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THE PHOTOELECTRON ANGULAR DISTRIBUTIONS
OF HBr AND HI AT $h\nu = 21.2$ eV

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ABSTRACT

Photoelectron angular distributions for the
$2\Pi_{3/2,1/2}(p\Pi)^{-1}$ and $2\Sigma_{1/2}(p\sigma)^{-1}$ ionic states of HBr and HI have been measured at a photon energy of 21.2 eV. The asymmetry parameters for the highly localized $p\Pi$ orbitals closely follow those of the "lone pair" orbitals of the related CH$_3$X molecules and the outer np atomic orbitals of the corresponding united atoms. Furthermore, the asymmetry parameters for the $2\Pi_{3/2}$ and $2\Pi_{1/2}$ states were found to be equal within experimental uncertainty, despite the large spin-orbit splittings of these heavy molecules. The asymmetry parameters for the $2\Sigma^{+}(p\sigma)^{-1}$ ionic states are significantly smaller than for the $2\Pi(p\Pi)^{-1}$ states, in contrast to recent predictions based on the angular momentum transfer theory.
I. Introduction

The importance of relativistic effects in atomic photoionization processes has been the subject of considerable theoretical and experimental work in recent years. These studies, including measurements of partial cross-sections,\(^1\) angular distributions,\(^2\) and spin-polarization,\(^3\) have yielded important new information about spin-orbit interactions in continuum processes. Overall, the atomic work indicates that spin-orbit effects are usually small and can be treated as a perturbation on the nonrelativistic picture.\(^4\) At certain energies, however, particularly near Cooper minima and autoionization resonances, spin-orbit effects are "amplified," leading to very different cross-sections or angular distributions from those predicted nonrelativistically.\(^4,5\)

In contrast, only a few experiments and virtually no calculations have been performed on the photoionization of molecules containing heavy atoms. Furthermore, most of the photoelectron measurements on relativistic molecules have been primarily concerned with the spin-orbit interactions in the bound states of the neutral\(^6\) or the ionic core.\(^7\) More detailed information, including the effects of spin-orbit interactions in the continuum, could be obtained from angular distribution measurements on these same molecules. To date, only the measurements of Carlson et al.\(^8\) on the methyl halides (CH\(_3\)X, X = F, Cl, Br, I) have addressed the angular distribu-
tions of relativistic molecules. For CH$_3$Br and CH$_3$I only small differences were observed for the asymmetry parameters for the spin-orbit split $^2E_{3/2}$ and $^2E_{1/2}$ ionic states, similar to the results obtained for atomic systems.

To investigate further the effects of spin-orbit coupling on the angular distribution of photoelectrons from relativistic molecules, we have determined the asymmetry parameters for HBr and HI at the He I photon energy, $h\nu = 21.2$ eV. These molecules are prime candidates for such studies, because they have relatively simple valence electronic structures and exhibit large energy separations between the spin-orbit split $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ionic states. In addition, these data permit comparisons to be made with the existing data on HCl$^8$ and the related CH$_3$X molecular series.

II. Experimental

The experiments were performed on the 8° beam line at the Stanford Synchrotron Radiation Laboratory (SSRL). A monochromatic beam of highly (>97%) plane-polarized synchrotron radiation (21.24 eV, 8.7 Å band pass) intersected a gas jet formed by effusive expansion through a microchannel array. Sample densities were $2 \times 10^{-3}$ Torr in the interaction volume, compared with a background pressure of $5 \times 10^{-5}$ Torr, giving negligible electron-molecule scattering. Photoelectrons were detected by two time-of-flight (TOF) analyzers at 0° and 54.7° from the photon polarization vector. The TOF analyzers
utilized the unique time structure of the SPEAR storage ring (300 psec FWHM pulse duration, 780 nsec repetition period). They are orders of magnitude more efficient than conventional single channel deflection-type analyzers, with lower noise. The outputs of the two detectors were simultaneously analyzed with a single time-to-amplitude converter and stored separately in a multichannel analyzer. The $\beta$ values were derived after correcting for the relative counting efficiencies of the two TOF detectors by calibrating the apparatus with the He(ls $\rightarrow$ ep) transition, for which $\beta = 2$.

The HI gas sample was obtained commercially (Matheson) and used without further purification. Although the original intent was to run HI and HBr separately, the HI gas sample contained sufficient HBr impurity that the HBr spectrum could be obtained simultaneously. A small amount of HCl impurity was also observed.

Peak areas were obtained by computer deconvolution of the spectra to gaussian distributions. Since the vibrational structure of the ionic states was not well-resolved, the reported asymmetry parameters are vibrationally averaged values.

