

## Electric dipole moment and quadrupole hyperfine structure of OC–HCl and OC–DCI

R. S. Altman, M. D. Marshall, W. Klemperer, and Andrei Krupnov

Citation: *The Journal of Chemical Physics* **79**, 52 (1983); doi: 10.1063/1.445511

View online: <http://dx.doi.org/10.1063/1.445511>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/79/1?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

Nuclear quadrupole hyperfine structure in the microwave spectrum of HCl–N<sub>2</sub>O : Electric field gradient perturbation of N<sub>2</sub>O by HCl

*J. Chem. Phys.* **121**, 237 (2004); 10.1063/1.1756871

Molecular g values, magnetic susceptibility anisotropies, and molecular quadrupole moments in 1 5N<sub>2</sub>–HF, 1 5N<sub>2</sub>–DF, OC–HF, OC–DF, and OC–HCl van der Waals complexes

*J. Chem. Phys.* **78**, 6515 (1983); 10.1063/1.444691

Magnetic Susceptibility Anisotropy, Molecular Quadrupole Moment, and the Sign of the Electric Dipole Moment in OCS

*J. Chem. Phys.* **50**, 1714 (1969); 10.1063/1.1671264

Quadrupole Moment of OCS

*J. Chem. Phys.* **41**, 2201 (1964); 10.1063/1.1726232

Infrared Line and Band Strengths and Dipole Moment Function in HCl and DCI

*J. Chem. Phys.* **26**, 1671 (1957); 10.1063/1.1743604

---

An advertisement for AIP Applied Physics Reviews. It features a blue background with a molecular model of a crystal lattice. On the left, there is a small image of the journal cover. The main text reads 'NEW Special Topic Sections' in large white letters. Below this, it says 'NOW ONLINE' in orange, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

AIP Applied Physics Reviews

# NEW Special Topic Sections

**NOW ONLINE**  
Lithium Niobate Properties and Applications:  
Reviews of Emerging Trends

AIP Applied Physics Reviews

# Electric dipole moment and quadrupole hyperfine structure of OC-HCl and OC-DCI<sup>a)</sup>

R. S. Altman, M. D. Marshall, and W. Klemperer

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Andrei Krupnov

Institute of Applied Physics, Academy of Sciences, 603 600 Gorky, USSR

(Received 14 February 1983; accepted 25 March 1983)

Microwave and radio frequency spectra of the weakly bound complex OC-HCl and two of its isotopes measured in static electric field are reported. The values of the dipole moments and the hyperfine constants determined are

	OC-H <sup>35</sup> Cl	OC-H <sup>37</sup> Cl	OC-D <sup>35</sup> Cl
$\mu_a$ (D)	1, 517 83(6)	1, 518 23(26)	1, 562 31(18)
$eqQ_a^{C1}$ (MHz)	-52, 071 9(14)	...	-55, 247 3(7)
$eqQ_a^D$ (MHz)	...	...	0, 150 9(32)

This molecular complex is shown to have a significant induced dipole moment which is much larger than elementary electrostatic calculations predict. The ratio of the electric quadrupole coupling constant in the DCI complex to that of free DCI is shown to be the same using either the chlorine or the deuterium, indicating no measurable distortion in the electric field gradient at the deuterium nucleus.

## INTRODUCTION

Recently, Flygare *et al.*<sup>1</sup> have measured the microwave spectrum of the weakly bound complex formed between carbon monoxide and hydrogen chloride. They found the molecular geometry of the complex to be linear and hydrogen bonded. The hydrogen bond is formed at the carbon end of the CO, namely the atomic order is OC-HCl for this complex. From the value of the bond stretching force constant, they also have shown that this molecule is rather strongly bound. Collected in Table I are the bond stretching force constants of HCl complexes. We notice that the weak bond in OC-HCl is relatively strong.

