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The Helium-(I) Photoelectron Spectra of some Halogens and Diatomic Interhalogens

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Medium resolution helium(I) photoelectron spectra of the halogen molecules Cl_2, Br_2 and I_2, and of the diatomic interhalogens, ICl and IBr, are reported. Vibrational fine structure is discernible in the first photoionisation bands of Cl_2, Br_2 and ICl, while multiplet splittings are evident in the photoelectron spectra of Br_2, I_2, ICl and IBr. The details of the spectra are consistent with established qualitative concepts of molecular orbital theory.

Introduction

We describe in this communication the medium resolution photoelectron (PE) spectra excited by helium(I) 21.21 eV radiation in the halogen molecules Cl_2, Br_2 and I_2, and also in the simple binary interhalogens, ICl and IBr. The halogens themselves (including fluorine) have been previously studied by Frost *et al.*,[1] who have also measured the PE spectra of the hydrogen halides. However, Frost *et al* employed a retarding field grid spectrometer which produces low resolution integrated PE spectra. The spectra reported here are of the differential type with substantially improved resolution.

Experimental Section

The PE spectra were recorded on a spectrometer recently constructed in this Laboratory.[2] The design of this instrument is similar in principle to that described by Branton *et al.*,[3] though it employs a simplified retarding system and a 127° sector electrostatic analyser. The resolution (full width at half maximum height of the argon $^2P_{3/2}$ line) was about 50 meV when the spectra were measured. The spectra were calibrated in the usual way[4] using the inert gases Ar, Kr and Xe.

Commercial samples of the species investigated were purified immediately before use by sublimation or distillation *in vacuo* (10^{-3} torr).

All the measurements were made at ordinary temperatures (*ca.* 25°C). The sample pressures employed were about 0.02 torr, though the corrosive action of the materials on the pressure monitoring equipment made reliable measurement difficult. The main chamber pressure was between 6×10^{-5} and 10^{-4} torr.

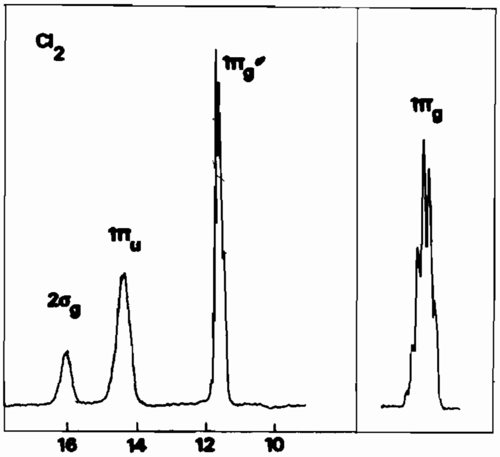

Figure 1. The He^I photoelectron spectrum of molecular chlorine.

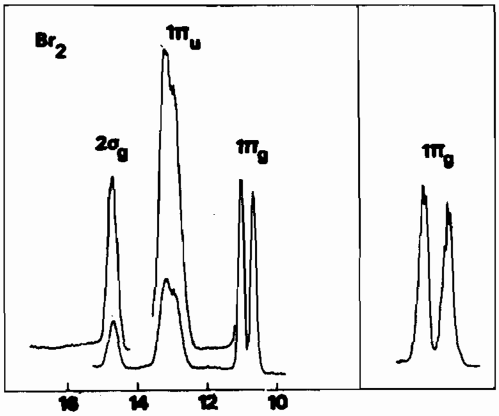

Figure 2. The He^I photoelectron spectrum of molecular bromine.

The spectra reproduced in Figures 1-5 are tracings of the original spectra, but spurious structures due to small amounts of unavoidable and obvious contaminants have been removed. (In particular, structure clearly attributable to Br_2 and I_2 is inevitably present in the IBr photoelectron spectrum since IBr

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[1] D. C. Frost, C. A. McDowell, and D. A. Vroom, *J. Chem. Phys.*, 46, 4255 (1967).
[2] S. Evans, A. F. Orchard, and D. W. Turner, to be described.
[3] G. R. Branton, D. C. Frost, T. Makita, C. A. McDowell, and I. A. Stenhouse, *J. Chem. Phys.*, 52, 802 (1970).
[4] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (B), 22, 1968.