### III. Results and Discussion

In ($\omega, \omega$) coupling,\(^9\) which is appropriate for describing the electronic structure of relativistic molecules, the ground state of the heavy HX diatomics can be written as
\[ \psi(1\Sigma^+;0^+) = A(N)|\cdots(s\sigma_{1/2})^2(p\sigma_{1/2})^2(p\pi_{1/2})^2(p\pi_{3/2})^2| \]

where \( A(N) \) is the \( N \)-electron antisymmetrizer and where we have indicated the united atom designations of the outer valence orbitals. Photoionization at \( h\nu = 21.2 \text{ eV} \) leads to the three ionic states—\( ^2\Pi_{3/2}, ^2\Pi_{1/2}, \) and \( ^2\Pi^+ \)—corresponding to ionization from the three outermost valence orbitals.\(^{10} \)

The \( 0^\circ \) and \( 54.7^\circ \) TOF spectra of \( \text{HBr}^+ \) and \( \text{HI}^+ \) are shown in Figure 1, assigned according to the photoelectron studies of Lemka et al.\(^{11} \) The \( ^2\Pi_{3/2,1/2} \) ionization bands consist primarily of strong vertical transitions, as expected from the nonbonding, "lone-pair" character of the \( \text{p}\sigma \) molecular orbital. The strong bonding nature of the \( \text{p}\sigma \) orbitals is confirmed by the broad Franck-Condon envelopes of the \( ^2\Pi^+ \) ionization bands.

Asymmetry parameters, \( \beta \), for the ionic states of these molecules are summarized in Table 1. The \( \text{HCl} \) results of Carlson et al.\(^{12} \) are included for comparison. The error limits of our \( \beta \) values for \( \text{HBr} \) and \( \text{HI} \) are the statistical errors incurred in the computer fits of the areas. The larger errors quoted for the \( \text{HBr} \) \( \beta \) values reflect the more severe overlapping of the \( ^2\Pi_{3/2} \) and \( ^2\Pi_{1/2} \) levels. From this table we note first that the \( \beta \) values for ionization from the \( \text{p}\pi_{3/2} \) and \( \text{p}\pi_{1/2} \) orbitals are equal within experimental uncertainty. This is expected for \( \text{HCl} \) where the spin-orbit interactions are small;
however, for HI this result is somewhat surprising, considering the large spin-orbit splitting (0.66 eV) of the $^2\Pi_{3/2} - ^2\Pi_{1/2}$ ionic states. Second, the $^2\Pi(p\pi)^{-1}$ asymmetry parameters are in every case significantly larger than the corresponding values for the $^2\Sigma^+(p\sigma)^{-1}$ ionic states. Both of these conclusions are qualitatively evident by inspection of Figure 1.

Because the $p\pi$ orbital is highly localized on the halogen, the asymmetry parameters for the $p\pi$ orbitals might be expected to be similar to other halogen-containing molecules that have lone-pair orbitals. In Table 2 we compare the $\beta$ values for the outer lone-pair orbitals for the HX and CH$_3$X series. In the bromine and iodine compounds, the $\beta$ values for these orbitals are essentially identical, although for HCl and CH$_3$Cl the asymmetry parameters are very different. This difference in the chlorine compounds was explained by Carlson et al. as resulting from the expectation that the $p\pi$ orbital in HCl is a "purer" lone-pair than the $e(p\chi)$ orbital in CH$_3$Cl. Based on the present results in the heavier molecules, this explanation can be further generalized. Since the $p\pi$ atomic orbitals of the bromine and iodine atoms are much larger and of lower energy than the atomic orbitals of the carbon and hydrogen atoms, they are not expected to mix strongly in molecule formation. Hence, the $p\pi$ and $e(p\chi)$ lone-pair orbitals retain their np atomic character, as reflected in their very similar $\beta$ values. For the chlorine and especially the fluorine atoms, however, the size and energy of the np atomic orbitals better
match those of the carbon and hydrogen atoms; hence, they can be expected to mix more strongly. Therefore, one might expect larger differences in the $\beta$ values of the lone-pairs of the HX and CH$_3$X molecules for the lighter halogens.

