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Roy E. Bruns and Willis B. Person

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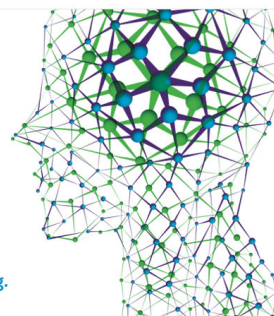
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## CNDO calculation of dipole moment derivatives and infrared intensities of formaldehyde\*

Roy E. Bruns

*Instituto de Quimica, Universidade Estadual de Campinas, Caixa Postal 1170, Campinas, S.P., Brazil*

and

Willis B. Person

*Department of Chemistry, University of Florida, Gainesville, Florida 32601*

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The complete neglect of differential overlap (CNDO) approximate wavefunctions for formaldehyde have been applied to the calculation of the derivatives of the dipole moment with respect to the symmetry coordinates ( $\partial p/\partial S_j$ ). Agreement between the calculated derivatives and the experimental values given by Hisatsune and Eggers for the  $A_1$  symmetry species is exceptionally good, permitting an interpretation of the experimental results in terms of electronic distributions in the molecule. The agreement for the  $B_1$  and  $B_2$  symmetry species is also very good except for the asymmetric in-plane CH bend. However, the theory successfully predicts that charge reorientation for this motion is quite different from that which occurs in the out-of-plane CH bend, so that these motions are represented by CH bond moments of opposite polarity. An analysis is given of the results in terms of derivatives with respect to internal coordinates ( $\partial p/\partial r_k$ ). Comparison of  $\partial p/\partial r_{CO}$  values from a series of  $X_2CO$  molecules (and also with  $\partial p/\partial r_{CS}$  for  $X_2CS$  molecules) reveals an interesting trend. An analysis of the various contributions to the calculated  $\partial p/\partial r_k$  values is presented, with an explanation of the calculated results for the out-of-plane bending coordinate  $\partial p/\partial \gamma$ .

## INTRODUCTION

The success of the CNDO (complete neglect of differential overlap) method in predicting dipole moment derivatives for vibrations of  $F_2CO$ ,<sup>1</sup>  $BF_3$ ,<sup>2</sup> and other molecules<sup>3,4</sup> encourages further testing of the model. The formaldehyde molecule  $H_2CO$  provides a particularly useful test of the method for several reasons. The calculated values of derivatives for hydrogen-containing compounds, such as HCN<sup>5</sup> and  $C_2H_4$ ,<sup>6</sup> have not always been as successful, in general, as the calculations for molecules containing fluorine atoms. (However, the calculated values for benzene<sup>7</sup> form a particularly spectacular set of results violating the generalization.) Secondly, the experimental investigation of the intensity perturbation due to Coriolis coupling between the  $\nu_5$  and  $\nu_6$  fundamentals of formaldehyde is interpreted in terms of in-plane and out-of-plane CH bond moments that have opposite polarities,

providing an interesting test for the theory. The  $H_2CO$  molecule contains a carbon-oxygen double bond that may contribute substantially to the magnitude of the  $\partial p/\partial S_j$  values for symmetry coordinates involving the CH bond. This effect has been previously studied in  $F_2CO$ <sup>1</sup> and  $Cl_2CO$ .<sup>8</sup> Finally, it is of some interest to compare the properties of  $\partial p/\partial r_{CO}$  values for the series of  $X_2CO$  molecules that have now been studied.