Another class of carbon monoxide complexes is the metal carbonyls.<sup>2</sup> There are several similarities between these complexes and the weakly bound "carbonyl" complex of OC-HCl. The bond formed with the metal is typically made to the carbon end of the CO molecule as in CO bound to HX (X = F, Cl, Br) and BF<sub>3</sub>. Carbon monoxide as a ligand in these metal carbonyls retains its basic molecular structure. The bond between the metal atom and the carbon monoxide is always seen to be linear. Although there is no chemical bond formed between CO and HCl, the geometry of the weak bond parallels the metal carbonyl bond.

A further comparison of weakly bound CO complexes is obtained for CO bound to BF<sub>3</sub>,<sup>3</sup> a B-C bond is formed to give the complex C<sub>3v</sub> symmetry. The complex of argon bound to BF<sub>3</sub> was also studied. As seen in Table I, the stretching force constant of ArBF<sub>3</sub> is over twice

that of ArHCl while the stretching force constant for OC-BF<sub>3</sub> is about the same as that of OC-HCl. BF<sub>3</sub> is thought to be a strong Lewis acid, certainly stronger than HCl, and this is seen to be the case with argon. Yet with CO both HCl and BF<sub>3</sub> form a weak bond with similar strength. It would appear to us that since there is a large induced dipole moment in OC-BF<sub>3</sub> of 0.482 D, a large induced dipole moment most likely exists in the OC-HCl complex. Measurement of this electrical distortion is a primary purpose of the present study.

Recently an *ab initio* SCF-MO study was performed on complexes between CO and HCl<sup>4</sup> (as well as HF). In this study the optimized geometry of lowest energy corresponded to the system with a linear hydrogen bonded structure. Calculations were done on the oxygen-hydrogen bond form as well as the carbon-hydrogen bond form. The isomer with the carbon-hydrogen bond, the isomer seen in the experiment, had the lower total energy with the energy difference between the isomers being only 17 cm<sup>-1</sup>. This theoretical study includes a dipole moment calculation for the complex which can be tested against experiment.

## EXPERIMENTAL

Microwave ( $\Delta J = 1$ ) and radio frequency ( $\Delta J = 0$ ) spectra were taken using a Rabi-type molecular beam electric resonance spectrometer which is operated in the flopout mode.<sup>5</sup> The spectrometer is equipped with a supersonic nozzle source and a mass spectrometer detector. The three electric fields in the spectroscopy region (A, B, C) have recently been rebuilt. The quadrupolar A and B fields each have lengths of 33 cm and the rod diameter is 0.500 cm. The C field (resonance

<sup>a)</sup>Research supported by the National Science Foundation.

TABLE I. Bond stretching force constants for molecular complexes of hydrogen chloride.

Complex	Structure	$k_s$ (mdyn/Å)
Ne DCl <sup>a</sup>	$C_{\infty v}$	0.0038
Ar HCl <sup>b</sup>	$C_{\infty v}$	0.012
Kr HCl <sup>c</sup>	$C_{\infty v}$	0.016
Xe HCl <sup>d</sup>	$C_{\infty v}$	0.017
HF HCl <sup>e</sup>	$C_{\infty v}$	0.057
CO <sub>2</sub> HCl <sup>f</sup>	$C_{\infty v}$	0.014
OC HCl <sup>g</sup>	$C_{\infty v}$	0.045
C <sub>2</sub> H <sub>2</sub> HCl <sup>h</sup>	$C_{2v}$	0.069
C <sub>2</sub> H <sub>4</sub> HCl <sup>i</sup>	$C_{2v}$	0.066
Ar BF <sub>3</sub> <sup>j</sup>	$C_{3v}$	0.029
OC BF <sub>3</sub> <sup>j</sup>	$C_{3v}$	0.050

<sup>a</sup>A. E. Barton, D. J. B. Howlett, and B. J. Howard, *Mol. Phys.* **41**, 619 (1980).

<sup>b</sup>Reference 6.

<sup>c</sup>A. E. Barton, T. J. Henderson, P. R. R. Langridge-Smith, and B. J. Howard, *Chem. Phys.* **45**, 429 (1980).