In Table 2 we have also listed the asymmetry parameters for the outermost np shells of the rare gases, which represent the united atom limits of the HX molecules. Except for the HCl value of Carlson et al., the lone-pair asymmetry parameters are smaller by 15-30% than the corresponding atomic values, although they do follow the same trend of increasing magnitude with increasing size. The decrease in $\beta$(np) from atom to molecule can be attributed in part to "$\lambda$-spoiling" resulting from the reduction of symmetry. Since only the projection of the orbital angular momentum on the internuclear axis ($m_\lambda$ or $\lambda$) is well-defined, higher $\ell$ components can mix with the atomic p orbitals in the $\pi(\lambda = m_\lambda = \pm 1)$ molecular orbital. In general, it has been found that for atoms, the higher the $\lambda$ value of the initial orbital is, the lower the $\beta$ value will be. This generalization has been used by Carlson to interpret a wide range of asymmetry parameters for various small molecules, by expanding the molecular orbitals over spherical harmonics about a center of symmetry. Although this generalization is more appropriate in the x-ray limit of photoionization, any admixture of higher $\lambda$-wave components into the $\pi$-orbital can be expected to alter the $\beta$ value away from the atomic value. A recent one-center expansion
calculation on HBr,\textsuperscript{17} in which the molecular orbitals were expanded over basic functions centered on the Br atom, indicated some small 4d, 5d, and 4f character in the outer π molecular orbital, in support of the above arguments. The "anomalously" large $\beta(p_{3/2}^\pi)$ and $\beta(p_{1/2}^\pi)$ values for HCl do not follow the above trends for the other HX and CH$_3$X molecules, including CH$_3$Cl.

From Table 2 we also note that for the heavy HX and CH$_3$X molecules and the heavy rare-gas atoms, the differences between the asymmetry parameters for the spin-orbit components of the $p^\pi$ and np orbitals are very small. At these kinetic energies even Xe, with a $^2$P$_{3/2} - ^2$P$_{1/2}$ energy separation of 1.31 eV and a branching ratio, $^2$P$_{3/2} : ^2$P$_{1/2}$, of 1.6:1 (compared to the nonrelativistic value of 2:1),\textsuperscript{18} has $\beta$ values for the spin-orbit split $^2$P$_{3/2}$ and $^2$P$_{1/2}$ ionic states that differ by only 2%. From recent fully relativistic calculations on Kr and Xe\textsuperscript{4,19} one finds that for photon energies below $\sim$50 eV, the energy dependences of $\beta(np_{3/2})$ and $\beta(np_{1/2})$ are very similar. The small differences between $\beta(np_{3/2})$ and $\beta(np_{1/2})$ has therefore been interpreted as resulting primarily from the displacement of the two curves by their difference in binding energies. This simple argument correctly predicts that $\beta(np_{3/2}) > \beta(np_{1/2})$ at photon energies below $\sim$33 eV and $\beta(np_{3/2}) < \beta(np_{1/2})$ at higher energies. Similar behavior is expected for the heavy molecules and from Table 2 we see that $\beta(\omega = \frac{3}{2}) > \beta(\omega = \frac{1}{2})$ for the lone-pair orbitals for those experiments where the error
limits are reasonably small. Hence, the small differences in
the asymmetry parameters for ionization of the \( p_{3/2}^\pi \) and \( p_{1/2}^\pi \) orbitals are most likely a result of kinetic energy effects and not of variations in their continuum matrix elements or phase shifts. We note, however, that at the kinetic energies at which the comparisons of Table 2 are made, the atomic \( np_{3/2} \) and \( np_{1/2} \) asymmetry parameters are converging.\(^{19}\) At higher or lower kinetic energies the difference between the \( \beta(np_{3/2}) \) and \( \beta(np_{1/2}) \) parameters are larger; this is particularly true at higher kinetic energies where differences between the radial functions of the more penetrating \( np_{1/2} \) and more diffuse \( np_{3/2} \) orbitals become important.\(^{4}\) This suggests that larger deviations between the asymmetry parameters for the \( p_{3/2}^\pi \) and \( p_{1/2}^\pi \) orbitals of the HX molecules may also be observed at other photon energies. Higher-energy experiments would be highly desirable, because they could yield important information concerning both the bound and continuum wavefunctions.

As noted above, \( \beta \) values for the \( ^2\Sigma^+(3\sigma)\) ionic states were consistently lower than those found for the \( ^2\Pi(p\pi)\) levels. This result is in disagreement with the qualitative predictions of Cheng\(^{20}\) in which the asymmetry parameters for \( \Sigma^+ \rightarrow \Sigma^+ \) ionization transitions should always be greater than that for \( \Sigma^+ \rightarrow \Pi \) transitions. This conclusion was based on the application of the angular momentum transfer theory (AMTT)\(^{21}\) to molecular photoionization. By conservation of parity and total angular momentum, \( \Sigma^+ \rightarrow \Sigma^+ \) transitions should include
only parity favored contributions while $\Sigma^\pm \rightarrow \Pi$ transitions include both parity favored and unfavored processes. Because $\beta = -1$ for a parity unfavored process, these contributions will tend to lower the overall asymmetry parameters for $\Sigma^\pm \rightarrow \Pi$ transitions. This analysis is consistent with much of the existing data on small molecules, e.g., $N_2$, CO, and $O_2$. However, it ignores the details of the dynamical factors; i.e., the dipole matrix elements and phase shifts, which determine the relative weights of the parity favored-to-unfavored contributions to the overall measured value of $\beta$. The deviation from the Cheng prediction is most likely a result of the fact that $pm$ orbitals are essentially atomic and hence have large $\beta$ values consistent with their atomic counterparts. The asymmetry parameters for the $2\Sigma^+(p\sigma)^{-1}$ ionic states of the $HX^+$ ions are more like those obtained for ionization of strongly bonding $\sigma$ type orbitals of other small molecules with $\beta_{\text{avg}}(\sigma) \sim 1.12,10$

