Gas Phase Molecular Complexes. Multiple Charge-Transfer Bands in the Spectra of Alkyl Halide–Iodine Atom Systems

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Abstract: The charge-transfer spectra of transient complexes between acceptor iodine atoms, produced by the flash photolysis of molecular iodine, and a series of five alkyl iodide and seven alkyl bromide donors have been measured. In each case two bands are observed in the near ultraviolet and/or blue spectral regions. This multiplicity is attributed to coupled spin-orbit splitting of the first ionization potential of the alkyl halide donor molecule. Satisfactory correlation between the charge transfer energy ($h\nu_{CT}$) and donor ionization potential (I_D) results for each series of alkyl halides if it is assumed that the decoupling of spin and orbital precession in the donor ion (which leads to the observed splitting in the photoelectron spectra in the free alkyl halide molecule) does not occur in the complexed donor species. The observed spectral transitions can also be correlated for each alkyl halide series on the basis solely of contact charge transfer.

Multiple charge-transfer bands have been observed in many liquid-phase systems.[2] In general, this behavior may result from transitions from more than one energy level of the donor, from transitions to more than one energy level of the acceptor, or from differences in the interaction energy between the donor and acceptor species. As such, the difference in energy between the two transitions as a function of donor and acceptor species provides an indication of the type of transitions occurring in charge transfer photoexcitation. For example, the twofold-degenerate highest occupied E_{1g} orbital of benzene loses its degeneracy on ring substitution, with the extent of splitting depending on the number and type of substituents and on the position of substitution.[3a] The charge-transfer transition energies should thus be proportional to the first two ionization potentials of the donor and correlative with the electron donor–acceptor properties of the substituents; this has been shown to be generally true, for example, with tetracyanoethylene (TCNE) acceptor–aromatic donor complexes.[3b]

Although most of the studies of multiple charge-transfer spectra have been done in solution or solid state, it is well recognized that theoretical treatments of charge-transfer interactions[4] strictly apply to isolated entities existing only in the gas phase at low pressures and that solvent–complex interactions influence all properties of the complex.[5] Specifically, solvent molecules can drastically affect the charge-transfer band position because of the large differences in polarity of the "no-bond" and "dative" charge-transfer forms, with most complexes having only small dative structure in the ground state and primarily ionic structure in the excited state. For iodine complexes, there is a vapor-to-solution red shift; in general, the weaker the complex, the greater the shift.[5] This trend is not observed with other acceptors such as carbonyl cyanide, however, and is not predictable for different types of donors. Furthermore, in some cases there is actually a blue shift in going from the vapor to solution phase, as with the relatively strong alkyl amine–sulfur dioxide systems.[6]

In an earlier paper involving the study of transient halogen atom charge-transfer complexes in the vapor phase,[7] we observed two peaks when I_2 was flash photolyzed in the presence of methyl or ethyl iodide vapors. The two bands in each case correlated reasonably well with the spin-orbit splitting of the first ionization potential of the alkyl iodide,[8] and therefore these bands were attributed to charge transfer between the iodine atom acceptor and the alkyl iodide doublet first ionization potential donor. We report here a detailed extension of this gas-phase study to two homologous alkyl halide series consisting of the five alkyl iodides and seven alkyl bromides that could effectively be studied in the vapor phase at sufficient pressures to generate detectable charge-transfer absorption spectra.

A recent paper[9] gives spectral results for the interaction between molecular iodine and a series of alkyl iodides, *n*-propyl bromide, and *n*-propyl chloride in the liquid (*n*-heptane solvent) phase. Multiple bands are observed with the alkyl iodides; again good correlation between the band maxima and ionization potentials clearly identifies the charge-transfer character of these transitions, although a somewhat arbitrary solvent correction has to be applied to compare the spectral and thermodynamic results with theory.