<sup>d</sup>K. V. Chance, K. H. Bowen, J. S. Winn, and W. Klemperer, *J. Chem. Phys.* **70**, 5157 (1979).

<sup>e</sup>Reference 9.

<sup>f</sup>R. S. Altman, M. D. Marshall and W. Klemperer, *J. Chem. Phys.* **77**, 4344 (1982).

<sup>g</sup>Reference 1.

<sup>h</sup>P. D. Aldrich, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.* **75**, 2126 (1981).

<sup>i</sup>A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Chem. Phys.* **75**, 625 (1981).

<sup>j</sup>Reference 3.

TABLE II. Stark effect data for OC-H<sup>35</sup>Cl and OC-H<sup>37</sup>Cl.

Transition	Voltage	Frequency (MHz)	Obs.-Calc. (kHz)
$JF \rightarrow J'F'$			
1 5/2 → 2 7/2	0	6687.858	0.6
1 3/2 → 2 5/2			
	150.65	6687.835	-1.3
1 5/2 → 2 7/2	250.64	6687.667	-3.4
2 3/2	329.96	6687.278	-1.9
	400.30	6686.613	0.7
	450.19	6685.905	-0.9
	500.02	6684.988	-0.2
2 1/2 → 5/2	150.00	22.269	0.2
	400.02	22.067	-0.1
$M_F = 1/2$	600.02	22.129	-1.4
	700.03	22.412	-0.3
1 1/2 → 1 3/2,	150.00	23.780	1.9
	300.03	25.225	1.1
$M_F = 1/2$	500.07	30.816	-2.1
	600.05	35.647	0.8
OC-H <sup>37</sup> Cl			
1 5/2 → 2 7/2	0	6534.322	2.1
1 3/2 → 2 5/2			
	250.55	6534.079	2.2
1 5/2 → 2 7/2	400.03	6532.712	-3.0
2 3/2	499.86	6530.769	1.3

TABLE III. Stark effect of the  $J=1 \rightarrow 2$ ,  $F_1=5/2 \rightarrow 7/2$ ,  $M_{F_1}=3/2$  transition in OC-D<sup>35</sup>Cl.

Voltage	Frequency (MHz)	Obs.-Calc. (kHz)
0	6704.253	-0.2
150.05	6704.266	-0.2
250.03	6704.057	-0.5
325.04	6703.681	1.1
425.02	6702.612	9.1

region) has a length of 12.7 cm.

The complex OC-HCl was prepared by expanding a gas mixture, 7% HCl, 25% CO, and 68% argon through a 25  $\mu$  orifice. The stagnation pressure was 2 atm and the temperature was -30 °C. In these studies rotational resonances were monitored at the  $m/e=29$  (HCO<sup>+</sup>) crack for OC-H<sup>35,37</sup>Cl and the  $m/e=30$  (DCO<sup>+</sup>) crack for OC-D<sup>35</sup>Cl. The parent species of these complexes were not seen in the mass spectrum in contrast to CO<sub>2</sub>-HCl, where resonances were monitored at both the parent and the daughter (CO<sub>2</sub>H<sup>+</sup>, CO<sub>2</sub><sup>+</sup>) mass peaks with similar signal to noise ratios.

## RESULTS

Transitions were observed for three isotopic species of OC-HCl. Their frequencies and assignments are reported in Tables II, III, and IV. Both  $\Delta J=1$  microwave and  $\Delta J=0$  radio frequency transitions were used in this work. The zero-field microwave transition frequencies were generated from the spectroscopic constants determined by Flygare *et al.*<sup>1</sup> One  $J=2 \rightarrow 1$  transition (~6.7 GHz) was measured at several electric field settings for each of the three isotopes studied. Dipole moments were determined from these microwave spectra and were then used for predicting the frequencies of the radio frequency transitions. The radio frequency transitions in our experiments have a much narrower linewidth than the microwave transitions as shown in Fig. 1. The inclusion of the radio frequency lines in the analysis allows the spectroscopic constants to be determined with greater precision.

