived from data on the lowest five vibrational levels of the molecule. Classical motion in these levels is confined to the range $R = R_e + 0.50$ Å to $R_e - 0.25$ Å (with $R_e = 2.0855$ Å), i.e., highly localized near R_e. Nevertheless, the long range induction forces (and their distance dependence) are recoverable from such localized data, at least for this molecule, and one is confident in stating that $BeAr^+$ is bound by little more than the polarizing effects of Be^+ and, more importantly,

that these effects continue to dominate near R_e.

For $BeAr^+$ $X^2\Sigma^+$, one finds p = 3.156. How can one recognize that this is, in some sense, a special or an anticipated value? First, 3.156 is close to, but less than the asympototic induction exponent of 4. The polynomial nature of Eq.(6) requires p to be different from the anticipated integral leading exponent (call it n), and we have found p to be in the range n to n-1 when long range forces persist near R_e.

A more interesting test comes when one computes p values (via Eq.(10)) for chemically bound diatomics and compares these to p values for weakly bound diatomics, as is shown in Fig. 4. Note that chemically bound diatomics have p values in the range 1-3, clustered sharply near p=2, while p values for weakly-bound systems extend throughout the range 3-7. On comparing Fig.'s 2 and 4, one notes that p and κ are somewhat correlated, even for chemically bound species. One can use Eq.'s (1) and (8) to derive an expression for the reduced third derivative of the potential, yielding

$$\lambda_e \equiv \frac{R_e}{D_e} \ell_e = -3\kappa(p+1). \tag{13}$$

From Fig.'s 2 and 4 and this expression, one can see that the weak bond is relatively more anharmonic than the chemical bond. (A somewhat related phenomenon is the fact that the zero point energy of a weakly bound molecule is typically a much greater fraction of the bond energy than for a chemically bound molecule. For instance, for Ar_2, the level v=0 is found 15% of the way up the potential well. The corresponding figures for Cl_2, K_2, and the light H_2 molecule are 1.4%, 1.1%, and 5.7%, respectively.)

A PHYSICAL INTERPRETATION OF POTENTIAL PARAMETERS

One can generate these functions and tabulate their parameters, but at some point, one is obliged to remember exactly what these functions are supposed to be representing and to interpret the parameters accordingly. The phrase "potential energy function" usually means, and certainly in the context of this article means, the Born-Oppenheimer total energy of both atoms as a function of R. Two opposing effects combine to produce binding: the variation with R of the total Coulombic potential energy and the variation with R of the total kinetic energy of the electrons. One can discuss any type of diatomic bond in these terms by means of the virial theorem.[38]

Let $\langle P.E. \rangle$ be the expectation value of the total Coulombic potential energy operator (which is a function of R) and let $\langle K.E. \rangle$ be the expectation value of the operator for the total kinetic energy of the electrons (also a function of R). The virial theorem states

$$\langle P.E. \rangle = 2V(R) + R \frac{dV(R)}{dR} \tag{14}$$

and

$$\langle K.E. \rangle = -V(R) - R \frac{dV(R)}{dR} . \tag{15}$$

Therefore, given any accurate V(R), one can deduce the functions $\langle P.E. \rangle$ and $\langle K.E. \rangle$. These functions are more illuminating than V(R) alone when one wishes to discuss the changes in electronic structure that occur on binding.

Qualitatively, $\langle P.E. \rangle$ and $\langle K.E. \rangle$ behave as follows for any bound diatomic, with the exception of purely ionic attraction. As the atoms approach, $\langle P.E. \rangle$ begins to rise, but $\langle K.E. \rangle$ falls at a greater rate. At some distance, $\langle K.E. \rangle$ reaches a minimum and begins to rise. At a slightly smaller distance, $\langle P.E. \rangle$ reaches a maximum and begins to fall. These trends continue up to $R = R_e$

where the decrease in <P.E.> is exactly twice the increase in <K.E.>. For $R<R_e$, <K.E.> continues to increase and <P.E.> to decrease until at some $R<<R_e$, <P.E.> finally begins to increase due to nuclear-nuclear repulsion.