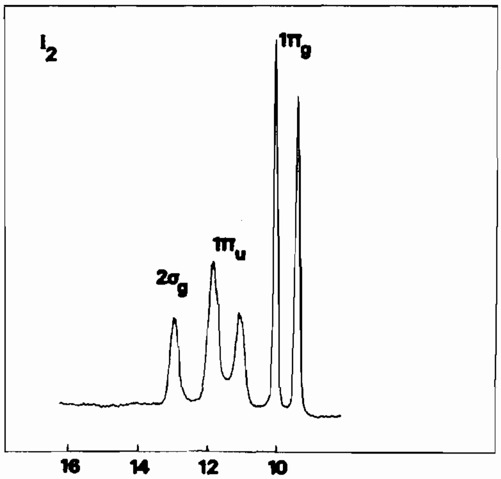

Figure 3. The He^I photoelectron spectrum of molecular iodine.

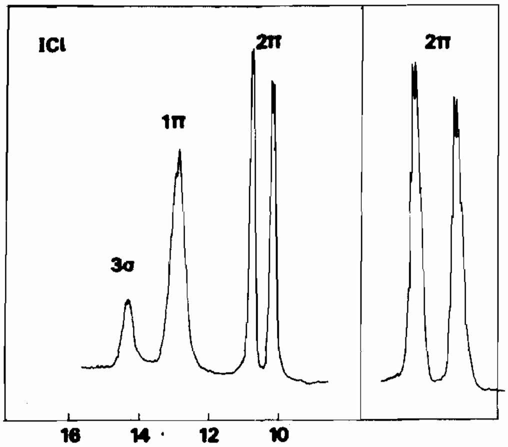

Figure 4. The He^I photoelectron spectrum of iodine monochloride.

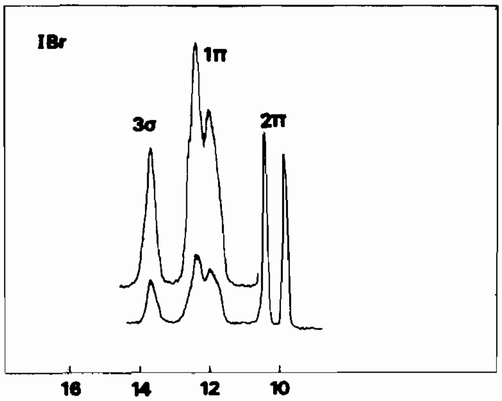

Figure 5. The He^I photoelectron spectrum of iodine monobromide.

is some 8% dissociated at ordinary temperatures[5]). No further structure was detected in the 16-21 eV range. In the case of Cl_2, Br_2 and ICl (Figures 1, 2 and 4, respectively) we also reproduce two-fold expanded scale traces of the first PE bands. The horizontal scale in each of the Figures relates to ionisation energy (IE) in eV. The vertical-scale concerns electron count rate: the maxima of the most intense PE bands in the spectra lie in the range 400-1000 counts/sec.

Results and Discussion

Assignment of the spectra. The valence electronic structures of the diatomic X_2 and XY molecules are of the general form[6,7]

$$X_2:\ \ldots\ (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$$

$$XY:\ \ldots\ (1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(2\pi)^4$$

The $1\sigma_g$ and $1\sigma_u$ MOs of X_2, and the corresponding MOs of XY, 1σ and 2σ, are usually assumed[7] to derive mainly from the halogen *s* valence AOs: the remaining high energy MOs are then of predominantly halogen *p* AO character.

A $^2\Pi$ term of a molecular ion, X_2^+ or XY^+, produced on ionisation of a molecular π subshell, will be split as a result of spin-orbit interaction into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ multiplet states (the $^2\Pi_{3/2}$ state being the more stable in first order).[8] The magnitude of the multiplet separation should increase with atomic number of the halogen, X or Y. Now multiplet structure is clearly present in the PE spectra of Figures 2-5, and its variation with atomic number of halogen strongly suggests the band assignments given in Tables I and 2, and on the actual spectra. These assignments conform with our expectations from simple electronegativity considerations.

No high IE structure, attributable to ionisation of the essentially *s* σ molecular orbitals, is observed in any of the PE spectra reported here. But this is not unexpected in view of the large energy separation of the halogen *p* and *s* valence AOs: even in I^+ the average of configuration *s*-*p* orbital energy difference is as much as 9.63 eV.[9]

Comparison with previous work. The ostensibly adiabatic IEs quoted for Cl_2, Br_2 and I_2 by Frost *et al.*[1] (Table I) are consistently intermediate in value between the vertical IEs and adiabatic IEs of the present work. The data reported here are probably more reliable.[10] The integrated PE band intensities of Table III are however in very satisfactory agreement with the intensity data given by Frost *et al.* with the sole exception of the relative areas of the $^2\Pi_{3/2u}$ and $^2\Pi_{1/2u}$ bands in the I_2 photoelectron spectrum, which were quoted in the earlier work as $0.77:1.00\pm0.01$. The discrepancy between this figure and our value of 0.60 ± 0.05 (Table III) is well outside the limits of error estimated by Frost *et al.*

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(5) M. C. Sneed, J. L. Maynard, and R. C. Brasted, *Comprehensive Inorganic Chemistry*, vol. III, Van Nostrand, 1954.

