Zero electron kinetic energy and photoelectron spectroscopy of the XeI\(^{-}\) anion

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The XeI\(^{-}\) anion and the corresponding neutral X1/2, I3/2, and I11/2 electronic states have been studied by means of zero electron kinetic energy (ZEKE) and photoelectron spectroscopy. The ZEKE spectra show rich and well-resolved progressions in the low-frequency vibrations of the anion and the neutral van der Waals complexes. From our spectroscopic data we construct model potentials for the anion and three neutral states, which are compared to previously obtained potential functions for this system. The intensity of the I3/2—anion transitions relative to the X1/2—anion transitions in the XeI\(^{-}\) ZEKE spectrum is considerably lower than expected from a Franck-Condon simulation based on the model potentials. Comparison with the photoelectron spectrum of XeI\(^{-}\) indicates this is due to a small s-wave partial cross section for photodetachment to the I3/2 state. © 1998 American Institute of Physics. [S0021-9606(98)00148-2]

I. INTRODUCTION

The characterization of the potential energy function between weakly interacting species has been the subject of extensive experimental and theoretical effort over the past decades. As a result, many key features governing the interaction between closed shell neutral species are now well understood both experimentally and theoretically.\(^{1−3}\) However, considerably less is known about the interactions between open and closed shell species with their manifold of available potential energy surfaces. A similar statement holds for the intermolecular forces between ions and neutrals, where from the experimental point of view the implementation of sensitive spectroscopic techniques with adequate resolution is far from straightforward. Although high-frequency, intramolecular vibrational modes in ion-neutral clusters have been characterized by a variety of infrared action spectroscopy experiments,\(^{4−11}\) the low-frequency modes characteristic of ion-neutral binding are more difficult to observe.

For negatively charged species, the development of anion ZEKE (zero electron kinetic energy) spectroscopy\(^{12}\) (based on the original design for the photoionization of neutrals as introduced by Schlag and co-workers\(^{13−15}\)) has proven to be a powerful means of characterizing the low-frequency vibrational modes involved in weak ion-neutral interactions. Rare gas halides (RgX\(^{-}\)) are particularly well-suited for such studies, and ZEKE spectra for KrBr\(^{-}\), XeBr\(^{-}\), KrCl\(^{-}\), KrI\(^{-}\), ArI\(^{-}\), ArBr\(^{-}\), \(n\) as well as the larger clusters Ar\(_n\)I\(^{-}\) \((n = 2−9)\) and Ar\(_n\)Br\(^{-}\) \((n = 2−9)\) have already been investigated in this laboratory. The present study on XeI\(^{-}\) is a continuation of this work and part of the ongoing effort in our group to obtain anion ZEKE spectra for the complete RgX\(^{-}\) series.

The charged Rg\(_n\)X\(^{-}\) species represent the simplest solvated ionic chromophores and are therefore important prototypical systems for understanding the influence of the surrounding on the photophysical properties and reactivity of ions in solution. ZEKE spectroscopy of the RgX\(^{-}\) diatomics yields accurate pair potentials, which are needed as a reliable basis to quantitatively assess the structure, energetics and dynamics of larger halide clusters,\(^{18,19}\) as well as the importance of many-body effects in these and related systems.\(^{18}\) From a more practical standpoint the RgX\(^{-}\) interaction potentials determine the transport properties of halide ions in rare gases, and are, for instance, important for the understanding and modeling of processes in plasmas and discharges.

As far as the XeI\(^{-}\) anion is concerned, the only experimental information available so far comes from photoelectron spectra and photodetachment action spectra of Cheshnovsky and co-workers, who obtained electron binding energies for Xe\(_n\)I\(^{-}\) clusters up to \(n = 12.\)^\(^{20}\) However, no experimental data on the interaction potential of XeI\(^{-}\) exist, and the only available information in this respect comes from coupled cluster calculations,\(^{21}\) the scaled electron gas theory,\(^{22}\) and various (semi-)empirical models\(^{23−26}\).

The interactions in neutral RgX complexes are particularly interesting, because they represent textbook examples of open shell—closed shell interactions. Three molecular electronic states arise from the \(^2P\) halogen atom—rare gas interaction, as shown in Fig. 1.\(^{27,28}\) The lower \(^2P_{3/2}\) state is split by the electrostatic interaction into two components, corresponding to the two possible projections of the total electronic angular momentum \(\Omega\) along the internuclear axis: \(\Omega = 1/2\) (the \(X1/2\) state or ‘‘X’’ state in the notation used here) and \(\Omega = 3/2\) (the \(I3/2\) or ‘‘I’’ state). The upper \(^2P_{1/2}\) halogen spin-orbit state correlates with the \(II1/2\) state (‘‘II’’ state) in the complex \((\Omega = 1/2)\).

Although these interactions are in general fairly weak, especially when compared to chemical forces in reactive processes, their influence on reaction dynamics can be significant, as shown in recent quantum mechanical and quasiclass-
The practical importance of several members of the neutral \( \text{RgX} \) series originates from their use in excimer lasers (the most prominent examples being \( \text{XeCl}, \text{ArF}, \) and \( \text{KrF} \)). The lasing process is due to transitions between electronically excited, deeply bound charge transfer states ("\( \text{Rg}^+ \text{X}^- \)"") and the repulsive wall of the weakly bound covalent ground states.

In the case of \( \text{XeI} \) the strongest of these transitions \( (X \leftarrow B) \) has been studied extensively in emission, and was first observed by Ewing and Brau. In a subsequent study, Tellinghuisen et al. recorded the strong diffuse ultraviolet emission bands, and quantitatively analyzed the spectrum for the first time, treating the transition from the \( B \) to the \( X \) state as bound-free. This yielded the curvature and slope of the \( X \) state potential in the Franck-Condon region, the latter being apparently steeper than the estimate given by Ewing and Brau.

In a subsequent study, Casassa et al. observed the \( II \leftarrow B \) transition in emission for the first time: however, no potential function for the \( II \) state could be extracted from this experiment. A detailed analysis of the \( \text{XeI} \) emission spectrum was carried out by Tamagake et al. From the simulation of their spectra they extracted very approximate potentials for the \( X, I, \) and \( II \) states, which were constructed from a combination of earlier \textit{ab initio} results and an additional dispersion term.

Lee and co-workers determined elastic differential cross sections (DCS) for collisions between \( \text{I}_2^2P_{3/2} \) and \( \text{Xe}^1S_0^+ \) in a crossed molecular beams experiment. The measured DCS contain contributions from the \( X \) and \( I \) states. Individual potential curvatures for these states were therefore determined by an appropriate mathematical inversion procedure. For the \( X \) and \( I \) states they extracted well depths of \( 241 \) cm\(^{-1} \) and \( 168 \) cm\(^{-1} \), respectively. However, no information on the \( II \) state could be obtained, because the higher \( ^2P_{1/2} \) spin-orbit state of iodine is not populated under their experimental conditions.

Jones et al. measured photoassociation spectra for \( \text{Xe–I} \) collision pairs. Unfortunately, their bound-free simulations of the highly structured spectra neglected the shallow \( X \) state well found in the scattering study. The most recent investigation of \( \text{XeI} \) came from Tellinghuisen’s laboratory, where the \( X \leftarrow B \) emission spectrum was recorded for the single isotopomer \( ^{129}\text{Xe}^{127}\text{I} \) with much higher resolution than in their previous work. Their study confirmed that this transition is primarily bound-free. However, extensive weak vibrational structure was also found on top of the broad emission, originating from transitions between higher vibrational levels of the \( B \) state and the bound region of the \( X \) state. This study yielded a complete potential curve for the \( X \) state, unambiguously showing that it possesses a well depth of at least \( 267 \) cm\(^{-1} \), already exceeding the well depth extracted from the scattering study. Due to uncertainties in the vibrational level numbering, the well may be even deeper.