A distinguishing feature of weakly bound diatomics, when viewed in terms of the virial theorem, is the persistance of the initial behavior (<P.E.> rising, <K.E.> falling) to R values quite near R_e followed by a very rapid switch of these trends. It is easy to show[33] that

$$\left(\frac{d\langle P.E.\rangle}{dR}\right)_{R_e} = -\left(\frac{d\langle K.E.\rangle}{dR}\right)_{R_e} = k_e R_e, \tag{16}$$

$$\left(\frac{d^2\langle P.E.\rangle}{dR^2}\right)_{R_e} = (1-3p)k_e, \tag{17}$$

and

$$\left(\frac{d^2\langle K.E.\rangle}{dR^2}\right)_{R_e} = 3pk_e \tag{18}$$

where Eq.(8) is the relevant definition for p. One can see from these relations and from the data in Fig.'s 2 and 4 that, near R_e, <K.E.> is increasing and <P.E.> decreasing at <u>relatively</u> much greater rates for weakly bound species (κ and p both large) than for chemically bound species.

All of these observations indicate that weakly bound molecules establish their equilibrium position over a relatively shorter distance (when distance is measured in units of R_e) than do chemically bound molecules, and that the onset of repulsion is relatively more abrupt for a weak bond. These effects are what one expects in the absence of extensive charge delocalization during bonding. But even among weakly bound diatomics themselves, curious variations are found in the degree to which long range forces persist toward R_e, in the relative rates at which repulsive forces appear, and in the failure of homologous families

to display simple trends in bond energies or bond lengths.

Table II presents the evidence. In this Table, bond energies, lengths, κ, and p values have been collected from various sources as indicated. Note that different model potentials can exhibit rather different shape parameters (κ and p) while still reproducing the type of data to which the model was fit. Few potentials have been compared to a truly wide variety of data types (such as bulk properties, differential scattering, spectroscopic, etc.) and fewer still have been constructed from direct spectroscopic observation of many bound levels, making some of the data in Table II uncertain if only because of model dependency.

Now we look at a few specific examples. First, compare Ar_2 with NaAr. The strong bond in Na_2 and the greater polarizability of Na might lead one to expect NaAr to be more strongly bound than Ar_2 and to have a shorter bond length. How can one understand why neither expectation is realized? At long range, the NaAr potential function must fall at a greater rate than the Ar_2 potential because of the greater dispersion interaction. But the virial theorem indicates that repulsion involves an abrupt increase in electron kinetic energy near R_e. The 3s electron on Na is spatially quite diffuse, and when it first encounters the Ar atom (i.e., when electron overlap becomes appreciable), this electron will increase its kinetic energy. The effect is analogous to confining a particle in a box and then slightly decreasing the box dimensions. Since the 3s electron is diffuse, the encounter occurs at a large distance, before the attractive dispersion force has had an opportunity to become appreciable. Near R_e, Ar is moving under the influence of this single diffuse electron. Hence, the long range shape of the potential is lost (p is much smaller than 6) and the curvature of the potential is relatively gentle (κ is 51). Note that the bond length for NaNe is <u>larger</u> than that for NaAr. This is to be

expected, since the NaNe attraction is weaker than for NaAr, but the 3s repulsion should grow at roughly the same rate for both molecules.

Next, we turn to the alkaline earth diatomics and the alkali-mercury diatomics.[34] It is here we encounter "first row anomalies" in the species Be_2 and LiHg. The p values clearly indicate a more chemical nature to the bonding; p ranges from 2.5 to 3.6 (except for Be_2), values far smaller than simple long range attraction allows. The curvatures are also small, especially for LiHg. These species appear to be incipiently covalent, at least to the extent that one can measure such a concept by the shape of the potential well near R_e. Even though the bond energies are very small, these diatomics are showing the features which dominate the bulk metals and alloys. The alkaline earths are showing the influence of low lying nsnp and/or ns(n-1)d configurations[8] (which seem[3a] to make their influence felt rather abruptly in Be_2 - hence the larger κ value). The anomalously high bond energies of Be_2 and LiHg and their anomalous shape parameters probably cannot be "blamed" on any one factor, but atomic size and unusually low first-excited state energies must play a role.