(6) R S. Mulliken, *Rev. Mod. Phys.*, *4*, 1 (1932).

(7) C. A. Coulson, *Valence*, Oxford 1961.

(8) G. Herzberg, *The Spectra of Diatomic Molecules*, Van Nostrand 1950.

(9) C. E. Moore, *Nat. Bur. Stand.* (U. S.) Circ. no. 467, 1949, 1952 and 1958.

(10) D. W. Turner, in *Physical Methods in Advanced Inorganic Chemistry*, Ed. H. A O. Hill, and P. Day, Interscience 1968.

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Table I. Ionisation energy data[a] (eV) for Cl_2, Br_2 and I_2

X_2	Vertical IE		Adiabatic IE[b]	Frost *et al.*[c]	Assignment[d] (ion state)
Cl_2	11.46 11.52 11.59 11.67 11.75 11.83	±0.02	11.30	11.50	$^2\Pi_g$
	14.33±0.03		13.85	14.11	$^2\Pi_u$
	15.97±0.03		15.65	15.94	$^2\Sigma_g^+$
Br_2	10.56 10.60 10.64 (10.68) (10.72)	±0.02	10.33	10.51	$^2\Pi_{3/2g}$
	10.92 10.96 (11.00) (11.04) (11.08)	±0.02	—	10.90	$^2\Pi_{1/2g}$
	(12.89)±0.05		12.30	12.52	$^2\Pi_{3/2u}$
	13.11 ±0.05		—		$^2\Pi_{1/2u}$
	14.65 ±0.03		14.20	14.44	$^2\Sigma_g^+$
I_2	9.38 10.02	±0.02	9.18 9.83	9.33 9.96	$^2\Pi_{3/2g}$ $^2\Pi_{1/2g}$
	11.03 11.80 12.93	±0.03	10.71 — 12.58	10.87 11.68 12.79	$^2\Pi_{3/2u}$ $^2\Pi_{1/2u}$ $^2\Sigma_g^+$

[a] Incompletely resolved structure is indicated by parentheses. [b] ±0.05 eV. [c] Ref. 1, accuracy quoted as ±0.01 eV. [d] This assignment of the PE spectra is given by Frost *et al.* (Ref. 1).

Table II. Ionisation energy data[a] (eV) for ICl and IBr

IX	Vertical IE		Adiabatic IE		Assignment (ion state)
ICl	(9.98) (10.03) 10.08 10.13 (10.18) (10.23)	±0.02	9.80±0.1		$^2\Pi_{3/2}$
	(10.62) 10.67 10.72 10.77 (10.82) (10.87)	±0.015	10.45±0.1		$^2\Pi_{1/2}$
	12.83±0.03		12.35±0.1		$^2\Pi$
	14.29±0.03		13.90±0.05		$^2\Sigma^+$
IBr	9.83±0.04 10.41±0.04 12.00±0.03 12.36±0.05 13.70±0.04		9.58 10.22 11.50 — 13.40	±0.06	$^2\Pi_{3/2}$ $^2\Pi_{1/2}$ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$ $^2\Sigma^+$

[a] Incompletely resolved structure is indicated by parentheses.

Table III. Relative PE band areas (ionisation probabilities)

X_2			
	$^2\Pi_g$	$^2\Pi_u$	$^2\Sigma_g^+$
Cl_2	1.00	0.76±0.03	0.24±0.04
Br_2	1.00	0.75±0.05	0.25±0.03
I_2	1.00	0.75±0.05	0.25±0.03
	$^2\Pi_{1/2}$	$^2\Pi_{3/2g}$	$^2\Pi_{3/2u}$
Br_2	1.00	0.92±0.04	—
I_2	1.00	0.95±0.04	0.60±0.05
IX	$^2\Pi(2\pi)$	$^2\Pi(1\pi)$	$^2\Sigma^+$
ICl	1.00	0.93±0.05	0.25±0.03
IBr	1.00	0.80±0.05	0.24±0.04
	$^2\Pi_{1/2}$	$^2\Pi_{3/2}(2\pi)$	$^2\Pi_{3/2}(1\pi)$
ICl	1.00	0.96±0.04	—
IBr	1.00	1.00±0.04	0.75±0.06