Experimental Section

The characteristics of the flash spectrophotometer and method of reaction cell preparation have been described previously.[7] In the present study the cylindrical fused quartz reaction cells (100 mm optical light path, 28 mm o.d.) were completely immersed in a transite circulating air thermostat capable of attaining temperatures up to ca. 180 °C, with a vertical temperature variation of approximately ±2 °C (although temperature control within the cell may have been better). The thermostat was positioned between the two flash lamps along the optical bench axis of the continuous analyzing beam from the 450-W Osram xenon arc. The flash light was filtered through 10-mm optical path length rectangular Pyrex cells containing saturated uranyl nitrate solution (lower wavelength cutoff at 490 nm), and the analyzing light was passed through either a 3-mm plate glass filter (alkyl iodides) or 10 mm of CCl_4 (alkyl bromides) before illuminating the reaction cell to prevent direct excitation of the alkyl halide. Transient changes in absorbance were measured 35 μs after flash initiation from voltage–time oscillograms, and spectral curves were obtained from point-by-point measurements taken every 2 or 5 nm; the Zeiss MM12 monochromator bandwidth was maintained at ca. 2 nm by appropriate entrance slit selection.

With the exception of 2-iodopropane, all the alkyl halides (Eastman, Matheson, or Fisher Certified) were clear and colorless or only very slightly yellow (for liquids). They were used without further purification other than for outgassing by repeated pump–thaw cycles, passage under vacuum through a P_2O_5 drying tube, and trap-to-trap fractional distillation prior to introduction into the evacuated reaction cell (transferred material colorless in all cases). Eastman 2-iodopropane contained appreciable iodine and was washed twice with 0.1 M sodium thiosulfate and twice with distilled water before outgassing, drying, vacuum distillation, and transfer to the reaction cell. For the room-temperature liquid alkyl halide donors, the desired amount of donor was introduced into the cell by freeze transferring under vacuum the appropriate number of aliquots of vapor from a calibrated reservoir on the vacuum transfer system at a pressure below the vapor pressure of the halide in such a manner that no vapor in contact or above the mercury manometer was actually transferred to the cell. Similarly, the appropriate number of iodine aliquots to give the desired I_2 concentration were transferred to the reaction cell from another calibrated chamber, with however the solid iodine reservoir attached to the

Table I. Spectral Parameters of Transient Absorption Following Flash Photodissociation of I_2 in Alkyl Halide Vapors

Alkyl halide (RX)	$[RX] \times 10^2$, mol/l.	$[I_2] \times 10^5$, mol/l.	t, °C	λ_{max}, nm	$\Delta\bar{\nu}_{1/2}$, cm^{-1}	% of total peak area
Methyl iodide	4.1	5.6	88	418	1270	40
				351	2480	60
Ethyl iodide	3.4	5.7	84	428	1820	37
				360	2220	63
1-Iodopropane	3.2	4.4	125	431	1660	29
				365	2380	71
2-Iodopropane	4.0	10.0	91	437	1320	27
				370	3110	73
1-Iodo-2-methylpropane	3.7	6	153	434	1770	30
				368	2550	70
Methyl bromide	4.0	7.6	61	322	2680	50
				300	1990	50
Ethyl bromide	4.0	8.0	55	332	2060	47
				308	2110	53
1-Bromopropane	4.0	7.6	78	336	2080	41
				312	2560	59
2-Bromopropane	4.0	7.9	63	339	1160	26
				316	2190	74
1-Bromo-2-methylpropane	4.2	7.3	107	338	2110	46
				315	2220	54
2-Bromo-2-methylpropane	4.0	3.3	73	347	1560	32
				322	2230	68
1-Bromobutane	4.0	6.7	110	338	2230	44
				315	2720	56

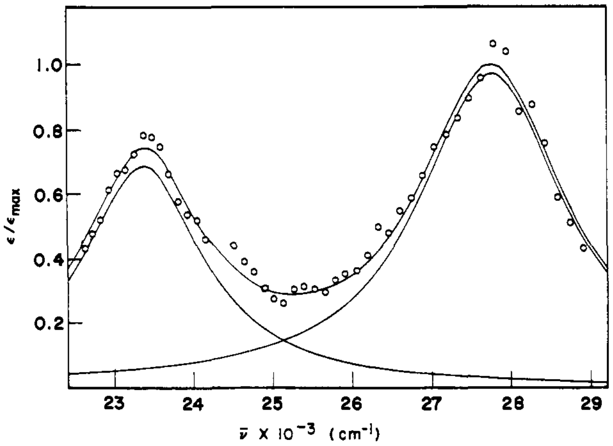

Figure 1. Transient spectrum following vapor-phase flash photolysis of I_2 in C_2H_5I. Open circles are experimental points, and solid lines are the two resolved bands and their summation.