The Ne-containing rare gas dimers deserve comment. Note the steady increase in κ and p through the series HeNe-NeXe accompanied by a saturation in D_e at NeAr. As with NaAr, the virial theorem indicates the increasing role of electron kinetic energy rise as Ne contacts larger and larger atoms. Unlike NaAr, however, the electrons on the rare gases are less diffuse; the repulsion is increasingly more abrupt as reflected by κ and p. The nearly constant bond energies of NeAr-NeXe is somewhat accidental; the regular changes in potential shapes are not.

Finally, we come to one of the outstanding questions posed by Table II. Why is XeF so remarkably different from other rare gas halides? The large

curvature implies a very abrupt onset of repulsion. The large well depth and short bond length indicate an important bonding mechanism not available to other rare gas halides. Whether this mechanism can be uniquely identified is not clear.

CONCLUDING REMARKS

When two atoms or molecules which would appear to have no great chemical interest in one another are bound to form a weak dimer, and when the binding interaction turns out to have properties with periodic variations, or, as with XeF, element-specific surprises, one must look beyond classical electrostatics. The role of electron delocalization in weak bonding may serve to enhance the bonding energy, but an equally valid indicator of delocalization is the change it causes in the shape of the potential well near R_e. The term "delocalization" is used here rather loosely. It is meant to imply those changes in electronic structure that occur in the vicinity of R_e which contribute to binding by reducing the relative rate of increase of the total electron kinetic energy. The curvature of the potential becomes more gentle in such a case (examples are the alkaline earth dimers), which is to be contrasted with, for instance, the heteronuclear rare gas dimers where the onset of repulsion is much more abrupt.

For polyatomic complexes, the prospects of obtaining details of the entire potential energy surface are greatly reduced, although considerable progress has been made.[35] Even without the detail offered by diatomics, the structural and internal dynamics data on polyatomic complexes show the need for "chemical" language to explain even the grossest features (such as the anisotropy of the weak bond) in certain cases.

It is likely that the precision of language used to describe weakly bound

species will sharpen as the body and diversity of data on them grow. We are currently in a transition period. The old rules are known to be insufficient, but the new rules are not yet clearly defined.[36] The challenge of finding these rules is an interesting one, since there are N(N+1)/2 weakly bound dimers for every N stable compounds! The extension of a small set of rules to such a large body of species (and one should not forget trimers, etc.) is the intellectual equivalent of, for instance, the concept of sp^3 hybridization to the theory of hydrocarbons.

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36. An amusing consequence of our current uncertainty in describing weak bonds is the general lack of a systematic nomenclature for weakly bound species. Should NaAr be considered an "argide" or a "natride"?

Table 1. Binding Energies of Weakly Bound Diatomics (in cm^{-1}). Values in parentheses are estimated.

Molecule	D_e[a]	Atomic ground state configuration	Reference
He_2	7.65 ± 0.15	$1s^2$	b
Ne_2	29.7 ± 2	ns^2np^6	9
Ar_2	100. ± 1		2
Kr_2	140. ± 2		c
Xe_2	196. ± 2		c
Rn_2	(250)		c
Be_2	800. ± 80	ns^2	3
Mg_2	430. ± 1		3
Ca_2	1095. ± 0.5		3
Sr_2	1100. ± 100		3
Ba_2	(2000)		8
Ra_2	(1400)		8
Zn_2	1400. ± 300	$(n-1)d^{10}ns^2$	3
Cd_2	760. ± 150		3
Hg_2	630. ± 100		3
Mn_2	3500. ± 2000	$3d^54s^2$	5

Table 1. (cont'd). Binding Energies of Weakly Bound Diatomics (in cm^{-1}). Values in parentheses are estimated.