All transitions were observed with the radiation polarized parallel to the static electric field giving  $\Delta M_F = 0$  selection rules.

The Hamiltonian used to analyze the data is given below:

$$H = H_R + H_S + H_Q,$$

$H_R$  is the rigid rotor Hamiltonian,  $H_S$  contains the Stark effect term,  $\mu \cdot E$ , and  $H_Q$  accounts for the interaction of the electric quadrupole moment of the chlorine nucleus ( $I=3/2$ ) with the surrounding electric field gradient. For the complex containing DCl, an additional term is required for the quadrupole moment of the deuterium nucleus ( $I=1$ ). Matrix elements of the Hamiltonian are calculated in a coupled basis using standard techniques. The basis used is

$$F_1 = J + I_{Cl}, \quad F = F_1 + I_D,$$

TABLE IV. OC-D<sup>35</sup>Cl radio frequency transitions.

Voltage	Transition		Frequency (MHz)	Obs. - Calc. (kHz)
$J=1, F_1=3/2 \rightarrow 1/2$	$F \rightarrow F'$	$M_F$		
10.031	3/2 → 1/2	1/2	24.890	-0.6
	3/2 → 3/2	1/2		
	3/2 → 3/2	3/2		
	5/2 → 1/2	1/2	24.861	0.2
	5/2 → 3/2	1/2		
	5/2 → 3/2	3/2		
	1/2 → 1/2	1/2	24.835	-1.4
25.017	1/2 → 3/2	1/2		
	5/2 → 1/2	1/2	24.869	1.6
	5/2 → 1/2	3/2		
	5/2 → 3/2	3/2	24.859	0.2
	1/2 → 1/2	1/2	24.832	-2.4
40.028	1/2 → 3/2	1/2		
	3/2 → 1/2	1/2	24.902	0.7
	3/2 → 3/2	1/2		
	3/2 → 3/2	3/2		
	5/2 → 1/2	1/2	24.880	-0.2
	5/2 → 3/2	1/2		
	5/2 → 3/2	3/2	24.850	0.9
	1/2 → 1/2	1/2	24.824	-2.0
50.005	1/2 → 3/2	1/2		
	3/2 → 1/2	1/2	24.913	0.3
	3/2 → 3/2	1/2		
	3/2 → 3/2	3/2		
150.00	5/2 → 1/2	1/2	24.892	-0.7
	5/2 → 3/2	1/2		
	5/2 → 3/2	3/2		
300.04	3/2 → 3/2	1/2	25.228	-3.2
399.98	5/2 → 1/2	1/2	26.741	-0.3
	5/2 → 3/2	1/2	28.974	0.5
$J=2, F_1=5/2 \rightarrow 1/2$				
25.000	7/2 → 3/2	1/2	23.673	0.6
	5/2 → 3/2	1/2	23.660	-0.2
	5/2 → 3/2	1/2		
	5/2 → 3/2	3/2		
150.02	7/2 → 3/2	1/2	23.632	-0.7
	5/2 → 3/2	1/2	23.623	-0.2
	5/2 → 1/2	1/2		
	5/2 → 3/2	3/2		

where  $J$  is the rotational angular momentum of the complex and  $I$  is the nuclear spin angular momentum. The matrix includes coupling to rotational states with the  $J$  quantum number two less than the lowest  $J$  state of interest and to states with  $J$  two greater than the highest  $J$  of interest. Inclusion of additional rotational states did not affect the numerical values of the energies obtained by diagonalization.