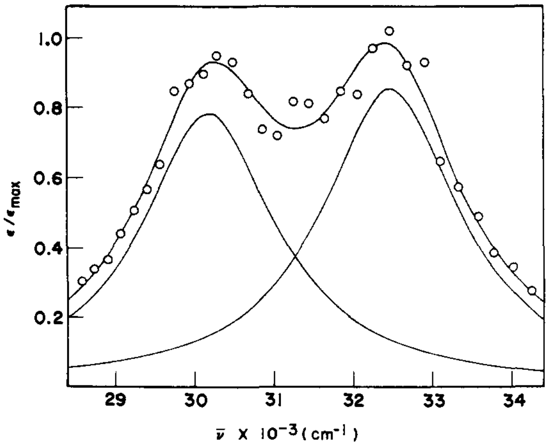

Figure 2. Transient spectrum following vapor-phase flash photolysis of I_2 in C_2H_5Br. Open circles are experimental points, and solid lines are the two resolved bands and their summation.

chamber through a greaseless stopcock maintained at a temperature slightly below that of the room. The actual I_2 concentration was determined spectrophotometrically, after sealing-off removal from the vacuum transfer apparatus, with an air-thermostated Beckman DU spectrophotometer. No irreversible reaction could be detected spectrophotometrically with any of the alkyl halides after the large number of flashes needed to get the complete transient spectrum (generally at least three at each wavelength), neither by iodine disappearance nor by appearance of any permanent new absorption band.

Results

The vapor-phase transient absorption spectra following flash photodissociation of I_2 in the presence of alkyl halides have been determined for 12 alkyl iodides and bromides. Typical results are shown in Figures 1 (ethyl iodide) and 2 (ethyl bromide). In each case studied two maxima are indicated, although band separation is greater with the iodides than with the bromides.

The resolution of each spectrum into two component bands was accomplished by means of a computer program modified from one originally written by Jones.[10,11] Basically, the experimental data are fitted to an equation containing Lorentzian and Gaussian terms. The best fit, determined by iterative least-squares analysis, also gives the fraction of Lorentzian character, which in all cases analyzed here was unity in agreement with usual behavior of gas-phase spectral bands.[12] The best fit absorption curve and the two resolved Lorentzian bands are also shown in Figures 1 and 2.

The choice of resolution into only two bands is somewhat arbitrary, and indeed in some cases there is the indication of a third peak possibility (as shown, for example, on Figure 1 at ca. 24 500 cm^{-1}). However, in no case did resolution into three bands improve the statistical least-squares fit, and therefore resolution into more than two peaks is not justified.

Spectral results for the 12 alkyl halide systems are summarized in Table I, the results for methyl iodide and ethyl iodide being in agreement with those reported earlier.[7] Consistent with previous interpretations, we conclude that these transient spectra arise from charge-transfer interactions be-

Table II

Alkyl halide (RX)	I_D, eV	$h\nu_{CT}$, eV	$\Delta h\nu_{CT}$, eV	r_{DA}, Å
Methyl iodide	9.54[a]	2.97	0.56	4.11
	10.17	3.53		4.03
Ethyl iodide	9.34[b]	2.90	0.54	4.26
	9.93	3.44		4.20
1-Iodopropane	9.27[b]	2.88	0.52	4.33
	9.82	3.40		4.29
2-Iodopropane	9.18[a]	2.84	0.51	4.40
	9.69	3.35		4.40
1-Iodo-2-methylpropane	9.18[a]	2.86	0.51	4.42
	9.73	3.37		4.37
Methyl bromide	10.53[c]	3.85	0.28	3.98
	10.85	4.13		3.94
Ethyl bromide	10.28[b]	3.74	0.29	4.14
	10.60	4.03		4.11
1-Bromopropane	10.18[b]	3.69	0.28	4.20
	10.50	3.97		4.15
2-Bromopropane	10.07[d]	3.66	0.27	4.30
	(10.39)	3.93		(4.24)
1-Bromo-2-methylpropane	10.09[d]	3.67	0.27	4.29
	(10.38)	3.94		(4.26)
2-Bromo-2-methylpropane	9.89[d]	3.57	0.28	4.42
	(10.18)	3.85		(4.41)
1-Bromobutane	10.15[b]	3.67	0.27	4.21
	10.44	3.94		4.19

[a] B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc. B*, 790 (1971). [b] K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 373 (1973). [c] J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.*, **53**, 178 (1970). [d] Lower ionization potential from K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962); higher ionization potential estimated from average spin-orbit splitting.

tween acceptor (A) iodine atoms and the alkyl halide donors (D).