Molecule	D_e[a]		Atomic ground state configuration	Reference
Eu_2	2800	± 1400	$4f^7 6s^2$	7
Yb_2	1400	± 1400	$4f^{14} 6s^2$	7
Pu_2, Am_2	(2000)		$5f^x 6d^o 7s^2$	8
Bk_2-No_2	(1500)		|	8

[a]See references 4 and 6. Values in cm^{-1}.

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Table II. Potential well parameters for several weakly bound diatomics. Energies in cm^{-1}, R_e in Å.

Molecule	D_e	R_e	κ	p	Method[a]	Reference
He_2	7.65	2.96	77	5.2	E	c
Ne_2	29.7	3.03	80	5.6	E	9
Ar_2	100.	3.76	88.4	5.62	ESB	2
Kr_2	140.	4.01	81.4	6.33	ESB	d
	138.	4.11	(72-87)[b]	(5-5.6)	E	e
Xe_2	196.	4.36	78.3	6.69	ESB	d
	192.	4.45	(88-84)	(5.6-5.5)	E	e
HeNe	9.9	3.21	43	3.64	E	f
HeAr	16.8	3.54	59	4.43	E	f
HeKr	17.2	3.75	57	4.34	E	f
HeXe	17.5	4.15	56	4.29	E	f
NeAr	50.	3.43	87	5.60	E	9
NeKr	52.	3.58	98	6.00	E	9
NeXe	52.	3.75	125	6.91	E	9
Be_2	800.	2.49	59.5	4.94	A	3(a,b)
Mg_2	430.	3.89	32.7	3.59	S	3(a,c)
Ca_2	1095.	4.28	41.9	3.56	S	3(a,d)
Sr_2	1100.	4.50	38	3.35	S	3(a,e)
NaNe	8.1	5.29	48	4.66	S	11
NaAr	41.	4.99	51	4.31	S	10
LiHg	871.	3.00	23.5	2.54	E	34(a)
NaHg	444.	4.72	40.9	3.10	E	34(b)
KHg	420.	4.91	40.0	3.00	E	34(c)

Table II. (cont'd). Potential well parameters for weakly bound diatomics. Energies in cm^{-1}, R_e in Å.

Molecule	D_e	R_e	κ	p	Method	Reference
CsHg	403.	5.09	46.2	3.40	E	34(c)
NeF	42.	2.85	(110-92)	(6.4-5.8)	E	g
ArF	98.	2.95	37.0	3.30	E	g
KrF	108.	3.00	37.0	3.30	E	g
XeF	1175.	2.32	(144-92)	(7.5-5.8)	E	h
	1175.	2.32	116.6	5.53	S	i
XeCl	280.	3.23	(54-22)	(4.2-2.3)	E	j
$HeNe^+$	6200.	1.33	48.9	4.30	S	16
$BeAr^+$	4536.	2.09	27.5	3.16	S	12(a,b)
$BeKr^+$	5511.	2.22	29.1	2.84	S	12(a),13
$CaAr^+$	1000.	2.80	36.3	3.93	S	15

[a]Methods - E, elastic scattering; S, optical spectroscopy; B, bulk data used in fit; A, ab initio calculation.

[b]If the model potential has two Morse functions joined at R_e, κ and p are not well defined. Data in parentheses list values for the inner Morse function and the outer Morse function, respectively.