The results reported here provide a more complete view of the anion and neutral potentials. Anion ZEKE spectroscopy is a very powerful tool in this respect, because photo-detachment from the \( \text{XeI}^- \) anion allows us to extract detailed information about the anion, as well as the neutral \( X, I, \) and \( II \) states. The capability of probing the anion and \( II \) states is particularly important due to the almost total lack of spectroscopic information.

We have organized this paper as follows: In Sec. II we briefly describe the experimental setup used for studying the \( \text{XeI}^- \) anion, and in Sec. III our ZEKE spectra are presented and complete assignments are given. Section IV deals with the construction of model potentials for fitting the vibrational and rotational contours of the ZEKE spectra. Finally, in Sec. V we compare our potentials to the available data from theoretical calculations and (semi-)empirical approaches. Special attention is paid to the observed relative intensities of the transitions to the different neutral electronic states in the ZEKE spectra. We also present \( \text{XeI}^- \) anion photoelectron spectra recorded for comparison with the ZEKE results for the \( X \) and \( I \) states.

**II. EXPERIMENT**

The anion zero electron kinetic energy (ZEKE) spectrometer has been described in detail previously, and only the specific details relevant to this study will be considered here. Briefly, \( \text{XeI}^- \) anions are generated by passing a mixture of 10%–20% \( \text{Xe} \) in \( \text{Ar} \) over \( \text{CH}_3\text{I} \) (0 °C), which is then expanded into vacuum through a 0.5 mm aperture in a pulsed valve (General Valve Series 9), typically applying a backing pressure of 10–30 psi.
The expansion is crossed just in front of the valve by an 1 keV electron beam. Anions are formed through dissociative attachment (and other secondary processes), and undergo clustering in the continuum flow region of the free-jet expansion. The negative cluster ions formed during these processes are effectively cooled as the expansion progresses, and then pass through two skimmers into a differentially pumped region. In our setup, the additional second skimmer in the source chamber, placed close (1–2 mm) to the beam valve and about 10 mm away from the first skimmer, is found to substantially enhance the amount of all clusters, especially the larger ones, suggesting an additional cooling effect.

The clusters are then accelerated to 1 keV into a 1 m collinear time-of-flight mass spectrometer, where they separate according to their mass. After entering the detector region the XeI− anions are photodetached by an excimer-pumped dye laser (Lambda Physik FL3002). In contrast to previous work carried out on this instrument, a weak dc field of −15 mV/cm is applied across the electron detachment region at all times; the negative sign indicates the field is anti-parallel to the ion beam propagation direction, so that this field slightly decelerates electrons in the laboratory frame.

After a delay of 200–500 ns, the electrons are extracted coaxially to the ion beam by applying a pulsed extraction field of 4 V/cm across the extraction region. Higher energy electrons with velocity components perpendicular to the ion beam axis are discriminated against geometrically by the extraction plates acting as apertures. The electrons with (nearly) zero kinetic energy and the higher energy electrons ejected forward and backward on axis travel different distances in the extraction field and gain different amounts of energy. They therefore separate in the following drift region, and those electrons having nearly zero electron kinetic energy relative to the anion packet can be selectively detected in a 35–100 ns wide temporal gate using a microchannel plate detector positioned approximately 1 m away from the extraction region.

The addition of a weak dc field enhances the amount of ZEKE electrons by roughly a factor of three, with no degradation of the spectral resolution of 1–2 cm−1 for atomic anions. The peaks observed in this study are broader than those electrons with nearly zero electron kinetic energy and the higher energy electrons ejected forward and backward on axis travel different distances in the extraction field and gain different amounts of energy. They therefore separate in the following drift region, and those electrons having nearly zero electron kinetic energy relative to the anion packet can be selectively detected in a 35–100 ns wide temporal gate using a microchannel plate detector positioned approximately 1 m away from the extraction region.

The time-of-flight anion photoelectron spectrometer has already been described at length elsewhere. XeI− anions are produced using the same mixture as noted above. However, in this case only a single skimmer (1 mm diameter) in conjunction with higher backing pressures (40–80 psi) is used. The ions are extracted from the beam and then enter a time-of-flight mass spectrometer with a linear reflectron stage.

The ions separate in time and space according to their mass-to-charge ratios, and the XeI− ions are then selectively detached by the third harmonic of a pulsed Nd:YAG laser (355 nm corresponding to 3.493 eV; Quanta-Ray DCR-3), running at 20 Hz. The energy of the photoelectrons is measured by time-of-flight in a field-free flight tube 100 cm in length. The instrumental resolution under these conditions (electron kinetic energy around 0.4 eV) is about 8 meV. The polarization dependence of the features in the XeI− photoelectron spectra is investigated by varying the angle θ between the laser polarization and the direction of electron collection, using a half-wave plate. In this way, photoelectron spectra at θ = 0° and 90° ("horizontal" and "vertical" polarization, respectively) are obtained.

II. ZEKE SPECTRA AND ASSIGNMENTS

As is already clear from the remarks in Sec. I and Fig. 1, we expect to observe two band systems, which are separated by approximately the spin-orbit constant of atomic iodine (0.942 eV/7603.0 cm−1). The lower energy band system is shown in Fig. 2, and results from transitions to the

![FIG. 2. Experimental and simulated XeI− ZEKE spectra for the X1/2 and X3/2 states (^1P3/2 asymptote). Solid lines: experimental data; dotted lines: best fit spectral simulation based on MMSV model potentials, as described in text. Peaks 1 and 3 belong to the X state and peaks 2 and 4 to the I state; see Tables I and II for complete assignments of all features. The two insets on the left and on the right show magnifications of the experimental and simulated spectra in the corresponding energy regions.](Image)
TABLE I. Peak assignments for the XeI⁻—anion transitions in the XeI⁻ ZEKE spectrum (left part of Fig. 2). All energies are in cm⁻¹. The assignment listed first contributes the most to the peak intensity. Assignments in parentheses are additional transitions needed to account for at least two third of the total peak intensity, listed in order of decreasing magnitude of their contribution.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position</th>
<th>Relative energy</th>
<th>(v' (XeI^-)\rightarrow v'' (anion)) assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25 235.9</td>
<td>0.0</td>
<td>0→0</td>
</tr>
<tr>
<td>(a_1)</td>
<td>25 225.7</td>
<td>−10.2</td>
<td>1→1</td>
</tr>
<tr>
<td>(b_1)</td>
<td>25 215.3</td>
<td>−20.6</td>
<td>2→2</td>
</tr>
<tr>
<td>(c_1)</td>
<td>25 204.8</td>
<td>−31.1</td>
<td>3→3</td>
</tr>
<tr>
<td>(d_1)</td>
<td>25 194.2</td>
<td>−41.7</td>
<td>4→4</td>
</tr>
<tr>
<td>(e_1)</td>
<td>25 184.1</td>
<td>−51.8</td>
<td>5→5</td>
</tr>
<tr>
<td>(f_1) (broad)</td>
<td>25 169.8</td>
<td>−66.1</td>
<td>6→6</td>
</tr>
<tr>
<td>(g_1)</td>
<td>25 155.9</td>
<td>−80.0</td>
<td>7→7</td>
</tr>
<tr>
<td>(h_1)</td>
<td>25 145.1</td>
<td>−90.8</td>
<td>8→8</td>
</tr>
<tr>
<td>(i_1)</td>
<td>25 136.2</td>
<td>−99.7</td>
<td>9→9</td>
</tr>
<tr>
<td>(j_1)</td>
<td>25 126.1</td>
<td>−109.8</td>
<td>10→10</td>
</tr>
<tr>
<td>(k_1)</td>
<td>25 115.3</td>
<td>−120.6</td>
<td>11→11</td>
</tr>
<tr>
<td>(l_1) (broad)</td>
<td>25 256.0</td>
<td>+20.1</td>
<td>12→12</td>
</tr>
</tbody>
</table>