The spectroscopic constants were determined using a nonlinear least squares fit to the data and they are given in Table V. Also included in the table is a measure of the angle between the HCl subunit and the  $a$  axis of the complex. This angle is calculated from the following equation<sup>6</sup>:

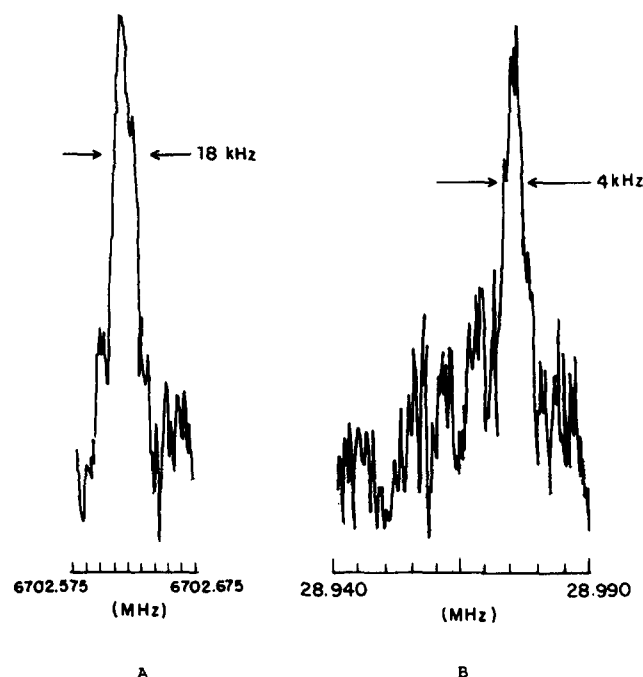


FIG. 1. Comparison of linewidths in the microwave and radio frequency regions. Both of these transitions are in OC-DCI. The microwave spectrum A is the  $J=2 \rightarrow 1, F_1=7/2-5/2, M_{F_1}=3/2$  transition measured at 425.02 V/cm. The radio frequency spectrum B is the  $J=1, F_1=5/2-3/2, M_F=1/2$  transition measured at 399.98 V/cm. From the observed (typical) linewidths, it is apparent that the resolution of the spectrometer is greater in the radio frequency region.

$$eqQ_a^{Cl \text{ or } D} = eqQ_{fr \dots \text{molecule}}^{Cl \text{ or } D} \frac{(3 < \cos^2 \theta > - 1)}{2}. \quad (1)$$

The utility of low  $J$  radio frequency transitions in determining the quadrupole coupling constant of deuterium is graphically depicted in Fig. 2. The figure shows the electric field dependence of the components of the  $J=1, F_1=1/2-3/2, \Delta M_F=0$  transition. This transition is split into three components at zero field by the hyperfine interaction of the deuterium. Application of a homogeneous dc Stark field in the resonance region further split the transitions into various  $M_F$  components. As  $J$  increases, the analogous set of radio frequency transitions becomes much more complicated.

## DISCUSSION

As in CO<sub>2</sub>-HCl, there is quite a large induced dipole moment in OC-HCl. If the induced dipole moment is

TABLE V. Spectroscopic constants of OC-HCl.

	OC-H <sup>35</sup> Cl	OC-H <sup>37</sup> Cl	OC-D <sup>35</sup> Cl
$\mu_a$ (D)	1.51783(6)	1.51823(36)	1.56231(18)
$eqQ_a^{Cl}$ (MHz)	-52.0719(14) -52.086(9) <sup>a</sup>	-41.070 <sup>a</sup>	-55.2473(7) -55.254(7) <sup>a</sup>
$eqQ_a^D$ (MHz)	...	...	0.1509(32)
$\theta_a^{Cl}$	23.05	23.02 <sup>a</sup>	20.28
$\theta_a^D$	...	...	21.11(1)

<sup>a</sup>This is the value reported in Ref. 1.