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FIGURE CAPTIONS

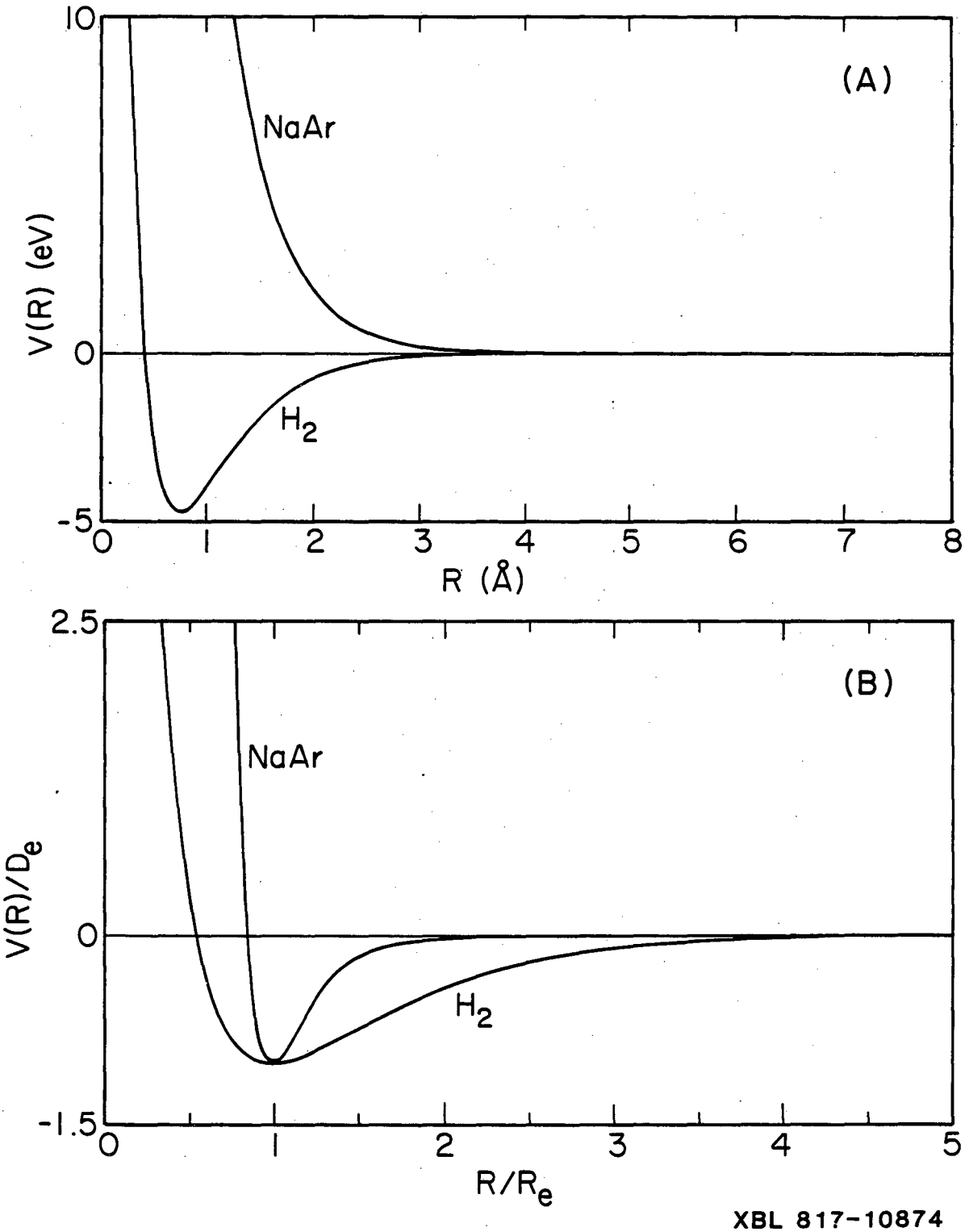
Fig. 1. (a) Potential energy curves for the ground electronic states of H_2 and NaAr. The potential well for NaAr has its minimum at 5 Å, but being only 5 meV deep, it is invisible on this drawing.

(b) Potential curves redrawn in reduced coordinates. Note the relative narrowness of the NaAr potential compared to the H_2 potential.

Fig. 2. A histogram of reduced curvature values.

Fig. 3. Potential curves for $BeAr^+ X^2\Sigma^+$. The solid line is an (EXP-Z4) potential fit to a six parameter Thakkar function (dashed line) obtained by spectroscopic inversion. From the point where the two curves meet (near 1.0 Å) to larger R, the two functions are virtually identical.

Fig. 4. A histogram of p values.