TABLE II. Peak assignments for the I3/2—anion transitions in the XeI⁻ ZEKE spectrum (right part of Fig. 2). All energies are in cm⁻¹. The assignment listed first contributes the most to the peak intensity. Assignments in parentheses are additional transitions needed to account for at least two third of the total peak intensity.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position</th>
<th>Relative energy</th>
<th>(v' (I3/2^-)\rightarrow v'' (anion)) assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>25 295.9</td>
<td>0.0</td>
<td>0→0</td>
</tr>
<tr>
<td>(a_2)</td>
<td>25 282.8</td>
<td>−13.1</td>
<td>1→1</td>
</tr>
<tr>
<td>(b_2)</td>
<td>25 263.4</td>
<td>−32.5</td>
<td>2→2</td>
</tr>
<tr>
<td>(c_2)</td>
<td>25 303.1</td>
<td>+7.2</td>
<td>3→3</td>
</tr>
<tr>
<td>(d_2)</td>
<td>25 316.8</td>
<td>+20.9</td>
<td>4→4</td>
</tr>
<tr>
<td>(e_2)</td>
<td>25 335.3</td>
<td>+39.4</td>
<td>5→5</td>
</tr>
<tr>
<td>(f_2)</td>
<td>25 352.9</td>
<td>+57.0</td>
<td>6→6</td>
</tr>
<tr>
<td>(g_2)</td>
<td>25 369.6</td>
<td>+73.7</td>
<td>7→7</td>
</tr>
<tr>
<td>(h_2)</td>
<td>25 385.7</td>
<td>+89.8</td>
<td>8→8</td>
</tr>
<tr>
<td>(i_2)</td>
<td>25 399.8</td>
<td>+103.9</td>
<td>9→9</td>
</tr>
<tr>
<td>(j_2)</td>
<td>25 412.0</td>
<td>+116.1</td>
<td>10→10</td>
</tr>
<tr>
<td>(k_2)</td>
<td>25 423.4</td>
<td>+127.5</td>
<td>11→11</td>
</tr>
</tbody>
</table>
many more lines than our previous spectra of other RgX−
anions, indicating a higher vibrational temperature. We estimate
T_{\text{vib}} \approx 160 \text{ K} and T_{\text{rot}} \approx 100 \text{ K} from our fit, compared,
e.g., to T_{\text{vib}} \approx 60–80 \text{ K} and T_{\text{rot}} \approx 40 \text{ K} in our
ArI−/KrI−/ArBr− anion ZEKE study. 15 While the reason for
this higher temperature is not entirely clear, the observation of
more spectral features does allow a more detailed character-
ization of the anion and neutral states.

The spectral features in Fig. 2 above 25 250 cm^{-1} are
due to 13/2− anion transitions. Only very weak lines are
observed over the whole energy range. A second inset has been
included in the upper right half of the figure, showing a
magnification of this part of the experimental spectrum and
the corresponding spectral simulation. The following assign-
ments are made primarily because they give the best fit in-
volving the optimized I state model potential, and at the
same time are the ones that are most consistent with the
parameters extracted for the anion and II state potentials
(Sec. IV C).

Peaks 2, d2, ..., g2 are assigned to a vibrational progress-
ion in the I state, with peak 2 assigned as the 0-0 transition
and the latter four peaks as (v′-0) transitions with v′ = 1−4.
With the help of the simulation one can extend this
progression up to v′ = 8 (peaks h2−k2). The extent of this
progression indicates that the bond length of the I state is
significantly different from the anion, in apparent contrast to
the X state. Moreover, the overall intensity of the I band is
much lower than expected from the simulated Franck-
Condon factors alone, as will be further addressed in Sec.
V B. Complete assignments of all the 13/2− anion
transitions can be found in Table II. The assignment of the
barely visible peak 2 to the 0-0 transition is supported by the
observation of peak c3 and its assignment to the 2-1 transition.

The ZEKE spectrum for photodetachment to the II/2 state
is shown in Fig. 3 (upper solid line). The resolution in
this case is worse than for the X and I states, because the
delay between photodetachment and electron extraction was
significantly reduced to about 200 ns in order to achieve
acceptable signal rates. This results in a ZEKE linewidth of
roughly 15 cm^{-1}, due to poorer discrimination against higher
energy electrons. The small signal results from the combina-
tion of much lower detachment laser power (frequency dou-
bling was required)

\begin{align*}
\text{IV. ANALYSIS}
\end{align*}

Peak 1 in Fig. 2 yields an accurate electron affinity of
25 235.9 ± 2.0 cm^{-1} for XeI−, compared to 25 250 ± 160 cm^{-1}
obtained from the photoelectron spectrum of
Cheshnovsky and co-workers. 20 Note that this value is larger
than the corresponding electron affinity for atomic iodine of
24 672.796 cm^{-1}. 45 This shows that the XeI−
dissociation energy is greater than that of XeI. Also, from the vibrational
assignments in Tables I–III we can deduce frequencies for
the anion and the three neutral states. To gain further insight
into the binding properties of the different XeI species (es-
specially the anion and II state potentials, for which no high
quality data exist) we construct sufficiently flexible model
potentials for the anion and neutral complexes. The eigen-
functions of these potentials and Franck-Condon factors are
then calculated, resulting in a vibrational stick spectrum,
which is convoluted with the rotational and ZEKE line
shapes to produce a simulated ZEKE spectrum. By itera-
tively adjusting the potential parameters the best possible fit
to the experimental ZEKE spectrum is sought. Finally, we
consider the uncertainties in the potential parameters ob-
tained from the best fit.

\begin{table}
\caption{Peak assignments for the II/2− anion transitions in the XeI−
ZEKE spectrum (Fig. 3). All energies are in cm^{-1}. Only approximate values
can be given with the aid of the spectral simulation due to the reduced
experimental resolution in this case (see text). For particularly broad fea-
tures the transitions contributing the most to the total peak intensity are
given.}
\begin{tabular}{cccc}
\hline
Peak & Position & Relative energy & \( v' (II/2) \rightarrow v'' (anion) \) \\
\hline
3 & 32 880 & 0 & 0−0 \\
3 & 32 850 & −30 & 0−1 \\
3 & 32 840 & −40 & 1−2 \\
3 & 32 820−32 790 & −60 to −90 & 0−2, 1−3, 2−4 \\
3 & 32 902 & +22 & 1−0 \\
3 & 32 910−32 930 & +30 to +50 & 3−1, 5−2, 2−0, 4−1 \\
\hline
\end{tabular}
\end{table}

\begin{align}
(\nu'−0 \text{ and } \nu'−1). \text{ See Table III for a compilation of all indi-
gual II− anion transitions.}
\end{align}

