Bonding in Donor–Acceptor Complexes. II. Electrostatic Contributions to Changes in the Infrared Spectrum of Benzene–Halogen Complexes[1]

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Abstract: A simple model, used previously to estimate electrostatic contributions to the energy of formation and dipole moment of benzene–halogen complexes, is applied to a calculation of electrostatic contributions to infrared spectral properties of these complexes. In particular, the enhancement of the intensity of the halogen stretching mode and the red shift of the frequency of this mode can be partly, if not mostly, attributed to changes in the electrostatic energy of the halogen as it vibrates. The interaction making the dominant contribution to these effects is the benzene quadrupole–halogen induced dipole interaction. A simple unparametrized model is used to calculate the electrostatic contribution to these infrared effects and good order of magnitude agreement with experiment is obtained. These results confirm our earlier conclusion that "charge-transfer" interactions are not as important in determining ground-state properties of these complexes as had been previously supposed.

Since the 1955 work of Collin and D'Or on solutions of Cl_2 in benzene,[2a] there has been considerable interest in the changes that take place in the infrared spectrum of aromatic–halogen complexes.[2b] There are three types of changes which have been observed. (1) The intensity of bands may be changed or bands which are not infrared allowed for the isolated molecule may be observed. (2) Some of the vibrational frequencies in the donor or acceptor may be shifted. (3) New low-frequency bands due to the "intermolecular" vibrations of one molecule against the other may be observed.[3,4] Much of the discussion in the literature has been about the implications that can be drawn from these results about the geometry of benzene–halogen[2b] complexes, but this discussion has resulted in considerable study being given to the origin of the intensity enhancements and frequency shifts.[5,6]

In what follows we will be concerned principally with the changes that take place in the halogen stretching mode when the halogen is complexed. There are two such changes: a shift in the frequency to lower energies and an increase in intensity which appears to be related to the strength of the interaction between the donor and the halogen.

These changes have been generally interpreted in terms of the charge-transfer model.[5,6] As is well known, in this model the ground state of the complex is described by a wave function[7]

$$\psi_N = a\psi_0 + b\psi_1 \qquad (1)$$

which is a linear combination of a no-bond wave function ψ_0 and a dative-bond wave function ψ_1 in which an electron has been transferred from donor to acceptor. Since the dipole moment of the complex depends on the relative magnitude of a and b, any vibration of donor or acceptor which changes the mixing coefficients in ψ_N will be reflected as an intensity change in the infrared spectrum. Since the states described by ψ_0 and ψ_1 will have different force constants, the force constant and infrared frequency will also depend on the extent of mixing. Thus the charge-transfer model predicts that frequency changes will occur upon complexation. Comparisons of calculated and experimental values of the intensity changes and frequency shifts in benzene–halogen complexes showed reasonably good agreement, but there was considerable uncertainty in evaluating two parameters necessary for the calculation $[(\partial E_A^v/\partial Q_1)$ and $\mu_{EN}]$.

In Mulliken's original paper it was pointed out that ψ_0 contains all of the classical electrostatic interactions between donor and acceptor.[7] It has been recently shown that benzene quadrupole–halogen induced dipole interactions make significant contributions to the energy of formation and the induced dipole moment of benzene–halogen complexes[8] and the purpose of this paper is to evaluate the importance of these and other electrostatic interactions in determining changes in the infrared spectrum. As a model we assume that the halogen molecule lies along the sixfold axis of the benzene ring at distances corresponding to those found for solid-state complexes.[9] In this position the halogen molecule experiences an electrostatic potential and a resulting electric field which is nonuniform and nonlinear along its molecular axis. Details of the calculation of this electric field are given in paper I.[8] As the halogen molecule vibrates the dipole moment induced by the benzene electric field will change and consequently the halogen stretching mode will be infrared active. We show below that these electrostatic effects make a nonnegligible contribution to both the intensity enhancement and frequency shift of benzene–halogen complexes.

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[1] Supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-65, and by the National Science Foundation.