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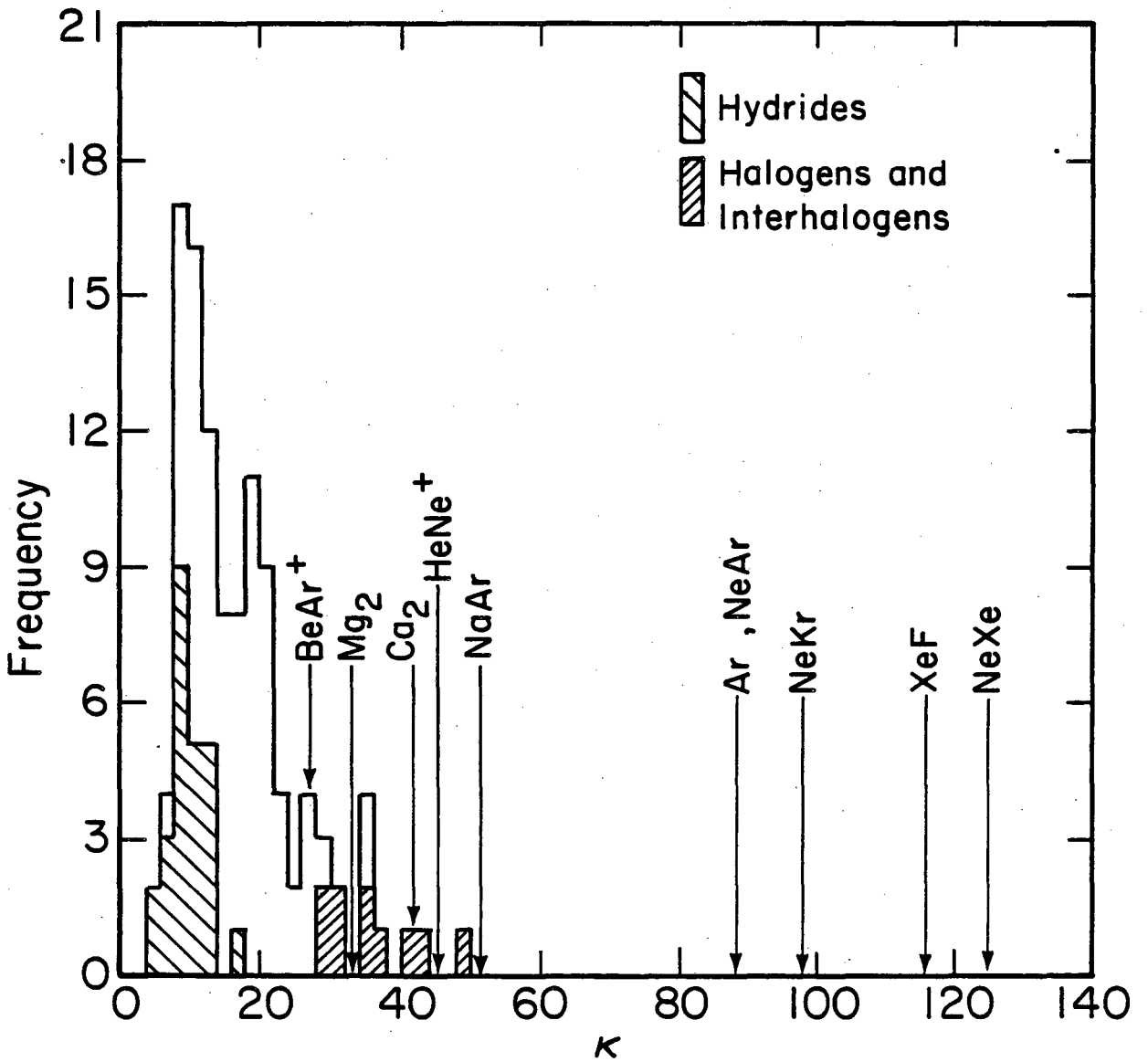