\begin{align}
\text{A. Potential functions}
\end{align}

As in previous work, 16, 17, 36 we use the flexible, piece-
wise Morse–Morse-switching function van der Waals
(MMSV) potential to fit our spectra. For neutral XeI, the
reduced form of this potential [with \( f(x) = V(R)/e \) and \( x = R/R_m \)] is:

\begin{align}
f(x) = e^{-2\beta_1(1−x)}−2e^{-\beta_1(1−x)}, \quad 0<x\leq1, \\
= e^{-2\beta_1(1−x)}−2e^{-2\beta_1(1−x)\equiv M_1(x)}, \quad 1<x\leq x_1, \\
\text{SW}(x)M_2(x) + [1−\text{SW}(x)]W(x), \quad x_1<x<x_2, \\
= −C_6x^{-6}−C_8x^{-8}\equiv W(x), \quad x_2<x<\infty,
\end{align}

where the switching function is given by

\begin{align}
\text{SW}(x) = \frac{1}{2} \left[ \cos \frac{\pi(x−x_1)}{(x_2−x_1)} + 1 \right],
\end{align}
and the reduced dispersion coefficients \( C_{6r} \) take the form:

\[
C_{6r} = \frac{C_6}{R_m^6}, \quad C_{8r} = \frac{C_8}{R_m^8}.
\]  

(3)

Here, \( \epsilon \) is the potential well depth and \( R_m \) represents the equilibrium bond length (position of the well minimum). \( C_6 \) is the induced dipole–induced dipole dispersion coefficient, and \( C_8 \) represents the corresponding coefficient for the induced dipole–induced quadrupole interaction. Higher dispersion terms are neglected, as is the small induction term, varying as \( R^{-8} \), due to the permanent quadrupole moment of the iodine atom. The \( \text{Xe}^- \) anion potential is of the same form, except that the dispersion terms are replaced by:

\[
f(x) = -B_{4r}x^{-4} - B_{6r}x^{-6} = W(x), \quad x_2 \leq x < \infty,
\]  

(4)

with

\[
B_{4r} = \frac{B_4}{eR_m^4}, \quad B_{6r} = \frac{B_6}{eR_m^6}.
\]  

(5)

and

\[
B_4 = \frac{1}{e^2} \alpha_d(Xe), \quad B_6 = \frac{2}{e^2} \alpha_q(Xe) + C_6.
\]  

(6)

Here, \( q \) represents the iodide charge and \( B_4 \) is the coefficient of the leading term in the long range \( \text{Xe}^- \) potential, reflecting the dipole induced in the \( \text{Xe}^- \) atom by \( \Gamma \). The \( B_6 \) term arises from quadrupole induction and dipole dispersion terms. \( \alpha_d(Xe) \) and \( \alpha_q(Xe) \) are the dipole and quadrupole polarizabilities of the \( \text{Xe}^- \) atom, respectively; these are given in Table IV.

The dispersion coefficients \( C_6 \) and \( C_8 \) for the neutral \( \text{Xe} \) \( 1/2, 3/2, \) and \( \text{II} 1/2, 3/2 \) states are estimated using the formulas of Koutselos and Hason. Their formulas involve the dipole and quadrupole polarizabilities of each interacting atom, and an effective number of electrons, \( N \), characteristic of each atom. These quantities were taken from experimental sources or semi-empirical approaches or \( \text{ab initio} \) calculations. The anisotropy of the dipole and quadrupole polarizabilities for the iodine atom is determined in the same manner used by us previously for the \( \text{Br} \) atom. The relevant parameters are listed in Table IV.

The \( C_6 \) parameter for the \( \text{Xe}^- \) anion is taken from the \( \text{ab initio} \) calculations of Hättig and Heß who determined dispersion coefficients for the whole series of rare gas halides. Note that all of their \( \text{ab initio} \) \( C_6 \) parameters are in excellent agreement with the values published by Koutselos, Mason, and Viehland, which were deduced via an universal scaling scheme for closed shell interactions involving rare gas–rare gas, alkali ion–noble gas, and halogen ion–noble gas interactions. All \( C_6 \) and \( C_8 \) dispersion coefficients are given together with the other potential parameters in Table V. Because the ZEKE spectra are not sensitive to the very

**Table IV. Dipole and quadrupole polarizabilities and effective numbers of electrons used to calculate dispersion and induction coefficients.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Corresponding spinless state of ( \text{Xe} ) neutral</th>
<th>( \alpha_d ) ( [\alpha_0] )</th>
<th>( \alpha_q ) ( [\alpha_0] )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( \Sigma )</td>
<td>30.05 (^a)</td>
<td>266.7 (^b)</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>( \Pi )</td>
<td>34.57 (^c)</td>
<td>314.5 (^d)</td>
<td>6.5</td>
</tr>
<tr>
<td>( \text{Xe} )</td>
<td>---</td>
<td>27.16 (^e)</td>
<td>202.8 (^f)</td>
<td>7.253 (^f)</td>
</tr>
</tbody>
</table>

\(^a\) Derived from the spherically averaged \( \alpha_d(\text{I}) \) value (Ref. 47) assuming the same anisotropy as for \( \alpha_d(\text{Cl}) \) (Ref. 50).

\(^b\) Derived from the spherically averaged \( \alpha_d(\text{I}) \) value assuming the same anisotropy as for \( \alpha_d(\text{Cl}) \) (Ref. 51). Spherically averaged \( \alpha_d(\text{I}) \) value itself calculated via the “hydrogenic relationship” (Ref. 52) using \( \alpha_d(\text{I}) \) from Ref. 47.

\(^c\) Reference 47.

\(^d\) Reference 48.

\(^e\) Reference 49.

\(^f\) Calculated from the \( C_6 \) value of Ref. 48.

**Table V. MMSV potential parameters and deduced spectroscopic constants for \( \text{Xe} \) and \( \text{Xe}^- \).** Term values \( T_0 \) are referenced to the anion vibrational ground state. \( \alpha_0 \) = zero point energy, \( \nu_0 \) = fundamental vibrational frequency. Assumed anion temperature in the spectral simulations for \( 1/2, 3/2(\text{II} 1/2): T_{\text{th}} = 160 \) (160) K and \( T_{\text{av}} = 100 \) (130) K. Error bars (\( \pm \)) estimated from multiparameter sensitivity analysis as described in text. Parameters given with more digits than are significant to prevent round-off errors. Scattering data also given for comparison.

|            | \( X/1 \) | \( X/2 \) | \( 3/2 \) | \( 3/2 \) | \( 1/2 \) | \( \text{Anion} \) |
|------------|----------|----------|----------|----------|----------|----------------|---|
| \( T_0 \) [cm\(^{-1}\)] | 25 235.9 (2.0) | --- | 25 295.9 (3.0) | --- | 32 880 (5) | 0 |
| \( \alpha_0 \) [cm\(^{-1}\)] | 11.98 | 9.72 | 10.74 | 10.21 | 10.75 | 16.50 |
| \( v_0 \) [cm\(^{-1}\)] | 23.06 | 19.3 | 20.18 | 19.5 | 21.16 | 32.45 |
| \( \epsilon \) [meV\(^{-1}\)] | 33.07 | 29.9 | 25.06 | 20.8 | 27.48 | 103.2 |
| \( R_a \) [Å] | 4.049 | 4.30 | 4.34 | 4.60 | 4.24 | 4.09 |
| \( \beta_1 \) | 16.8896−8.45566−R+1.2092−R\(^2\) \( 0.15 \) | 4.40 | 7.20 (0.15) | 7.10 | 5.20 (0.15) | 3.79 (0.15) |
| \( \beta_2 \) | 6.29 (0.15) | 6.50 | 5.95 (0.40) | 7.30 | 7.10 (0.40) | 6.03 (0.15) |
| \( \chi_1 \) | 1.091 (0.02) | 1.1066 | 1.100 (0.20) | 1.0950 | 1.095 (0.20) | 1.010 (0.02) |
| \( \chi_2 \) | 1.753 (0.04) | 1.800 | 1.588 (0.20) | 1.635 | 1.635 (0.20) | 1.435 (0.04) |
| \( C_6 \) [eV Å\(^6\)] | 185.5 (28) | 214.9 | 198.4 (30) | 214.9 | 192.0 (29) | --- |
| \( C_8 \) [eV Å\(^8\)] | 1982 (600) | 1499 | 2148 (600) | 1499 | 2065 (600) | --- |
| \( B_4 \) [eV Å\(^4\)] | --- | --- | --- | --- | 28.98 (4.3) | --- |
| \( B_6 \) [eV Å\(^6\)] | --- | --- | --- | --- | 365.4 (110) | --- |

\(^a\) Scattering data from Ref. 36.