[2] (a) J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955); (b) see W. B. Person, C. F. Cook, and H. B. Friedrich, *ibid.*, **46**, 2521 (1967), and references therein.

[3] H. Yada, J. Tanaka, and S. Nagakura, *J. Mol. Spectrosc.*, **9**, 461 (1962).

[4] J. Yarwood and W. B. Person, *J. Amer. Chem. Soc.*, **90**, 3930 (1968).

[5] E. E. Ferguson, *J. Chim. Phys.*, 257 (1964).

[6] H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

[7] R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952). For a recent review, see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[8] Paper I: M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

[9] O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **12**, 1146 (1958); **13**, 1781 (1959).

Theory

A. Intensity Enhancements. The starting point for this theory will be the result of Person's vibronic analysis of these complexes.[6] The transition moment for the *l*th vibration in the charge-transfer complex was shown to be

$$\mu_{\mathrm{N1,N0}} = \left(\frac{\partial \mu}{\partial Q_l}\right)_0 + 2\mu_{00}a_0\left(\frac{\partial a}{\partial Q_l}\right)_{Q_l=0} + 2\mu_{11}b_0\left(\frac{\partial b}{\partial Q_l}\right)_{Q_l=0} + \left[2a_0\left(\frac{\partial b}{\partial Q_l}\right) + 2b_0\left(\frac{\partial a}{\partial Q_l}\right)\right]\mu_{01} \quad (2)$$

where a_0 and b_0 are the coefficients defined in eq 1 and where μ_{00}, μ_{11}, and μ_{01} are the corresponding dipole matrix elements. The first term in eq 2 is the change in dipole moment if there is no mixing of the dative state and the last three terms give the delocalization moment due to the electronic rearrangements between donor and acceptor during a vibration.

For homonuclear halogens as acceptors, it is generally assumed that $(\partial\mu/\partial Q)_0 = 0$ and all of the intensity is then due to the delocalization moment. A consideration of the model discussed above indicates that this is not the case, however, and electrostatic contributions should be subtracted from the observed transition dipoles to obtain the delocalization contribution. We now wish to estimate the electrostatic contribution to the intensities of aromatic halogen complexes.

Consider a halogen molecule placed in the nonlinear electric field due to the quadrupole potential of an adjacent benzene ring. The situation for the four halogens to be considered is shown in Figure 1. To treat infrared intensities we assume that the parallel component of the polarizability tensor can be divided into two equal atomic contributions located at the halogen atoms.[10] The induced dipole moment is then

$$\mu_i = {}^1\!/_2\alpha_{\parallel}(E_1 + E_2) \quad (3)$$

where E_1 and E_2 are the electric field strengths at atoms 1 and 2 and where $\alpha_{\parallel}$ is the component of polarizability along the halogen bond. As the halogen molecule vibrates there will be two contributions to a change in the induced moment: a contribution due to the change of polarizability upon vibration and a contribution due to the fact that atoms 1 and 2 experience different fields. Thus

$$\left(\frac{\partial \mu_i}{\partial Q}\right)_0 = {}^1\!/_2(E_1 + E_2)\left(\frac{\partial \alpha_{\parallel}}{\partial Q}\right) + {}^1\!/_2\alpha_{\parallel}\left[\left(\frac{\partial E_1}{\partial Q}\right) + \left(\frac{\partial E_2}{\partial Q}\right)\right] \quad (4)$$

The importance of the first term in eq 4 was originally discussed by Condon in a discussion of the possibility of an electric field induced infrared spectrum,[11] a possibility verified later by the experiments of Crawford and Dagg.[12] This term is, of course, present in uniform fields while the second term in eq 4 vanishes for uniform or linear fields. It is important to point out here that eq 4 represents a way of calculating, for a specific orientation, one of the contributions responsible for the pressure-induced infrared spectrum of homonuclear diatomics.[13] There is an additional contribution to the infrared intensity in pressure-broadening studies that should also be important in donor–acceptor complexes—the contribution due to the mutual repulsion of electron clouds. This is a short-range interaction which depends on the overlap between the electronic wave functions of the two partners in the complex. For molecular hydrogen and deuterium these two sources make about equal contributions to the infrared intensity.[13,14] It is not at present clear how this overlap repulsion contribution should be handled for complex molecules like benzene and halogens, so it will be neglected in what follows.[15] This means that eq 4 may underestimate the noncharge-transfer contributions to $(\partial\mu_i/\partial Q)_0$.