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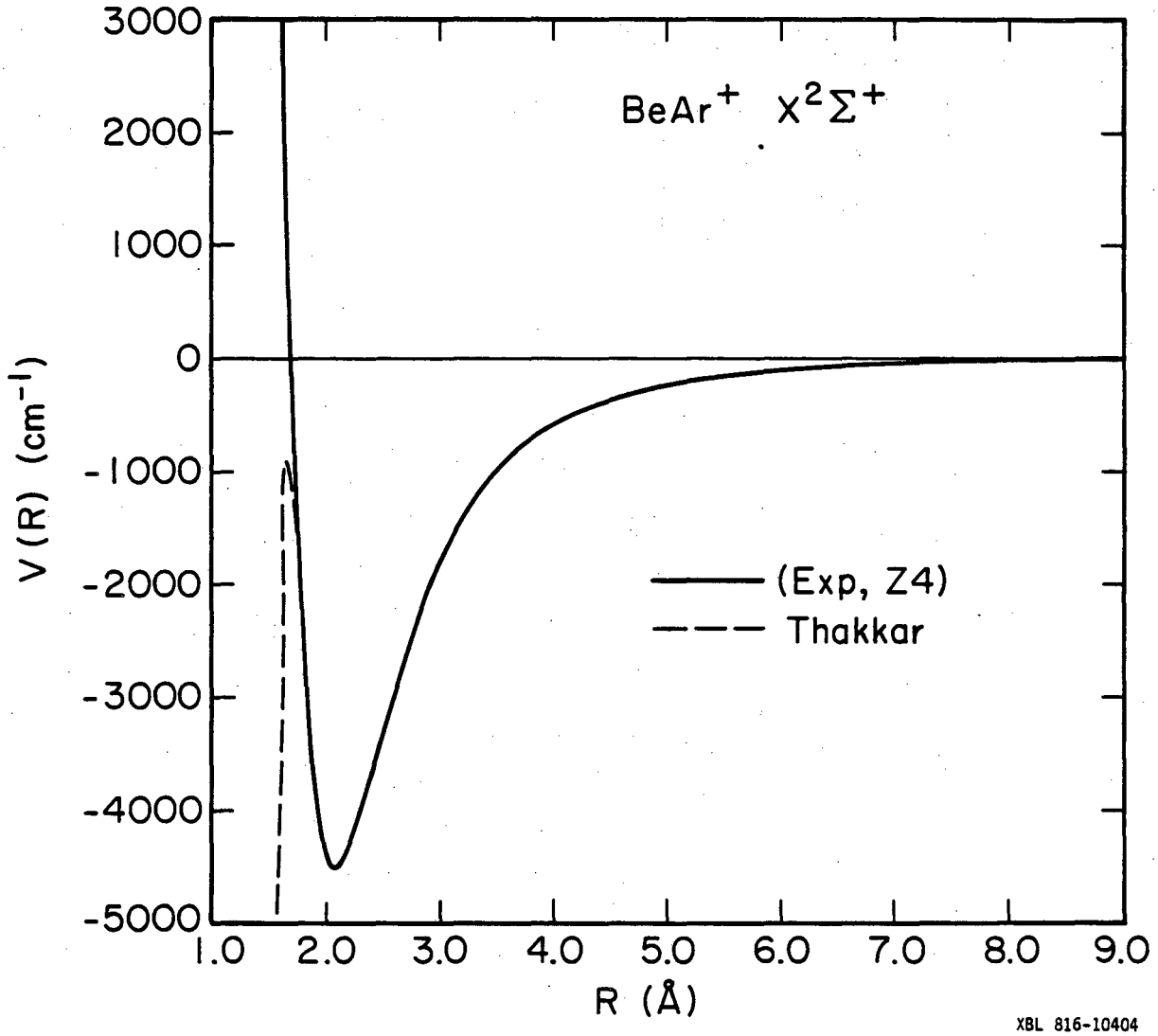
BeAr+ X2Σ+
(Exp, Z4)
Thakkar
V (R) (cm-1)
R (Å)
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