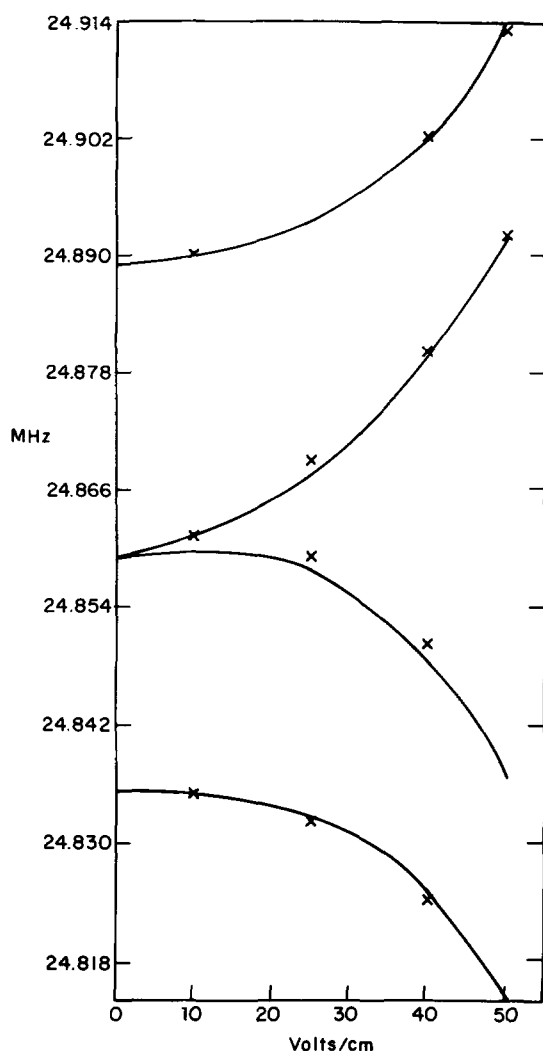


FIG. 2. The electric field dependence of the transition frequencies for the components of the  $J=1, F_1=1/2 \rightarrow 3/2, \Delta M_F=0$  radio frequency spectrum. The transition is split into three components at zero electric field by the spin of the deuterium. The application of a homogeneous dc Stark field splits the transitions into various  $M_F$  components. The measured transition frequencies are indicated by the 'x's on the graph. The fitted curves are shown also.

taken as

$$\mu_{\text{ind}} = \mu_{\text{OC-HCl}} - (\mu_{\text{HCl}} \cos \theta + \mu_{\text{CO}}) \quad (2)$$

then for OC-HCl and OC-DCI  $\mu_{\text{ind}}$  is equal to 0.39 and

TABLE VI. Dipole moment comparison.<sup>a</sup>

	OC-HCl	OC-DCI	OC-BF <sub>3</sub> <sup>b</sup>	CO <sub>2</sub> -HCl <sup>c</sup>
$\mu_a$	1.5178	1.5623	0.592	1.4509
$\mu_{\text{multipole}}$	1.303	1.327	...	1.251
$\mu_{\text{induced}}$	0.388	0.418	0.482	0.446
$\mu_{\text{induced}}^{\text{SCF}}$ (OC-HCl)	-0.112	...	...	...
$\mu_{\text{induced}}^{\text{SCF}}$ (CO-HCl)	0.254	...	...	...

<sup>a</sup>All values are in Debye units.

<sup>b</sup>Reference 3.

<sup>c</sup>R. S. Altman, M. D. Marshall, and W. Klemperer, J. Chem. Phys. 77, 4344 (1982).

TABLE VII. Electrostatic properties.

	H <sup>35</sup> Cl	D <sup>35</sup> Cl	<sup>12</sup> C <sup>16</sup> O
$\mu$ (D)	1.109 <sup>a</sup>	1.103 <sup>a</sup>	0.1098 <sup>b</sup>
$\Theta$ (D Å)	3.74 <sup>c</sup>	3.67 <sup>d</sup>	...
$\frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ (Å <sup>3</sup> )	2.6 <sup>e</sup>	f	1.977 <sup>e</sup>
$\alpha_{\parallel} - \alpha_{\perp}$ (Å <sup>3</sup> )	0.23 <sup>h</sup>	f	0.532 <sup>e</sup>

<sup>a</sup>E. W. Kaiser, J. Chem. Phys. 53, 1686 (1970).