Confirmation of the charge-transfer nature of absorption spectra for an homologous series of donors with a common acceptor is generally indicated by the approximately linear correlation between donor ionization potentials (I_D) and the absorption energies $h\nu_{CT}$, generally taken to be the maxima in the absorption curves.[13] It is seen from Table II that $\Delta h\nu_{CT}$, which is the energy gap between the two resolved peaks, is approximately constant for a given RX series but significantly different between the two structurally identical series; this shows that the multiple CT peaks in this case come from donations from different energy levels in RX rather than from specific properties of the acceptor or different orientations of the RX and I species in the charge transfer interactions. In this sense, the presence of the two peaks for each of the alkyl halide systems is interpreted as charge transfer from the two closely spaced components of the first ionization potential of the alkyl halide donors. This splitting of I_D results from strong spin-orbit interaction and should be roughly two-thirds of the energy separation between the free halogen ($^2P_{3/2}$) and ($^2P_{1/2}$) atoms.[14]

The pertinent data for $I_D - h\nu_{CT}$ plots are given in Table II and are plotted in Figure 3. It is evident that a reasonable correlation exists between I_D and $h\nu_{CT}$ for the alkyl iodides or the alkyl bromides alone using only the lower or the upper ionization potentials. However, there is no correlation using both ionization potentials for either halide series; similar behavior to this has recently been shown for liquid-phase (*n*-heptane solvent) charge transfer between molecular iodine and four alkyl iodides.[9] There is also no correlation between the alkyl iodides and alkyl bromides for either ionization potential series. It is now recognized that both of these effects were present in our previous paper[15] but were not obvious at that time on the basis of the limited number of alkyl halides covered.

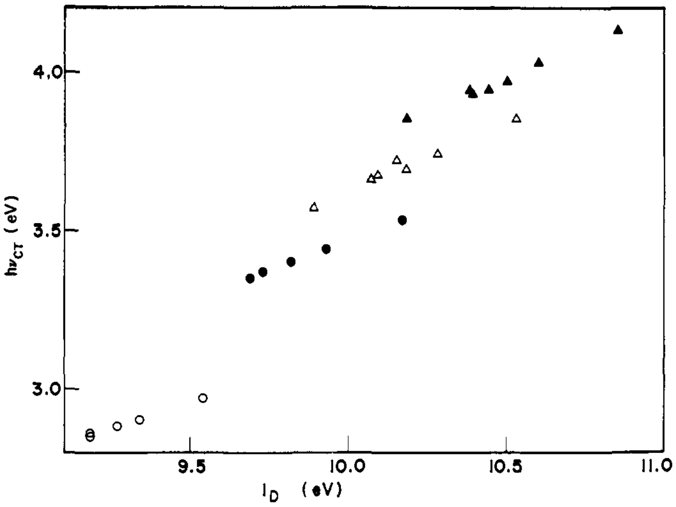

Figure 3. Plot of charge-transfer transition energies $h\nu_{CT}$ vs. alkyl halide ionization potentials, I_D. Circles: alkyl iodides. Triangles: alkyl bromides. Open symbols: lower component of donor first ionization potential. Closed symbols: upper component of donor first ionization potential.

The reason for the lack of correlation between the data for the two ionization potential series for a given alkyl halide series is not clear; it may involve modification of the spin-orbit splitting of the first ionization potential of the alkyl halide by the specific charge transfer interaction. The electronic configuration of the ground state of methyl halide (belonging to the C_{3v} point group), neglecting core electrons, is[14]

$$(sa_1)^2(ns_Xa_1)^2(\pi e)^4(\sigma a_1)^2(np\pi_Xe)^4,\ ^1A_1 \qquad (1)$$

The σ orbital is the chief C–X bonding orbital, and the π and s orbitals are the primary C–H bonding orbitals. The np_x and np_y orbitals of the halogen (with some contribution from C and H atomic orbitals) form the nonbonding (e) molecular orbital, which is the highest filled orbital of CH_3X. The first ionization potential thus corresponds to the energy required to remove one of these lone pair nonbonding electrons from the $np\pi_Xe$ orbital to form the CH_3X^+ ion with electronic configuration[14]

$$\ldots(np\pi_Xe)^3,\ ^2E \qquad (2)$$

with only minor change in the molecular binding.