\(^b\) Possible systematic \( \epsilon \) shift for all ZEKE potentials of +3 meV per unit if the \( 1/2 \) state level numbering is off (see Sec. IV A).

\(^c\) Possible systematic \( R_m \) shift of about \( \pm 0.3 \) Å for all ZEKE potentials, because experiment is only sensitive to relative differences in \( R_m \).

\(^d\) \( R \) dependent \( \beta_1 \) imperative to obtain the best MMSV fit to the Morse–RKR repulsive wall of the potential from Ref. 38.
long range part of the potential, \( B_4, B_6, C_6, \) and \( C_8 \) were kept fixed at the calculated values during the fitting procedure.

Since we cannot resolve any rotational structure due to our experimental ZEKE resolution of \( \approx 1 \text{ cm}^{-1} \), we are not able to independently extract information on the equilibrium bond length of any of the potentials determined in this study. A similar problem holds for the well depth \( \epsilon \), because we are only sensitive to the differences between two electronic states. We must therefore refer to other experiments to determine the absolute position and well depth of one of our potential curves. The bond lengths and well depths of the remaining potentials can then be determined with high precision.

Lee and co-workers\(^{36}\) extracted complete interaction potentials for the \( X1/2 \) and \( 13/2 \) states of neutral XeI through elastic differential cross section measurements at two collision energies. These represent the only measurements so far that contain information on the absolute Xe–I bond length. Since scattering on the \( X \) and \( I \) state potentials contributes to the differential cross section, the two potentials have to be extracted from a (not necessarily unique) inversion procedure. Their quoted error is about \( \pm 10\% \) for both \( \epsilon \) and \( R_m \).

More recently, the \( X \rightarrow B \) transition of the \(^{130}\text{Xe}^{127}\text{I}\) isotopomer was studied in emission by Radzykewycz and Tellinghuisen (in the following abbreviated as “R&T”),\(^{38}\) with superior resolution than their earlier studies.\(^{32}\) They observed transitions involving seventeen \( X \) state vibrational levels, tentatively assigned as \( v' = 0–16 \), with some uncertainty in the absolute numbering. With their “minimal” numbering they obtained a well depth of \( 267 \text{ cm}^{-1} \), which is already outside the quoted 10% error margin of the scattering result (\( 241 \text{ cm}^{-1} \)). The value from the emission studies can only increase (e.g., to 292 cm\(^{-1}\) or 21% difference, if the numbering is off by one unit). Based on their assumed functional form for the \( B \) state, they obtain a value of \( R_m = 4.049 \text{ Å} \) for the \( X \) state, which is 0.25 Å less than the scattering potential but still within the 10% error margin.

We use the R&T \( X \) state potential as a starting point for the analysis of our ZEKE spectra. The turning points from their study are fit using the MMSV potential form of Eq. (1), with only one slight modification: the low energy part of the repulsive wall from the Morse–RKR potential is not particularly well described by a simple Morse branch with a single constant parameter \( \beta_1 \). We have therefore chosen a polynomial of the form \( \beta_1 = \beta_0 + B_1 \cdot R + B_2 \cdot R^2 \) for the Morse parameter, where \( B_0, B_1, \) and \( B_2 \) are optimized to give the best fit to the left branch of their curve up to \( v' = 11 \).

The resulting fit employing a Levenberg–Marquardt least-squares fitting algorithm\(^{54}\) is excellent. For the levels \( v = 0–11 \) the \( R \) values of the classical turning points of the R&T Morse–RKR potential are reproduced within 0.03% and the average deviation of our eigenvalues from theirs is only 0.09%. This is more than sufficient for our purposes here. All \( X \) state MMSV potential parameters can be found in Table V.

### B. Fitting procedure

The vibrational eigenvalues and wave functions for the anion and neutral potentials involving a distinct set of parameters are calculated using a discrete variable representation (DVR) procedure\(^{55}\) based on a basis set of Morse potential eigenfunctions.\(^{56}\) Then, Franck-Condon factors are calculated, assuming a Boltzmann distribution for the anion vibrational population, and these are used to produce a simulated vibrational stick spectrum. Finally, a rotational simulation is performed to fit the observed asymmetric peak shapes.\(^{17}\) In this procedure, a set of rotational lines are calculated for each vibrational band, and these are convoluted with the ZEKE instrumental line shape.\(^{15}\) For further details of the rotational fitting analysis the reader is referred to our previous work.\(^{17}\)

Because of the accuracy of the R&T \( X \) state potential, its parameters are kept constant at the values obtained from our best fit as explained before. To determine \( \epsilon \) for the anion and the remaining electronic states we use the relationships implied by Fig. 1, namely:

\[
\epsilon_m = \nu_0(X1/2) + \epsilon_0^m + \epsilon_X - \omega_X^0 - \text{EA},
\]

\[
\epsilon_I = \epsilon_X - \Delta_{X,I} - \omega_X^0 + \omega_I^0,
\]

\[
\epsilon_{II} = \epsilon_X + \omega_{v=0} - \Delta_{X,II} - \omega_X^0 + \omega_{II}^0
\]

where \( \nu_0(X1/2) \) is the origin of the \( X1/2 \) state, \( \epsilon_0^m, \omega_X^0, \epsilon_X \) etc. represent zero point energies, \( \text{EA} \) is the electron affinity of the iodine atom, \( \Delta_{X,I} \) is the spin-orbit constant in atomic iodine, \( \Delta_{X,II} \) is the \( X1/2-13/2 \) state splitting (between the \( v = 0 \) levels), and \( \Delta_{X,II} \) is the \( X1/2-II1/2 \) state splitting.

Once all well depths are fixed, the potential parameters \( R_m, \beta_1, \beta_2, x_1, \) and \( x_2 \) of the anion, \( I \) and \( II \) state potentials, the ZEKE linewidth, and the vibrational and rotational temperature are iteratively adjusted by trial-and-error to produce the best agreement between the experimental and simulated ZEKE spectra. The anion potential is constructed first, to fit the \( X1/2 \)−anion band. Once this is fixed, the potentials for the \( I \) and \( II \) states are determined by their respective bands. Thus, even though the \( II1/2 \)−anion band is relatively unstructured, we obtain a reasonably precise potential for the \( II \) state because the anion potential has been independently determined.