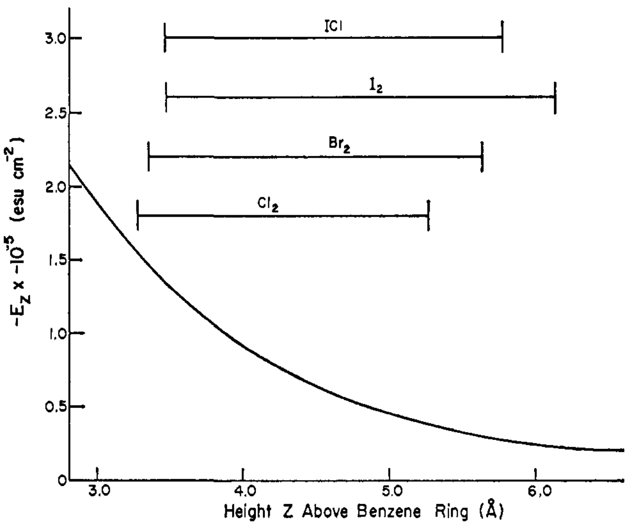

Figure 1. A plot of the electric field intensity along the sixfold axis of benzene as a function of distance above or below the benzene plane. The positions of the halogen molecules above the benzene plane are also given.

For ICl there is a permanent dipole moment and a nonvanishing value of $(\partial\mu/\partial Q)_0$ even in the absence of an electric field. Contributions from the effects discussed above will be in addition to the contribution from the permanent moment.

In Figure 1 the electric field strength is plotted *vs.* Z, the distance above the plane of the ring along the benzene hexagonal axis. For computational purposes it will be more convenient to write the last term in eq 4 in terms of derivatives with respect to Z. We thus have

$$\left(\frac{\partial E_1}{\partial Q}\right)_{Q=0} = -{}^1\!/_2\left(\frac{\partial E}{\partial Z}\right)_{Z_1} \quad (5a)$$

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[10] For a discussion of this point, see ref 8. ICl is an exception, of course, and here the polarizability is not divided equally.

[11] E. U. Condon, *Phys. Rev.*, 41, 759 (1932).

[12] M. F. Crawford and I. R. Dagg, *ibid.*, 91, 1569 (1953).

[13] J. Van Kranendonk, *Physica*, 24, 347 (1958). For a discussion of recent theory and experiments in this field, see R. G. Gordon and J. K. Cashion, *J. Chem. Phys.*, 44, 1190 (1966).

[14] S. Paddi Reddy and C. W. Cho, *Can. J. Phys.* 43, 793 (1965).

[15] In experimental studies this contribution is usually obtained by subtracting the calculated quadrupole-induced dipole contribution from the experimental value. The question might be raised as to whether this contribution is not identical with the delocalization moment part of eq 2. These are two different effects, however, the one involving a mutual repulsion of the electrons on the two partners, the other involving an electron transfer between partners. The situation is analogous to the exchange repulsion and charge-transfer contributions to intermolecular potential energies. Both depend on the same power of the overlap integrals, but they are different effects tending to cancel one another. For induced infrared spectra in benzene–halogen complexes they reinforce one another.

$$\left(\frac{\partial E_2}{\partial Q}\right)_{Q=0} = {}^1/_2\left(\frac{\partial E}{\partial Z}\right)_{Z_1} \tag{5b}$$

and eq 4 then becomes

$$\left(\frac{\partial \mu_i}{\partial Q}\right)_0 = {}^1/_2(E_1 + E_2)\left(\frac{\partial \alpha_{||}}{\partial Q}\right) - {}^1/_4\alpha_{||}\left[\left(\frac{\partial E}{\partial Z}\right)_{Z_1} - \left(\frac{\partial E}{\partial Z}\right)_{Z_2}\right] \tag{6}$$

B. Frequency Shifts. Placing a diatomic molecule in a nonuniform electric field will modify its potential energy function and, therefore, the frequency of vibrational transitions. To treat this effect semiquantitatively we assume the following.