Mulliken has treated the spin-orbit splitting of the first ionization potential of CH_3I[14] similar to that for ClI,[16] even though the two have different point group symmetry, since in both cases the influence of the electron removal is localized for the most part on the iodine atom. The electronic configuration of the ClI ground state is

$$\ldots(5p\pi_I)^4,\ ^1\Sigma^+ \qquad (3)$$

while that of the ClI$^+$ ion is

$$\ldots(5p\pi_I)^3,\ ^2\Pi \qquad (4)$$

Thus, both the ^2E state of CH_3I^+ and the $^2\Pi$ state of ClI$^+$ should be similar and comparable to an I$^+$ ion.[16]

The magnetic interaction energy, γ, for a free atom with a single p electron (other than those in closed shells) is primarily due to interaction between the spin of this electron and the magnetic field of its own orbital motion; this is given[17] by the Landé interval rule

$$\gamma = \frac{a}{2}\left[j(j+1) - l(l+1) - s(s+1)\right] \qquad (5)$$

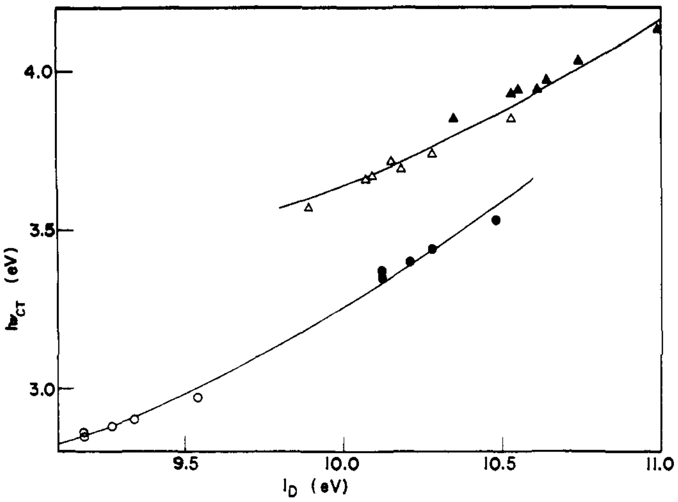

Figure 4. Plot of charge-transfer transition energies $h\nu_{CT}$ vs. alkyl halide ionization potentials, I_D. Circles: alkyl iodides. Triangles: alkyl bromides. Open symbols: lower component of donor first ionization potential. Closed symbols: calculated upper component of donor first ionization potential (see text). Solid lines calculated according to eq 8.

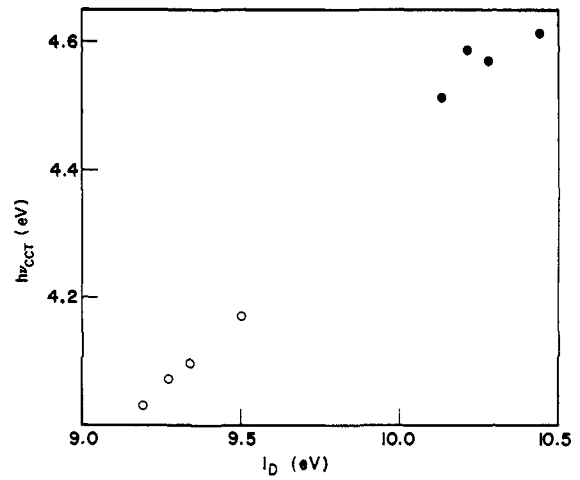

Figure 5. Plot of contact charge-transfer transition energies $h\nu_{CCT}$ vs. alkyl iodide ionization potentials I_D for RI-I_2 contacts (data from ref 9). Open circles: lower component of donor first ionization potential. Closed circles: calculated upper component of donor first ionization potential (see text).