One additional boundary condition is introduced during this procedure. As pointed out by Haberland\(^{28}\) and Aquilanti,\(^{57,58}\) the three neutral potentials are not independent from each other, and if one assumes that the iodine spin-orbit splitting \( \Delta_{vo} \) does not vary with the internuclear separation \( R \) (or, alternatively, if this dependence was known, which is usually not the case) and given that two of the three neutral potential functions are known, the third potential function can be calculated analytically. The present fits were therefore subjected to the additional restriction that the three potentials must yield an (almost) constant \( \Delta_{vo}(R) \) when applying the formulas of Haberland and Aquilanti.

This restriction increased the difficulty of finding an optimized fit even further. The iodine spin-orbit splitting \( \Delta_{vo}(R) \) for our best set of potential parameters obtained in this way varies by less than 0.2% for \( R > 4.0 \text{ Å} \). However, at shorter range it is necessary to allow a somewhat larger variation...
which was still less than 3% for $R > 3.7$ Å. The deviation at short range corresponds to a slightly smaller $\Delta_{so}$ than for atomic iodine.\textsuperscript{44} Such a reduction is not unexpected and was also observed for iodine in Xe matrices.\textsuperscript{59} Finally we note that if one uses two of the neutral potentials to determine the third, i.e., allowing no variation in $\Delta_{so}(R)$, then the repulsive wall of the generated potential deviates significantly from the “best fit” potential. This also yields a worse fit of the corresponding ZEKE spectrum.

C. Best fit and sensitivity of its parameters

The best fit potentials are shown in Fig. 4. Note that for a better representation of the well region of the neutral potential curves (preferentially sampled in our ZEKE experiment), the energy scale in the plot for the $X$, $I$, and $II$ states (40 meV) is different from that of the anion potential (120 meV). The anion potential is about a factor of three deeper, as the numbers on the energy axis indicate. Also, for all potential curves the vibrational levels contributing to visible transitions in the spectra of Figs. 2 and 3 have been indicated by short dashes on the side of the repulsive walls (see also Tables I–III) and partially numbered.

The best fit parameters of the potentials can be found in Table V, and the corresponding spectral simulations have been included in Figs. 2 and 3. While the assignment of features resulting from this fit has already been discussed in Sec. III, we want to assess in more detail how well the parameters in our potentials are defined.

The possible choice of parameters is highly restricted due to the rich line structure (especially of the $X$ and $I$ states), the interdependence of all potential curves (linked by the common anion electronic state), the imposed energetic restrictions [Eqs. (7)–(9)], and the assumption of an approximately $R$ independent iodine spin-orbit splitting. However, one might still argue that the considerable number of adjustable parameters introduces non-negligible uncertainties.

In Fig. 5 we show how the spectral simulation for the $X_{1/2}$ state depends on changes of individual anion potential parameters relative to the optimized set. The six vertical dotted lines mark the position of the 0-0 to 3-3 peaks of the $\Delta v = 0$ sequence band as well as the 4-6 and 5-7 peaks of the $\Delta v = -2$ sequence band in the experimental and best fit spectrum, and aid in showing shifts in the simulations resulting from varying single parameters. Note that the part of each curve left of the gap is scaled up by a factor of five. Details see text.
visibly. If one increases the Morse parameter \( b_1 \) of the anion repulsive wall to 4.17 (+0.38, 10%), the spacing of the same sequence band increases dramatically. This is understandable, because increasing \( b_1 \) increases the steepness of the anion repulsive wall [Eq. (1)] and therefore the anion level spacing (vibrational frequency). The next simulation results from a reduction in \( b_1 \) to 5.43 (-0.60, -10%), thereby decreasing the steepness of the anion Morse branch to the right of the minimum. In this case the anion level spacing is reduced, resulting in a much narrower \( \Delta v = 0 \) sequence band.

Increasing \( x_1 \) to 1.11 (+0.10, +10%) shifts the left boundary of the switching region between the second Morse function and the long range multipole interaction to larger \( R \), i.e., essentially extends the Morse region of the anion potential on the right of the minimum. This results in a steepening of the potential, and therefore an increase of the anion level spacing and the \( \Delta v = 0 \) sequence band spacing. Finally, we investigate the effect of increasing \( x_2 \) (which determines the right boundary of the switching region) to 1.58 (+0.15, +10%). This is expected to have an effect only on the medium range part of the anion potential. Nevertheless, deviations from the experimentally observed level spacing are found already for the 2-2 peak, and are even more apparent for the \( \Delta v = -2 \) sequence band (4-6, 5-7, i.e., the high \( v' - v'' \) region). All of these examples show how restricted the choice for each anion parameter is, and the high sensitivity of the simulation with respect to the \( x_2 \) variation clearly demonstrates in what detail the population of higher anion vibrational levels allows a characterization of the anion potential even at values of \( R \) considerably larger than \( R_m \).

Similar analyses of the parameter sensitivity have been carried out for the potentials of the \( I \) and \( II \) states. The potential diagram in Fig. 4 clearly shows that the equilibrium bond lengths of both neutral states are considerably larger than that of the anion (see also Table V). Photodetachment from the anion (mainly the \( v'' = 0 \) level) therefore predominantly samples the repulsive wall of these states. Consequently, it is found that the key features visible in the spectra, in these cases the length and spacing of the neutral progressions in the \( I \) and \( II \) state spectra (Figs. 2 and 3 as well as Tables II and III), are particularly sensitive to the steepness of the neutral repulsive wall (\( b_1 \)) and to the relative position of the potential curves (\( R_m \)). However, the spectral simulation is less sensitive with respect to the parameters \( b_2, x_1 \), and \( x_2 \) which determine the shape of the potentials at increasingly larger \( R \).

For sake of clarity, the foregoing discussion has focused on the variation of only a single parameter relative to the best fit. We have also carried out extensive multiparameter variations to be sure that we fully explore the whole parameter space in the search for the global optimum. We have found that the narrow boundaries obtained in the single parameter variations do not change very much, i.e., counteracting deviations caused by detuning of a single parameter through changing a second or even third parameter works only for a very limited range of values. The estimated uncertainties from the latter analysis have been included in Table V.

From the location of the turning points corresponding to the highest energy levels contributing to transitions in our spectra we estimate that our XeI anion, \( X, I, \) and \( II \) state potentials are very well defined over the intervals \( R = 3.6-4.8 \, \text{Å}, 3.5-5.4 \, \text{Å}, 4.0-5.6 \, \text{Å}, \) and \( 3.8-5.0 \, \text{Å}, \) respectively. This corresponds to 34%, 76%, 63%, 48% of the total well depth of these potentials (Fig. 4). Because the parameters \( b_4 \) and \( b_6 \) (\( C_6 \) and \( C_8 \)) characterize the anion (neutral) long range interactions are well-established from either experimental or \( \text{ab initio} \) data (Sec. IV A), and should be reliable within the range of \( \pm 15\% \) to \( \pm 30\% \), the behavior of our model potentials at large \( R \) should also be realistic. However, the XeI `ZEKE spectra are insensitive to the high energy region of the repulsive wall which is therefore less well characterized.

Considering the small error margins from our analysis, the largest uncertainty in our potentials is probably systematic in nature and linked to the uncertainties of \( R_m \) and \( \epsilon \) in our reference potential, the \( X \) state potential of R&T. For example, each increase in the X state vibrational level numbering\(^{38} \) by one quantum will increase \( \epsilon \) by about 24 cm\(^{-1} \). The same increase will apply to the well depths of all the other states [Eqs. (7)–(9)], presumably accompanied by minor adjustments of the other potential parameters. In any case our well depths are certainly lower bounds to the “real” values.