1. The potential energy function for the molecule with electrostatic interactions can be written as the sum of a Morse potential energy function for the unperturbed molecule, $V_M(Q)$, and an electrostatic potential energy function, $V_{el}(Q)$. Thus

$$V(Q) = V_M(Q) + V_{el}(Q) = D(1 - e^{\beta Q})^2 + V_{el}(Q) \tag{7}$$

2. Both parts of the potential energy function can be expanded in a power series about the equilibrium internuclear distance in the absence of electrostatic interactions. Thus

$$V(Q) = V_M(0) + V_{el}(0) + \left(\frac{\partial V_{el}}{\partial Q}\right)_{Q=0} + {}^1/_2\left[\left(\frac{\partial^2 V^M}{\partial Q^2}\right) + \left(\frac{\partial^2 V_{el}}{\partial Q^2}\right)_{Q=0}\right]Q^2 + \ldots \tag{8}$$

Such an expansion will be good as long as the electrostatic contributions are small, a condition certainly satisfied in the benzene halogen complexes.

The two most important things to notice from eq 8 are that the electrostatic interactions introduce a term in the expansion linear in vibrational coordinate and a correction to the force constant. (There will be a correction to the anharmonicity constant and to higher derivatives as well, but these corrections will be neglected in this work.) The presence in eq 8 of the term linear in Q means, of course, that the electrostatic interactions change the internuclear distance somewhat from its unperturbed equilibrium value. In the development that follows we will examine the effect of the term linear in Q by solving the Schroedinger equation for a Morse oscillator with such a linear term included. It will be shown that this term will always give a red shift if the quantity $(\partial V_{el}/\partial Q)_{Q=0}$ is negative. The correction to the force constant will then be estimated independently.

The solution to the problem of a Morse oscillator with linear Q term has been used by Coggeshall to calculate infrared frequency shifts in hydrogen-bonded alcohols,[16] and is formally identical with solving the quantum mechanical problem of a Morse oscillator with the inclusion of vibration rotation interaction.[17] Using a potential function of the form

$$V = D(1 - e^{-\beta Q})^2 - V_E Q \tag{9}$$

where D is the dissociate energy from the potential minimum and where

$$-V_E = (\partial V_{el}/\partial Q)_{Q=0} \tag{10}$$

the Schroedinger equation becomes

$$\frac{d^2\psi_v}{dQ^2} + \frac{2\mu}{\hbar^2}[W - D(1 - e^{-\beta Q})^2 + V_E Q]\psi_v = 0 \tag{11}$$

After considerable algebraic manipulation,[17] one obtains the energy level expression

$$W(V_E,v) = \left[D + C_0 - \frac{(D - {}^1/_2C_1)^2}{D + C_2} + \frac{\beta\hbar(D - {}^1/_2C_1)}{\pi[2\mu(D + C_2)]^{1/2}}(v + {}^1/_2) - \frac{\beta^2\hbar^2}{2\mu}(v + {}^1/_2)^2\right. \tag{12}$$

where $C_0 = ({}^3/_2)(V_E/\beta)$, $C_1 = 2(V_E/\beta)$, and $C_2 = -{}^1/_2(V_E/\beta)$. The corresponding expression for the unperturbed Morse oscillator is

$$W(v) = \frac{\beta\hbar D}{\pi(2\mu D)^{1/2}}(v + {}^1/_2) - \frac{\beta^2\hbar^2}{2\mu}(v + {}^1/_2)^2 \tag{13}$$