Earlier ionisation data for the halogens, obtained by other techniques such as electron impact spectroscopy, have been reviewed by Frost *et al.*[1]

We observe vibrational fine structure in the first $^2\Pi$ bands of the PE spectra of Cl_2, Br_2 and ICl, whereas Frost *et al.* detect such detail only in the case of F_2. The vibrational frequencies estimated from the PE spectra (Table IV) are entirely consistent with the values obtained by more conventional spectroscopy.[8] We also see, in the data of Table IV, the familiar[10] increase of vibrational frequency on ionisation of antibonding electrons: the effect is however rather small and within experimental error in the case of Br_2 and ICl. The spectrometer proved incapable of resolving vibrational fine structure for the first $^2\Pi$ ionisations of I_2 and IBr (with expected vibrational spacings of about 27 and 34 meV, respectively, as indicated by the data of Table IV).

Table IV. Vibrational frequencies (meV)[a] in the ground states of X_2 and IX species and in the ground $^2\Pi$ states of their molecular ions

	Present work	Ref. 8
Cl_2	—	70.03
Cl_2^+	78±4	80.00
Br_2	—	40.07
Br_2^+	42±4	—
I_2	—	26.60
I_2^+	[b]	—
ICl	—	47.63
ICl^+	48±3	—
IBr	—	33.28
IBr^+	[b]	—

[a] 1 meV = 8.066 cm^{-1}. [b] Not resolved.

Table V. $^2\Pi_{1/2}$—$^2\Pi_{3/2}$ multiplet separations (estimated as vertical IE differences)[a]

	$^2\Pi_g(1\pi_g)$	$^2\Pi_u(1\pi_u)$
Br^{2+}	0.36±0.01	*ca.* 0.22[b]
	[0.39±0.01]	
I_2^+	0.64±0.01	0.77±0.03
	[0.63±0.01]	[0.82±0.01]
	$^2\Pi(2\pi)$	$^2\Pi(1\pi)$
ICl^+	0.58±0.01	—
IBr^+	0.58±0.01	0.36±0.02

[a] The multiplet splittings quoted by Frost *et al.*[1] are included in parentheses. [b] Poorly defined.

No vibrational structure was detected in the higher IE bands in any of the spectra. Here the lack of fine structure might be attributed to substantial decreases in vibrational frequency on ionisation of electrons from strongly bonding molecular orbitals. However such an explanation is not generally plausible: for example, the vibrational spacing in the Cl_2^+ $^2\Pi_u$ state is known[8] to be about 70.5 meV. In such cases the vibrational fine structure is probably obscured by the superimposed multiplet splittings (24.8 meV for the $^2\Pi_u$ state of Cl_2^+).[8] Also it may be that the individual vibrational bands are relatively broad for the higher ionisations.

The observed separation of the $^2\Pi_g$ and $^2\Pi_u$ states of Cl_2^+ (2.55 eV) agrees well with the spectroscopically determined value of 2.554 eV.[8]

Multiplet structure in the PE spectra. The observed $^2\Pi_{1/2}$–$^2\Pi_{3/2}$ multiplet widths are collected in Table 5. As regards the homonuclear X_2 molecules, each $^2\Pi(\pi^3)$ state of the molecular ions is expected to suffer a first-order multiplet splitting of the order ζ_X, the spin-orbit coupling constant for the halogen *p* atomic subshell.[a] The spin-orbit coupling parameters for neutral bromine and iodine atoms are $\zeta_{Br} = 0.305$ eV and $\zeta_I = 0.628$ eV,[9] so that the Br_2 and I_2 data of Table 5 are in fair agreement with the simplest predictions. Multiplet fine structure is not clearly discernible in the Cl_2 photoelectron spectrum, the vibrational intervals in Cl_2 (Table IV) being of comparable magnitude to the chlorine 3*p* spin-orbit coupling constant, $\zeta_{Cl} = 0.073$ eV.[9] The multiplet splittings in the ICl and IBr spectra are also intelligible in very simple terms. The $^2\Pi(2\pi)$ multiplet separations (each about 0.58 eV) are of a sensible magnitude for the ionisation of MOs which on electronegativity grounds are expected to be of predominantly iodine 5*p* character ($\zeta_I = 0.628$ eV): the multiplet intervals in ICl and IBr are moreover somewhat less than those observed in I_2. The $^2\Pi(1\pi)$ separations are similarly entirely reasonable for MOs composed largely of chlorine 3*p* or bromine 4*p* atomic orbitals.