V. DISCUSSION

In this section we discuss our results for the XeI neutral and anion potentials and compare them to previously published results. Moreover, the surprisingly low \( I \) state intensity (compared to the \( X \) state) will be considered in more detail.

A. ZEKE potentials and results from other studies

The parameters of the X and \( I \) state potentials obtained from Lee’s scattering study\(^{36} \) have already been included in Table V for comparison. Our \( X \) state potential is essentially identical with that determined by R&T, differing only in the type of potential form employed (and the very long range part, which will not be further considered here). In contrast, the \( X \) state potential from the scattering experiment has a shallower well (difference >10%), and \( R_m \) is about 0.25 Å larger. Nonetheless, this can still be termed complete agreement considering the uncertainties in \( R_m \) of Lee’s study and our study (both roughly ±10%). The Morse parameter \( \beta_1 \) of 6.29 is close to Lee’s value of 6.50. However, \( \beta_1 \) (5.93 at the minimum and 4.70 at 3.50 Å, according to our fit) is larger than in Lee’s potential (4.40), so our potential rises more rapidly for \( R < R_m \).

Comparing our \( I \) state potential to that deduced from the scattering experiment, we see that our well depth is larger by about 4.3 meV. This is expected, however, because our potential is referenced to the deeper R&T \( X \) state potential. A more meaningful comparison would therefore involve the well depth difference between the \( X \) and \( I \) states; the difference between Lee’s well depths is only about 1 meV larger than ours. When comparing the differences in the equilibrium distance \( R_m \) of the same states, the ZEKE results yield 0.29 Å, in nearly perfect agreement with the scattering measurements (0.30 Å). The \( \beta_1 \) Morse parameter of our \( I \) state
TABLE VI. Characteristic quantities of the ZEKE XeI anion potential compared to literature potentials. Uncertainties (±) given in parentheses as reported in each work cited, if available.

<table>
<thead>
<tr>
<th>Source</th>
<th>$\epsilon$ [meV]</th>
<th>$R_m$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>present work$^a$</td>
<td>103.2</td>
<td>4.09</td>
</tr>
<tr>
<td>scaled electron gas$^b$</td>
<td>144</td>
<td>3.85</td>
</tr>
<tr>
<td>CCSD(T)$^c$</td>
<td>100 (43)</td>
<td>4.34</td>
</tr>
<tr>
<td>polarizability correlations$^d$</td>
<td>133</td>
<td>4.27</td>
</tr>
<tr>
<td>modified polarizability correlations$^e$</td>
<td>123</td>
<td>4.17</td>
</tr>
<tr>
<td>universal interaction potentials$^f$</td>
<td>261 (≥78)</td>
<td>3.41 (≥1.0)</td>
</tr>
<tr>
<td>rare gas halide surface potentials$^g$</td>
<td>75</td>
<td>4.20</td>
</tr>
<tr>
<td>unified perturbative approach$^h$</td>
<td>98</td>
<td>4.18</td>
</tr>
</tbody>
</table>

$^a$Possible absolute shift of +3 meV per unit in $\epsilon$, if $X$ state numbering changes as explained in the text, and of about ±0.3 Å in $R_m$.

$^b$Reference 22.

$^c$Reference 21.

$^d$Reference 23.

$^e$As (d), but using modified constants from Ref. 16.

$^f$Reference 24.

$^g$Reference 25.

$^h$Reference 26.

Potential agrees very well with the scattering result. Our value for $\beta_2$, however, is considerably smaller, indicating a less steeply rising potential for $R > R_m$. Although our $\beta_2$ value is less precise than for $\beta_1$, because we are more sensitive to the region of the potential for which $R < R_m$, Lee’s value for $\beta_2$ lies well outside our error bars; simulations using the higher value result in a significantly poorer fit to experiment.

The existing data for the $II$ state from other sources is extremely limited. The only information available comes from XeI bound-free emission spectra by Tamagake et al., which gave estimates of the $II$ state well depth and location ($\epsilon = 10.4$ meV and $R_m = 4.80$ Å, respectively). The potentials in their study are based on theoretical calculations by Hay and Dunning, including an ad hoc dispersion correction to improve the agreement between their experiments and spectral simulations. Considering their additional results for the $X$ state (17.4 meV, 4.34 Å) and $I$ state (6.8 meV, 5.12 Å) it appears that their potentials systematically underestimate the well depth and overestimate the equilibrium distance for these states. Although our $II/1/2$—anion ZEKE spectrum suffers from reduced resolution, our experiment yields the first reliable potential for the $II$ state, particularly for $R < R_m$.

We obtain more new information about the XeI anion potential, $R_m$ is slightly shortened upon photodetachment to the $X$ state (−0.04 Å), even though the anion binding energy is considerably larger (Table V). Obviously, the larger radius of the iodide anion compensates for the stronger attraction of the charge-induced multipole terms not present in the neutral.

For comparison with previous studies of this system, we have summarized available $R_m$ and $\epsilon$ data for the XeI anion in Table VI. There are no other experimental results to be found for the XeI anion, not even ion mobility data, which is available for most of the other rare gas halide pairs. The scaled electron gas theory of Waldman and Gordon yields a much higher well depth but a much shorter equilibrium bond length than we obtain.

In a very recent theoretical study by Schröder et al., potential well depths and equilibrium bond lengths were determined at the coupled cluster level of theory for the whole series of xenon halide anions (and the respective neutral X states). The XeI well depth is very close to ours, however, the cited uncertainty is substantial. For the equilibrium bond length the calculations yielded a value which exceeds ours by 0.25 Å, and unfortunately no error limits were given.

The results of Cappelletti et al. in Table VI were obtained by particularly simple formulas based on empirically determined polarizability correlations. Their values for $R_m$ and $\epsilon$ both significantly exceed our values. In a very recent publication we used our ZEKE data on the ArI, KrI, ArBr, KrBr, XeBr, and KrCl anion potentials to recalibrate the numerical coefficients in their formulas. When using these values the resulting well depth and equilibrium bond lengths come closer to our experimental values, but still show deviations in the same direction as observed with the original constants.

Several semi-empirical methods have been proposed in the literature. The best agreement in the case of XeI is found for Patil’s “unified perturbative approach,” whereas the “surface potential” of Wilson et al. yields a significantly lower well depth. Both $\epsilon$ and $R_m$ predicted from the “universal interaction potentials” of Koutselos, Mason, and Viehland deviate considerably from our values, particularly the well depth. Note also that for KrBr, XeBr, and KrCl the difference between our most recent ZEKE results and their values is less extreme, but nevertheless substantial.

In Table VII we compare the well depths and equilibrium bond lengths for the rare gas–iodine anions and corresponding neutral states studied in our group by anion ZEKE spectroscopy. For each individual rare gas iodine pair we observe the trend $R_m(X) < R_m(anion) < R_m(II) < R_m(I)$, and $\epsilon(I) < \epsilon(II) < \epsilon(X) < \epsilon(anion)$. The $X$ state acquires predominantly $\Sigma$ character at short range, which corresponds to the situation where the iodine atom approaches the rare gas with the unpaired electron on the internuclear axis. In contrast, the $I$ state is a pure $\Pi$ state (at all distances) and the $II$ state has predominantly $\Pi$ character; i.e., in these cases the unpaired electron is located perpendicular to the internuclear axis. The greater stabilization of the $\Sigma$ state relative to the $\Pi$
state in rare gas halogen systems has been attributed by Aquilanti and co-workers\textsuperscript{61} to charge transfer, resulting from configuration interaction between the lower lying neutral and higher lying ionic (Rg\textsuperscript{+}X\textsuperscript{−}) molecular states of the same symmetry. On the other hand, a recent \textit{ab initio} study by Burcl \textit{et al.}\textsuperscript{62} on the HeCl, NeCl, and ArCl potentials indicates that minimization of exchange repulsion is the primary reason for a more strongly bound Σ state. It is likely that both effects are important in XeI, due to the highly polarizable Xe atom.