where l and s are the single-electron quantum numbers, $j = l + s$, and a is the spin-orbit coupling coefficient. Accordingly, the doublet separation between the ($^2P_{3/2}$) and ($^2P_{1/2}$) states ($l = 1, s = \frac{1}{2}$) for I is

$$\Delta\gamma = \frac{a}{2}\left\{\left[\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right] - \left[\frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right]\right\} = \frac{3a}{2} \quad (6)$$

and $a = 2\Delta\gamma/3$. The observed separations for I and Br are 0.94 and 0.46 eV, respectively, hence $a \cong 0.63$ eV for I and 0.31 eV for Br.

For a molecular species also with only a single electron in other than closed shells, such as the $^2\Pi$ and ^2E ionized states of ClI and CH_3I, the approximate interaction energy is arrived at[17] by analogy to the Paschen-Back effect for atoms, in which l and s are uncoupled in a strong magnetic field and hence to a first approximation independently space quantized. The interaction energy is then $\gamma_m = am_lm_s$, where m_l and m_s are the respective component magnetic quantum numbers. Assuming that the electrical quantum number components i_l and i_s existing in the strong electrical field (Stark effect) associated with a molecule ion are analogous to the atomic m_l and m_s components and hence also uncoupled,[17] the interaction energy is $\gamma_i = ai_li_s$. Thus, the expected doublet separation for the $^2\Pi$ and ^2E ionic states ($i_l = 1$, $i_s = \pm\frac{1}{2}$) is

$$\Delta\gamma_i = a(1)(\tfrac{1}{2}) - a(1)(-\tfrac{1}{2}) = a \quad (7)$$

and the first ionization potential for CH_3I or CH_3Br corresponding to excitation from the $^1A_1$ to the ^2E state (electron removal) should consist of a doublet with separation of $a = 0.63$ eV or 0.31 eV, respectively, in agreement with the respective observed values of 0.63 and 0.32 eV (see Table II).

The above treatment for the doublet in the first ionization potential is strictly valid only for molecules with fixed nuclei.[17] The excellent agreement obtained with the experimental values for CH_3I and CH_3Br shows that molecular rotation makes a negligible contribution to the multiplet energy in these cases. This treatment also requires only a single electron (other than closed shells), with no interaction or coupling of orbital angular momenta with other electrons.

The situation existing in the charge-transfer state of an alkyl halide and an iodine atom complex is quite different than in the above model. Charge transfer in the complex occurs only over a distance of the order of 0.4 nm, and (at least for strong liquid-phase complexes) there is appreciable mixing of the no-bond and dative states in both the ground and excited states.[18] Presumably the local electric field in the complex will qualitatively be less than that associated with the molecular ionic $^2\Pi$ or ^2E state of the free halide, with the possible consequence that the molecular spin-orbit uncoupling assumed above does not occur in the complex. In the limiting case then the appropriate doublet splitting for the "ionized" donor is that for the strongly spin-orbit coupled free halogen atom, which is shown above (eq 6) to be $\Delta\gamma = 3a/2 = 0.94$ and 0.46 eV for the iodide and bromide, respectively (i.e., the splitting is the difference in energy between the $^2P_{3/2}$ and the $^2P_{1/2}$ states for the free halogen atom).

Figure 4 is a plot of the charge-transfer transition energy, $h\nu_{CT}$, as a function of the alkyl halide ionization potential, with however the higher I_D being a calculated value equal to $[(I_D)_{lower} + 0.94]$ for the alkyl iodide series and equal to $[(I_D)_{lower} + 0.46]$ for the alkyl bromide series. In view of the very approximate nature of the assumptions leading to this plot, the correlation is now quite good for all data for each alkyl halide series and is in support of the above interpretation of the magnitude of spin-orbit splitting in the complexed alkyl halides. In the same manner, we have plotted the data of Morita and Tamres[9] (Figure 5) for the liquid-phase alkyl iodide-I_2 charge-transfer contacts, again showing a reasonable correlation between the lower and (modified) upper ionization potentials.