Band intensities and band widths. The integrated PE band intensity data in Table III, which reflect the relative probabilities of ionisation of different molecular subshells, have a number of interesting features. In idealised circumstances one expects the cross-section for ionisation of a particular subshell to be simply proportional to its occupancy.[12] However it appears from Table III that the nominally antibonding π electrons have a larger ionisation cross-section than the bonding π electrons, a fact which may be correlated with the relatively more diffuse probability density expected for antibonding molecular orbitals. It is particularly evident that the probability of ionisation of a bonding σ electron (in the $2\sigma_g$ or 3σ orbitals) is considerably less than that for either species of π electron.

The transition probabilities to $^2\Pi_{1/2}$ multiplet states are in general distinctly greater than those characterising the corresponding $^2\Pi_{3/2}$ states, an effect which is most pronounced in the case of $1\pi_u$ or 1π ionisations. (This disparity in intensity is also observed in the multiplet structure of the first photoelectron bands of the hydrogen halides, HX[1,13]). The simplest arguments[12] would have led us to expect equal cross-sections for ionisation to the distinct multiplet states, each of these states having a two-fold spin-orbital degeneracy.

Turning to the photoelectron band widths, it can be seen in Figures 1-3 that the bands assigned to the $1\pi_g$ ionisations are substantially less broad than the bands to higher IE associated with ionisation of the $1\pi_u$ and $2\sigma_g$ electrons. The diffuse character of the latter bands (with relatively large vertical-adiabatic IE separations) is consistent with ionisation from strongly bonding MOs:[10] that the first bands in the PE spectra are of a somewhat sharper nature perhaps indicates that the $1\pi_g$ molecular orbitals of Cl_2, Br_2 and I_2 are only weakly antibonding.

(a) In particular, this approximation involves the neglect of matrix elements, $<p\pi_1|\mathbf{H}_{SO}|p\pi_2>$, of the spin-orbit Hamiltonian $\mathbf{H}_{SO}$ between $p\pi$ AOs on different centres (cf. ref. 11).

(12) P. A. Cox and A. F. Orchard, *Chem. Phys. Lett.*, *7*, 273 (1970).
(13) J. B. Atkinson and D. W. Turner, unpublished work.
(14) R. S. Mulliken, *J. Chem. Phys.*, *2*, 782 (1934) and *3*, 573 (1935).
(15) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, *3*, 458 (1965).
(16) R. S Berry and C. W. Riemann, *J. Chem. Phys.*, *38*, 1540 (1963).

Ionisation energy trends. The variations in the ionisation energies for production of the $^2\Pi_g$, $^2\Pi_u$ and $^2\Sigma_g{}^+$ states of the Cl_2, Br_2 and I_2 molecular ions (Table I), all of which diminish with increasing atomic number of halogen, correlate well with the atomic ionisation potentials and also with the halogen *p* orbital electronegativities (Figure 6 [b]): but the correlation becomes rather poor if we include the F_2 data of Frost *et al.*[1] The energy separation of the $1\pi_g$ and $1\pi_u$ molecular orbitals (as inferred from Koopmans' approximation[17]) is also seen to diminish from Cl_2 through to I_2, thus showing the expected progressive weakening in covalent interactions, in agreement with the decreasing dissociation energy[8] of the halogen molecule.

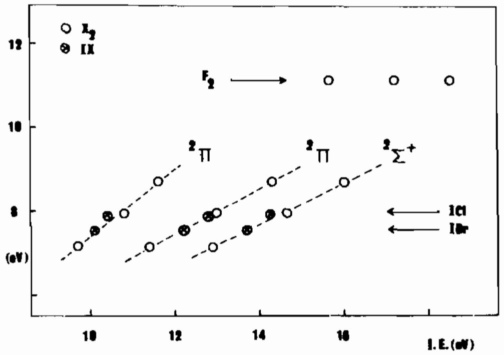

Figure 6. Plot of ionisation energy data for the halogens and diatomic interhalogens against halogen electronegativity [b].

The ICl and IBr ionisation energy data (Table II) are also readily comprehensible in similar terms. The iodine monochloride IEs are, not surprisingly, somewhat similar in magnitude to those of bromine.

Acknowledgments. We are grateful to Mr. D. I. King for experimental assistance. We also wish to thank the Science Research Council for financing the construction of the photoelectron spectrometer, and for a Research Studentship (to S.E.).

((b) We use the Mulliken electronegativity[14] calculated from average of configuration[15] atomic IE data,[9] and the electron affinities given by Berry and Riemann.[16] The points plotted in Figure 6 for the interhalogens, IX, correspond to the mean electronegativity of the I and X atoms. The $^2\Pi$ plots relate to the average IEs for separate multiplet states.

(17) T. Koopmans, *Physica*, *1*, 104 (1934).