Comparing eq 12 and 13 it can be seen that a potential energy term linear in Q will shift all levels by an amount given by the first term in eq 11 and will affect the transition energy as well. For comparison with experiment the difference in the transition energy between the $v = 0$ and $v = 1$ vibrational levels of the perturbed and unperturbed Morse oscillators will be needed. This difference is

$$\Delta W_{0\rightarrow 1} = W(V_E)_{0\rightarrow 1} - W_{0\rightarrow 1} = \frac{\beta\hbar(D - {}^1/_2C_1)}{\pi[2\mu(D + C_2)]^{1/2}} - \frac{\beta\hbar D}{\pi(2\mu D)^{1/2}} \tag{14a}$$

$$= \frac{\beta\hbar}{\pi(2\mu)^{1/2}} \times \frac{D^{1/2}[1 - (1 - C_2/D)^{1/2}] - {}^1/_2C_1/D^{1/2}}{(1 + C_2/D)^{1/2}} \tag{14b}$$

Assuming that $C_2/D \ll 1$ and expanding the square roots in a Maclaurin series one obtains

$$\Delta W_{0\rightarrow 1} = -\frac{\beta h}{2\pi(2\mu D)^{1/2}}(C_1 + C_2) \tag{15}$$

$$= -\frac{3}{4\pi}\frac{h}{(2\mu D)^{1/2}}V_E \tag{16}$$

Thus the contribution to the frequency shift from the linear term in eq 8 is directly proportional to V_E.

We now wish to evaluate this linear term contribution as well as the change in the force constant $(\partial^2 V_{el}/\partial Q^2)_{Q=0}$. The expression for the energy of a homonuclear diatomic molecule in an electric field is approximated by

$$V_{el} = -({}^1/_4)\alpha_{||}(E_1^2 + E_2^2) - {}^1/_2\Theta_A E'_A \tag{17}$$

where Θ_A and E_A' are the molecular quadrupole moment of the halogen and the electric field gradient at the center of the halogen bond. The justification of the first term was discussed in paper I.[8] The term due to the quadrupole interaction in eq 17 will contribute to both the first and second derivatives in eq 8, but since the authors can find no information on values of

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[16] N. D. Coggeshall, *J. Chem. Phys.*, 18, 978 (1950).

[17] L. Pauling and E. B. Wilson, "Introduction to Quantum Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p 271 ff.

Table I. Calculated Values of the Electrostatic Contribution to the Infrared Intensity of Benzene–Halogen Complexes along with the Necessary Parameters for the Calculation

Halogen	$-(E_1 + E_2)$,[a] esu cm^{-2} $\times 10^{-5}$	$(\partial E/\partial Z)_{Z_1}$,[a] esu cm^{-3} $\times 10^{-13}$	$(\partial E/\partial Z)_{Z_2}$,[a] esu cm^{-3} $\times 10^{-13}$	α_{11},[a] cm^3 $\times 10^{25}$	$(\partial\alpha/\partial R)_0$,[b] cm^2 $\times 10^{16}$	μ_A, amu	$(\partial\mu/\partial Q)_0$, esu amu$^{-1/2}$ $\times 10^{10}$	$(\partial\mu/\partial Q)_0$[c] (expt)
Cl_2	1.94	1.13	0.24	66	11.2	17.49	0.30	0.20
Br_2	1.77	1.07	0.18	99.5	14.8	39.96	0.24	0.32
I_2	1.57	1.00	0.13	175	20.7	63.47	0.26	0.17
ICl	1.63	1.00	0.17	136	14.3	27.42	0.30	0.67

[a] Taken from data in ref 8. [b] Calculated using a δ function model; see ref 20. [c] Taken from ref 6.

Table II. Calculated Values of the Frequency Shift Due to the Linear Term in the Potential Energy Expansion and of the Fractional Change in the Force Constant, along with the Necessary Parameters