As has been pointed out many times, the correlation between $h\nu_{CT}$ and I_D is only approximately linear, and for relatively strong interactions a better fit is provided by the parabolic relationship given by the following equation:[19]

$$(h\nu_{CT})^2 = \left[\frac{I_D - C_1}{1 - S_{01}{}^2}\right]^2\left[1 + \frac{4\beta_1\beta_0}{(I_D - C_1)^2}\right] \quad (8)$$

In this equation, which is based on the variation method, S_{01} is the overlap integral, and β_0 and β_1 are the resonance integrals $(H_{01} - S_{01}W_0)$ and $(H_{01} - S_{01}W_1)$, respectively. The best fit of the data from Figure 4 using the method and plot of Mulliken and Person[20] gives $S_{01} = 0.3$ for both RX series, and the quadratic least-squares fit of the data to eq 8 gives:[18] for RI·I, $\beta_0 = -1.3$ eV, $C_1 = 9.1$ eV; for RBr·I, $\beta_0 = -1.6$ eV, $C_1 = 9.8$ eV. Equation 8 is plotted on Figure 4 (solid lines) for the two alkyl halide series using these calculated parameters.

There is, however, another possibility for the lack of correlation in the $h\nu_{CT}$-I_D plots for the two series using the "free donor" ionization potentials. Morita and Tamres[9] have shown, on the basis of linear charge transfer absorbance dependence on either the donor or acceptor concentration, that the spectra observed for the alkyl halide–I_2 systems arise from contact charge transfer between donor–acceptor pairs in which the resonance interaction is essentially zero so that no actual complex molecule or specific entity is formed.[21] If there is no mixing of the charge-transfer state with donor or acceptor excited states, then the contact charge-transfer transition energy $h\nu_{CCT}$ is given by[22]

$$h\nu_{CCT} = I_D - E_A - (e^2/r_{DA}) \tag{9}$$

where E_A is the vertical electron affinity of the acceptor and $-e^2/r_{DA}$ is the strong coulombic attraction in the dative state occurring at a distance r_{DA}, which is taken to be the mean molecular (collision) diameter of D and A.

The electron affinity of atomic iodine is large (3.063 eV),[23] and therefore the actual slope of the $h\nu_{CCT}$–I_D plots will be quite sensitive to small changes in e^2/r_{DA} (and hence in r_{DA}) for different donors. It is not surprising, then, that plots of this type may be approximately linear and still have slopes that are appreciably less than unity (Figure 3) even for contact charge transfer involving a homologous donor series. Similarly, r_{DA} might be expected to be somewhat different for transitions in which different isomeric orientations occur for the two ionization potentials, such as for complexes with aromatic donors in which the degeneracy of the highest occupied orbital of benzene is removed by ring substitution. Different orientations would not be expected for the RX·I species, however, since the spin–orbit splitting in RX does not produce orbitals with different nodal planes, and for a given donor–acceptor pair r_{DA} should be the same for the two energies in the donor first ionization potential. That this is the case for all the alkyl iodide and bromide donors studied in this work is shown in the last column of Table II, which gives the same (within experimental uncertainty in $h\nu_{CT}$) values of r_{DA} calculated according to eq 9 for the two resolved charge-transfer bands.

The choice of an appropriate molecular collision diameter for D and A is somewhat arbitrary, since a specific orientation is required for maximum charge-transfer interaction whereas molecular diameters from van der Waals constants and critical phenomena are less specific. Assuming a configuration leading to maximum overlap between a nonbonding p orbital on the donor RX halogen atom and the singly occupied p orbital of the acceptor iodine atom,[24] a C–I bond distance of 2.133 Å[25] and a "constant energy distance" of 3.46 Å between two I atoms with zero bond energy[26] gives $r_{DA} \cong 4.1$ Å for the CH_3I–I species, in agreement with the average of the two values in Table II. Furthermore, the trends in r_{DA} between the two alkyl halide series and within each series are qualitatively as expected.

On this basis, then, the apparent noncorrelation between $h\nu_{CT}$ and the two ionization potentials for a given alkyl halide series shown in Figure 3 results simply from the lack of correspondence between I_D and r_{DA}, although for different donors in a common series this correspondence should still be roughly followed using the lowest ionization potential. Accurate absorbance data as a function of donor and free iodine atom concentrations are needed to establish the contact-complex nature of these charge-transfer species.

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