<sup>b</sup>J. S. Muentzer, J. Mol. Spectrosc. 55, 490 (1975).

<sup>c</sup>F. H. Deleew and A. Dymanus, J. Mol. Spectrosc. 48, 427 (1973).

<sup>d</sup>Calculated from the moment of HCl.

<sup>e</sup>N. J. Bridge and A. D. Buckingham, Proc. R. Soc. London Ser. A 295, 334 (1966).

<sup>f</sup>The value for HCl is used.

<sup>g</sup>M. P. Bogaard and B. J. Orr, MTP International Review of Science, Physical Chemistry, Series Two, Vol. 2. Molecular Structure and Properties, edited by A. D. Buckingham (Butterworths, London, 1975), Chap. 5.

<sup>h</sup>D. W. Johnson and N. F. Ramsey, J. Chem. Phys. 67, 941 (1977).

0.42 D, respectively, as seen in Table VI. The only other weakly bound carbon monoxide complex for which the dipole moment was measured is OC-BF<sub>3</sub>, where the induced dipole moment is 0.48 D, which also is quite large. Multipolar calculations for the dipole moment of OC-HCl were performed using the following equation with the constants given in Table VII<sup>7</sup>:

$$\begin{aligned} \mu_a \approx & \mu_{\text{HCl}} \cos \theta_{\text{HCl}} \left[ 1 + \frac{2\alpha_{\parallel\text{CO}}}{R_{\text{c.m.}}^3} \right] \\ & + 3\Theta_{\text{HCl}} \left[ \frac{\alpha_{\parallel\text{CO}}(3 \cos^2 \theta_{\text{HCl}} - 1)}{2R_{\text{c.m.}}^4} \right] \\ & + \mu_{\text{CO}} \left[ \cos \theta_{\text{CO}} + \frac{2\alpha_{\perp\text{HCl}} \sin^2 \theta_{\text{HCl}} + 2\alpha_{\parallel\text{HCl}} \cos^2 \theta_{\text{HCl}}}{R_{\text{c.m.}}^3} \right], \end{aligned}$$

where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the parallel and perpendicular components of the polarizability,  $\theta_{\text{HCl}}$  is the molecular quadrupole moment of HCl, and  $\theta_{\text{CO}} = 0^\circ$ . This calculation is performed for  $\theta_{\text{HCl}} = 23^\circ$ . The results of this simple calculation are in Table VI as well, and as was seen in CO<sub>2</sub>-HCl, the calculated moment is smaller than the experimental value. This same discrepancy was also observed in the BF<sub>3</sub> complexes.<sup>8</sup> There does not appear to be any simple low order electrostatic calculation which is quantitatively reliable. We shall discuss this point further in comparing the electric dipole moments of complexes of N<sub>2</sub> and CO where this effect is dramatically displayed.

The SCF-MO study of OC-HCl does give a value for the dipole moment of the complex (1.55 D) which is reasonably close to the experimental value (which has been extrapolated to  $\theta_{\text{HCl}} = 0^\circ$ ) of 1.595 D. This is probably fortuitous because the SCF-MO method used generally yields dipole moments which are larger than the experimental values (as pointed out in that paper). This is seen in the calculation of the dipole moments for HCl and CO. Although not mentioned in the paper, the sign of the dipole moment of CO calculated is incorrect. From the Mullikan population indices given,

the carbon end of the CO is seen to be positive. This implies that the calculated energetically favored isomer OC-HCl is antidipolar.<sup>1</sup> It was emphasized that the quantity of interest is the calculated change in dipole moment upon complexation and, for the HCN-HF hydrogen bound system, this quantity was determined quite well. The agreement between calculation and the experiment in the case of OC-HCl is quite poor, though. Listed in Table VI are the values of the induced dipole moments for the experiment and both isomers of the *ab initio* study. The calculated value of  $-0.112$  D (minus sign implying dipole moment depletion) for OC-HCl compares quite poorly with the experimental value of  $+0.388$  D. The value calculated for the other isomer CO-HCl, which is not observed in the experiment, is  $+0.253$  D.