Halogen	$(E_1^2 + E_2^2)$,[a] esu^2 cm^{-4} $\times 10^{-10}$	$\partial(E_1^2 + E_2^2)/\partial R$,[a] esu^2 cm^{-5} $\times 10^{-18}$	$-V_E \times 10^6$ erg cm^{-1}	$\Delta W_{0\rightarrow 1}{}^L$, cm^{-1}	$(\partial^2\alpha_{\|}/\partial R^2)$,[b] cm $\times 10^6$	$\Delta k \times 10^{-4}$, dyn cm^{-1}	$\Delta k/k_0$[c]	$\Delta k/k_0$[d] (expt)	$\Delta k/k_0$[e] (expt)
Cl_2	2.55	1.66	10.0	−5.2	16.9	0.22	−0.021	−0.120	−0.040
Br_2	2.23	1.50	12.0	−4.6	19.7	−0.25	−0.032	−0.091	−0.025
I_2	1.87	1.32	15.5	−5.4	23.4	−0.29	−0.053	−0.072	−0.010
ICl	1.90	1.30	15.5	−6.9	18.5	−0.27	−0.036	−0.121	−0.079

[a] From the data given in ref 8. [b] Calculated using δ function model; see ref 19. [c] k_0 values calculated from extrapolated vibrational frequencies given in ref 21. [d] Calculated using values of ν_0 given by Herzberg.[21] [e] Calculated using values of ν_0 in an inert solvent.[6]

$(\partial\Theta/\partial Q)$ and $(\partial^2\Theta/\partial Q^2)$, the effect of these terms will have to be neglected. Since the quadrupole–quadrupole contribution makes a nonnegligible contribution to the energy of formation of the complex,[18] it may also be important for frequency shifts.

It follows directly from eq 8 and 17

$$-V_E = \left(\frac{\partial V}{\partial Q}\right)_{Q=0} = -{}^1/_4\left\{(E_1{}^2 + E_2{}^2)\left(\frac{\partial\alpha_{\|}}{\partial Q}\right)_{Q=0} + \alpha_{\|}\left[\frac{\partial(E_1{}^2 + E_2{}^2)}{\partial Q}\right]\right\}_{Q=0} \tag{18}$$

$$\Delta k = \left(\frac{\partial^2 V}{\partial Q^2}\right)_{Q=0} - \left(\frac{\partial^2 V_0}{\partial Q^2}\right)_{Q=0} = -{}^1/_4\left\{(E_1{}^2 + E_2{}^2)\left(\frac{\partial^2\alpha_{\|}}{\partial Q^2}\right)_{Q=0} + 2\left(\frac{\partial\alpha_{\|}}{\partial Q}\right)_{Q=0}\left[\frac{\partial(E_1{}^2 + E_2{}^2)}{\partial Q}\right]_{Q=0} + \alpha_{\|}\left[\frac{\partial^2(E_1{}^2 + E_2{}^2)}{\partial Q^2}\right]_{Q=0}\right. \tag{19}$$

For ICl there will be an additional contribution to the electrostatic potential energy of the form

$$V_{el}{}^{ICl} = q(\phi_1 - \phi_2) \tag{20}$$

where q is the atomic charge on atoms 1 and 2 that accounts for the permanent dipole moment and where ϕ_1 and ϕ_2 are the electrostatic potentials at atoms 1 and 2, respectively. Contributions to V_E and to Δk come about because ϕ changes as the molecule vibrates. Since the polarizability and its derivatives can no longer be divided equally between the two atoms in ICl, a weighting procedure similar to that used in paper I was used for these quantities. Equations 18 and 19 must be modified appropriately to account for these unequal atomic contributions.

Results and Discussion

The calculated values of the electrostatic contributions to the infrared intensities and frequency shifts for the benzene–halogen complexes are given in Tables I and II along with the necessary parameters. Values of $(\partial\alpha_{\|}/\partial Q)$ are, in principal, obtainable from Raman studies of the halogens but such data do not appear to have been measured. In the absence of these data we have used the δ function model developed by Lippincott and coworkers[19] to estimate these quantities. For a large number of compounds, this model gives agreement with experiment within 30%.[20] This model has also been used to estimate $(\partial^2\alpha_{\|}/\partial Q^2)$ needed to calculate the change in the force constant. In this case there is no way to estimate the accuracy of the result but it should give the correct order of magnitude and reflect trends in the series of halogens.