ACKNOWLEDGMENTS

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References


10. The \((\sigma_1/2)\) molecular orbital is expected to be mainly ns atomic character of the halogen atom. The bromine 4s and iodine 5s atomic ionization potentials are 23.9 eV and 20.8 eV, respectively; these lines are too high in energy to be observed with 21.2 eV photons in our apparatus.


13. The designation of the "lone-pair" orbitals of the \(\text{CH}_3\text{X}\) molecules is given by the irreducible molecular symmetry designation \(e\) (in \(C_{3v}\) symmetry) and its major atomic orbital constituent, the outer np orbitals of the halogen atoms.


Table 1. Experimental asymmetry parameters for photoionization \((h\nu = 21.2 \text{ eV})\) from the \(p_{3/2}^\pi\), \(p_{1/2}^\pi\), and \(p_{1/2}^\sigma\) orbitals of the \(HX (X = \text{Cl, Br, I})\) molecules.

<table>
<thead>
<tr>
<th>X</th>
<th>(p_{3/2}^\pi)</th>
<th>(p_{1/2}^\pi)</th>
<th>(p_{1/2}^\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1.40(5)</td>
<td>1.40(5)</td>
<td>.75(10)</td>
</tr>
<tr>
<td>Br</td>
<td>1.2(2)</td>
<td>1.1(2)</td>
<td>.9(1)</td>
</tr>
<tr>
<td>I</td>
<td>1.47(9)</td>
<td>1.47(9)</td>
<td>.89(8)</td>
</tr>
</tbody>
</table>

\(a\) From Ref. 12.

\(b\) This work.
Table 2. Comparison of $\beta$ values for the outer "lone-pair" orbitals of the HX and CH$_3$X molecules and the outermost np orbitals of the corresponding rare-gas atoms, Å.

<table>
<thead>
<tr>
<th>X, A</th>
<th>HX</th>
<th>CH$_3$X</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_{\pi \frac{3}{2}}, p_{\pi \frac{1}{2}}$</td>
<td>$e(p_X)<em>{\frac{3}{2}}, e(p_X)</em>{\frac{1}{2}}$</td>
<td>np$<em>{\frac{3}{2}},$ np$</em>{\frac{1}{2}}$</td>
</tr>
<tr>
<td>Cl, Ar</td>
<td>1.40$^a$</td>
<td>.9</td>
<td>1.26</td>
</tr>
<tr>
<td>Br, Kr</td>
<td>1.2, 1.1$^b$</td>
<td>1.2, 1.15</td>
<td>1.43, 1.40</td>
</tr>
<tr>
<td>I, Xe</td>
<td>1.47, 1.47$^b$</td>
<td>1.5, 1.45</td>
<td>1.81, 1.77</td>
</tr>
</tbody>
</table>

$^a$ From Ref. 12.

$^b$ This work.

$^c$ From Ref. 8.

$^d$ The $\beta(np_{\frac{3}{2}})$ and $\beta(np_{\frac{1}{2}})$ are for the same kinetic energies as the $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ states of the HX$^+$ ions, respectively. The $\beta(npj)$ data were obtained from theoretical relativistic many-body calculations which are in excellent agreement with the few experimental points available for comparison (see Ref. 19).
Figure Caption

Figure 1. The 0° and 54.7° TOF spectra of HBr+ and HI+ taken at $h\nu = 21.24$ eV. The difference in resolution between the 0° ($\Delta E/E = 2.3\%$) and 54.7° ($\Delta E/E = 3.0\%$) TOF analyzers results from the 54.7° analyzer sampling a larger portion of the interaction volume. See M.G. White, R.A. Rosenberg, G. Gabor, G. Thornton, E.D. Poliakoff, S.H. Southworth, and D.A. Shirley, Rev. Sci. Instrum. 50, 53 (1979).
Figure 1

\[ HX^+ \]
\[ h\nu = 21.24 \text{ eV} \]
\[ \Theta = 54.7^\circ \]

- \( H^+_{1/2} \)
- \( H^+_{3/2} \)
- \( HBr^+_{1/2} \)
- \( HBr^+_{3/2} \)
- \( HCl^+ \)

Counts \( \times 10^2 \)

Binding energy (eV)
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