Angular information about the HCl and DCl subunits within the complex is derived from the  $eqQ_a^{C1}$  and  $eqQ_a^D$  as mentioned previously in the results section. In OC-DCl as in other DCl complexes, there are two measures of the angle that the DCl subunit makes with the *a* axis from the projections of the quadrupole coupling constants. If the angle calculated from the  $eqQ_a^D$  is different from the one calculated from  $eqQ_a^{C1}$ , then some charge distortion within the DCl molecule has occurred. From our experimental data, Eq. (1) can be solved for  $\langle \cos^2 \theta \rangle$ , and the values are:  $\langle \cos^2 \theta \rangle^{C1} = 0.819$  and  $\langle \cos^2 \theta \rangle^D = 0.805$  (17) which, to within the experimental error, gives the same angle for the DCl subunit. In a previous paper,<sup>9</sup> it was mentioned that this was not the case in HFDCl. That statement is not correct. Upon reanalysis of the data for that system, it was found that the results are actually very similar to those of OC-DCl, so for DCl bound to all of the following: Ar, Kr, HF, and CO, it appears that there is a redundancy in the DCl angle measurement. In these cases the assumption of individual moiety electrical field gradient integrity upon complexation seems to be a good one.

Aldrich and Flygare have recently reported measurements of the deuterium electric quadrupole coupling

constants  $eqQ_a^D$  for the acetylene-DCl and ethylene-DCl T-shaped, hydrogen-bound complexes.<sup>10</sup> In these complexes the angle associated with the zero point bending motion is derived from the  $eqQ_a^{C1}$  which is assumed to be unperturbed upon complexation as in OC-DCl. The application of this procedure to the deuterium  $eqQ$  which worked quite well in OC-DCl, gives a very different value for the angle and implies that there is an enhancement of this constant. That is, the electric field gradient at the deuterium  $q_{aa}$  is increased. The authors claim that this effect in these species cannot be explained in view of traditionally hydrogen-bound systems or by methods involving multipole expansions which have been applied to van der Waals complexes in the past. They do claim that these complexes form a third category which is "weakly bound species characterized as van der Waals molecules with overlapping van der Waals radii." It is quite interesting that in other DCl complexes where both the  $eqQ_a^{C1}$  and the  $eqQ_a^D$  have been measured, there is very little or no enhancement while there is considerable van der Waals radii overlap in all species.

<sup>1</sup>A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.* **73**, 583 (1980); P. D. Soper, A. C. Legon, and W. H. Flygare, *ibid.* **74**, 2138 (1981).

<sup>2</sup>*Advanced Inorganic Chemistry*, edited by P. A. Cotton and G. Wilkinson (Wiley, New York, 1972).

<sup>3</sup>K. C. Janda, L. S. Bernstein, J. M. Steed, S. E. Novick, and W. Klemperer, *J. Am. Chem. Soc.* **100**, 8074 (1978).

<sup>4</sup>A. Hinchliffe, *Adv. Mol. Relaxation Interact. Processes* **21**, 151 (1981).

<sup>5</sup>N. F. Ramsey, *Molecular Beams* (Oxford University, London, 1955).

<sup>6</sup>S. E. Novick, P. Davies, S. J. Harris, and W. Klemperer, *J. Chem. Phys.* **59**, 2273 (1973).

<sup>7</sup>S. E. Novick, K. C. Janda, and W. Klemperer, *J. Chem. Phys.* **65**, 5115 (1976).

<sup>8</sup>K. Janda, Ph.D. thesis, Harvard University, 1977.

<sup>9</sup>K. C. Janda, J. M. Steed, S. E. Novick, and W. Klemperer, *J. Chem. Phys.* **67**, 5162 (1977).

<sup>10</sup>P. D. Aldrich and W. H. Flygare, *Chem. Phys. Lett.* (submitted).