Comparison of these data with experimental values is difficult because of uncertainties in both the experimental data and in the parameters used for the electrostatic calculations. In addition there is uncertainty as to which experimental number to use. The results of the electrostatic model should be compared with changes in the infrared spectrum in going from a state in which the halogens are present in the gas phase at low pressure to one where the halogen is present in the pure complex in the gas phase at low pressure. While the appropriate data for the former state are known, those for the latter are not.

The comparison of calculated and experimental intensity enhancements should not be influenced by this reference state problem since the halogen stretching vibration is not observed in solutions of nonpolar and noncomplexing solvents. The comparisons of frequency shift data will be influenced by the reference state since there are infrared shifts observed in going from the gas to the liquid phase.

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(18) M. W. Hanna, P. J. Trotter, and J. L. Lippert, submitted for publication.

(19) See E. R. Lippincott, J. M. Stutman, and G. Nagarajan, *J. Phys. Chem.*, 70, 78 (1966), and references therein.

(20) E. R. Lippincott and G. Nagarajan, *Bull. Soc. Chim. Belges*, 74, 551 (1965).

It can be seen from Table I that the electrostatic model is capable of accounting for essentially all of the intensity enhancement in these complexes. Making a different approximation about the distribution of polarizability along the bond axis would reduce the values given in Table I by 13–15%, but even if this was done and if the polarizability derivatives were reduced by 30%, the calculated intensities would still account for a substantial portion of the observed enhancements. Thus the conclusion seems inescapable that electrostatic interactions make an appreciable contribution to the infrared intensity of the halogen stretching mode in benzene–halogen complexes.

The interpretation of the frequency shift due to electrostatic interactions is more complicated since in the present computational model there are two contributions to this shift. The first contribution is a red shift of about 5 cm^{-1} for the homonuclear halogens and about 7 cm^{-1} for ICl which comes from the coefficient of the term linear in the normal coordinate. The second contribution is a 2–5% decrease in the force constant. The calculated quantities are compared with experimental data in the following way. First, the observed shift is taken to be the difference between the observed absorption maximum in complexing media and the corresponding quantity in two different reference states—gas-phase values given by Herzberg[21] and values in an inert solvent given by Friedrick and Person.[6] Second, the linear contribution is subtracted from the total shift. Third, the remaining shift is used to calculate Δk. It can be seen from Table II that electrostatic contributions are again of the correct magnitude and, therefore, make important contributions to these frequency shifts. The detailed agreement is not good because of uncertainties in both the theoretical and experimental quantities, but it is probably fair to say that electrostatic contributions can account for between 20 and 80% of the total effect.

The agreement between calculated and experimental parameters for ICl is considerably worse than for the other halogens. There are at least two contributions to this poorer agreement. The first is that the approximation scheme used for evaluating the polarizability and its derivatives at the near and far atoms is more subject to error. The second is that the same intermolecule distance was used for benzene–ICl as was used for benzene–I_2. Since benzene–ICl is an appreciably stronger complex than benzene–I_2, it is probable that its intermolecular distance is smaller. This would lead to a substantial increase in the values of the intensity enhancement and the frequency shift.

Finally, it should be pointed out that the agreement reported in this work was accomplished essentially without parametrization. Electrostatic potentials and fields were calculated from a reasonable, albeit simplified, charge distribution in the benzene ring.[8] Polarizabilities were obtained from experimental data and polarizability derivatives were estimated by a semiempirical method not at all related to the present calculation. The order of magnitude agreement between calculated electrostatic contributions to intensity enhancements and frequency shifts with corresponding experimentally measured values becomes more suggestive of the importance of electrostatic interactions because of this.

The following conclusions can be drawn from this work.

1. Electrostatic interactions cannot be neglected in treating infrared effects in donor–acceptor complexes. This conclusion, no doubt, also applies to hydrogen-bonding systems where similar effects have been observed.

2. The contribution of charge-transfer resonance to the ground state of benzene–halogen complexes has been overestimated in the past.

3. More accurate experimental data and theoretical calculations are necessary before the relative contributions of electrostatic and charge-transfer effects to changes in the infrared spectrum can be unraveled.

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(21) G. Herzberg, "The Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950.