1.0
2.0
3.0
4.0
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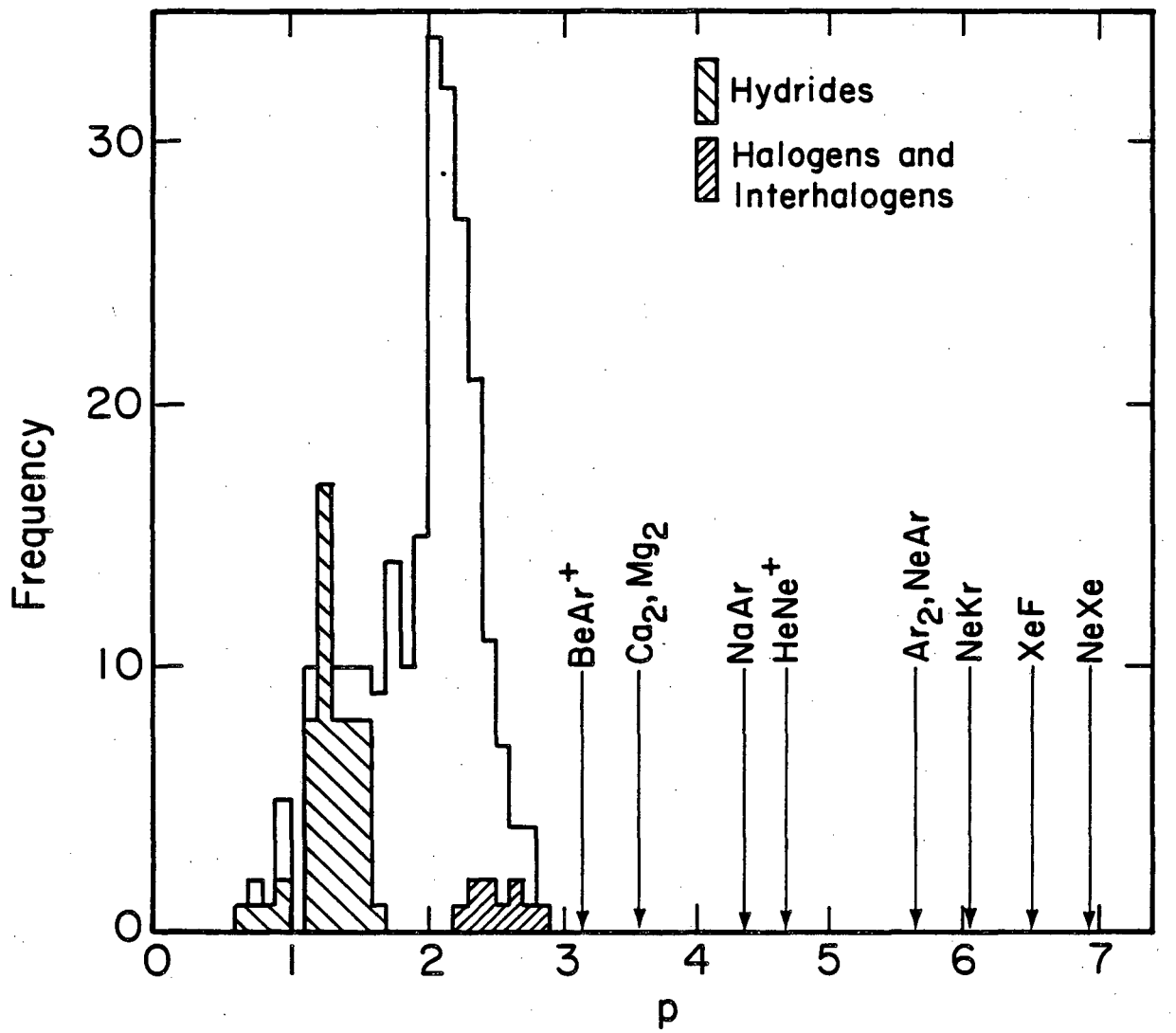
7.0
8.0
9.0
XBL 816-10404



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