Coming back to Table VII we find that in all cases the anions have by far the largest well depths, which is not surprising because of the much stronger attraction due to the leading charge-induced dipole term and the additional charge-induced quadrupole contribution [Eq. (5)], in contrast to the neutrals. The anion equilibrium bond length, however, is in each case slightly larger than that of the neutral X state, for the same reasons given above. We note that the decrease in $R_m$ associated with the $X1/2\rightarrow$ anion transition becomes smaller for the heavier rare gas atoms, whereas the increase in $R_m$ for the $I3/2\rightarrow$ anion transition becomes larger.

Comparing the same states for different rare gas iodine clusters, we see that in each case $e(ArI)<e(KrI)<e(XeI)$, which is due to the increasing rare gas polarizability from Ar to Xe. However, the bond lengths for KrI and XeI are very similar for all cases. This counterintuitive result is somewhat misleading because it relies on absolute $R_m$ values, for which the uncertainties are large. In general, the lack of precise (\:<1\%) absolute $R_m$ values represents the most significant defect in the rare gas halogen and halide potentials; the determination of these will require spectroscopy with rotational resolution.

B. Intensity of the $I3/2$ state in the ZEKE spectra

An interesting feature of our XeI− ZEKE spectra which has been only briefly mentioned so far is the surprisingly low intensity observed for the $I$ state relative to the $X$ state. To clarify this point, we show in Fig. 6 a comparison of the combined $X$ and $I$ state ZEKE spectra for the complete series of rare gas iodide anions (ArI\textsuperscript{−}, KrI\textsuperscript{−}, and XeI\textsuperscript{−}) studied by us so far.\textsuperscript{17} While in the case of ArI the 0-0 transition of the $I$ state is nearly as large as that of the $X$ state, it is already significantly smaller in the case of KrI and almost disappears in XeI.

Although the $I3/2\rightarrow$ anion band becomes more extended as the rare gas mass increases, Franck-Condon factors alone are insufficient to explain the trend in intensities. The vibrational stick spectrum representing the transitions to the $I$ state had to be rescaled by factors of 0.64, 0.46,\textsuperscript{17} and 0.10, respectively, relative to the $X$ state before convolution with the ZEKE and rotational line shape (Sec. IV B) in order to match the experimentally observed intensity pattern. There are at least two possible explanations. The observed effect may reflect either variations in the transition moments to the two neutral states or differences in the s-wave partial detachment cross sections; due to the Wigner threshold law,\textsuperscript{63} only those photoelectrons ejected with orbital angular momentum $l=0$ contribute to the ZEKE signal.\textsuperscript{12}

To study this effect further, we have measured polarization-dependent photoelectron spectra (PES) of XeI\textsuperscript{−} at a photodetachment wavelength of 355 nm, because electronic band intensities in a photoelectron spectrum depend primarily on transition moments. The results are shown in Fig. 7, along with the ZEKE spectrum. The energy scale for the PES represents the electron binding energy. PES data at angles of $θ=0^\circ$ (open circles) and $90^\circ$ (filled squares) between the plane of laser polarization and the direction of electron detection were recorded. Although the resolution of the photoelectron spectrum is clearly poorer than that of the ZEKE spectrum, we observe a large broad main peak where the $X$ state transitions in the ZEKE spectrum are located, and a smaller but pronounced shoulder at higher energy, where the $I$ state transitions in the ZEKE spectrum are found. The relative intensities of the PES features show only a small dependence upon laser polarization angle.

To compare the ZEKE results to the PES data, the ZEKE results have to be converted in an appropriate fashion. Because of the good quality of the spectral fit in Fig. 2 we have directly taken the vibrational stick spectrum forming the basis of this simulation (including the aforementioned scale factor of 0.10) and convoluted it with a Gaussian of 8 meV FWHM, which should accurately represent the resolution of the anion photoelectron spectrometer at this electron kinetic energy of roughly 0.4 eV. The resulting “ZEKE-based PES” is shown as a dotted line in Fig. 7, denoted as “Conv. 1”. The X band is fit quite well, but the I band in this con-
and suggests that the low intensity of the \( I \) state, which has mainly \( \Pi \) character, correlates with that of the \( I \) state, although this is more difficult to quantify because detachment to the \( I \) state generally requires frequency doubling of the dye laser output with an accompanying loss of laser pulse energy. Thus interactions in the anion and neutral which result in more differentiation of the \( \sigma \) and \( \pi \) orbitals from which detachment occurs (i.e., that correlate to the \( p \)-orbitals on the isolated halide) lead to differences in the \( s \)-wave partial detachment cross sections near threshold for the two types of orbitals.

**VI. CONCLUSIONS**

In our study of the Xe\(^{−}\) anion by ZEKE and photoelectron spectroscopy we have characterized the anion and neutral potentials involved in the photodetachment of this prototypical diatomic rare gas halide cluster in considerable detail. A simulation of the ZEKE spectra for the \( 1/2, 5/2 \), and \( 11/2 \) states accessible by the photodetachment process has allowed an assignment of essentially all features in the spectra, even those having very low intensity.

We have extracted model potentials for all states involved which define the *relative* positions and shapes of all electronic states in the Franck-Condon region with high accuracy. We have underlined this by an extensive test of the sensitivity of the potential parameters for each state. However, to be able to pinpoint the *absolute* position of all potentials, we need external experimental information on one of the four potential curves as a reference. In this case, we used the \( X \) state potential previously determined by Radzykewycz and Tellinghuisen, obtained from \( X \rightarrow B \) emission studies.\(^{38}\)

The ZEKE data are fully consistent with the \( X \) state potential from the emission study, whereas some differences between the ZEKE \( I \) state potential and the earlier \( I \) state potential from scattering data are observed. We obtain the first accurate potentials of the \( I \) state and the Xe\(^{−}\) anion, although worse experimental resolution in the case of the \( I \) state ZEKE spectrum makes this potential somewhat less reliable than the others. Characteristic quantities like the equilibrium bond length \( R_m \) and well depth \( \epsilon \) for all Xe\(^{−}\) anion and neutral potentials are consistent with trends observed in our previous ZEKE studies of the other rare gas iodides Kr\(^{−}\) and Ar\(^{−}\).\(^{17}\)

Another interesting feature is the very low intensity of the \( I \) state relative to the \( X \) state in the ZEKE spectra for Xe\(^{−}\) and some of the other rare gas halides. The intensity is found to decrease with increasing size of the rare gas and decreasing size of the halide. The photoelectron spectrum taken for Xe\(^{−}\), however, shows a much higher intensity in the \( I \) state region than the ZEKE spectrum, indicating that the low ZEKE intensity is probably due to pronounced differences in the \( s \)-wave partial detachment cross sections to both states. This trend appears to correlate with increasing binding energy in the anion and anisotropy in the neutral.

Very recently we obtained results for larger Xe\(_n\)I\(^{−}\) clusters up to \( n = 14 \). A preliminary analysis of the experimental data suggests that a slight systematic increase in \( R_m \) for all Xe\(^{−}\) potentials might describe the observed trends in the clus-
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