The main disadvantage of formaldehyde as a test case for the theory is that two sets of bands ( $\nu_1, \nu_4$ ) and ( $\nu_5, \nu_6$ ) are strongly overlapped and it is not clear exactly how these bands are to be separated experimentally to obtain a unique set of experimental  $\partial p/\partial S_j$  values. This problem and other complications encountered by Hisatsune and Eggers<sup>9</sup> in the measurement of the integrated intensities of formaldehyde resulted in estimated errors of about 20%–30% in the absolute values of the intensities of the fundamentals of  $H_2CO$ ,

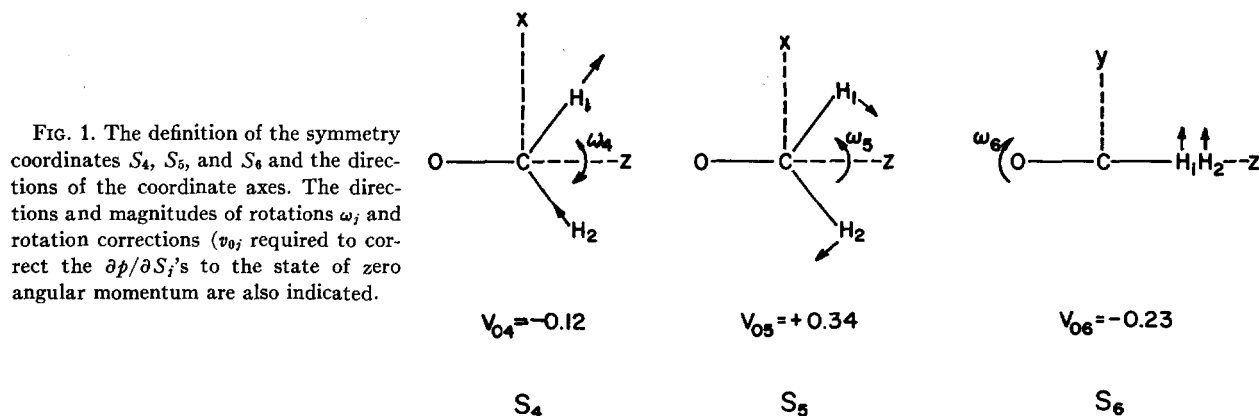


TABLE I. Comparison of calculated  $\partial p/\partial S_j$  values<sup>a</sup> with the experimental values for H<sub>2</sub>CO.

A <sub>1</sub> symmetry class			B <sub>1</sub> symmetry class			B <sub>2</sub> symmetry class		
Experimental	$\partial p_x/\partial S_1$ (D/Å)	$\partial p_x/\partial S_2$ (D/Å)	$\partial p_x/\partial S_3$ (D/rad)	Experimental	$\partial p_x/\partial S_4$ (D/Å)	$\partial p_x/\partial S_5$ (D/rad)	Experimental	$\partial p_x/\partial S_6$ (D/rad)
-+- <sup>b</sup>	-0.89±0.27	+1.87±0.08	-0.61±0.01	++	+1.35±0.29	-0.04±0.12	+	+0.43±0.07
++-	+1.45	+1.25	-0.56	--	-1.11	-0.64	-	+0.03
-++	<b>-0.86</b>	<b>+3.55</b>	<b>-0.09</b>	+-	+1.20	-0.74	CNDO	+0.26
+++	+1.51	+2.93	-0.04	-+	-0.97	+0.05		
CNDO	-0.57	+3.45	-0.06	CNDO	-1.20	+0.57		

<sup>a</sup> The symmetry coordinates are S<sub>1</sub>, C-H symmetric stretch; S<sub>2</sub>, C-O stretch; S<sub>3</sub>, CH symmetric bend; S<sub>4</sub>, CH asymmetric stretch; S<sub>5</sub>, CH asymmetric bend; and S<sub>6</sub>, out-of-plane CH bend.

<sup>b</sup> The signs are the signs of the  $\partial p/\partial Q_i$ 's. In the A<sub>1</sub> class, for example (+-+) would mean that the signs of  $\partial p/\partial Q_1$  and  $\partial p/\partial Q_2$  are positive while  $\partial p/\partial Q_3$  is negative. For that class, there are four other solutions, which are obtained from those listed by changing every sign in the row. The error limits indicate the extreme values for  $\partial p/\partial S_j$ , based on different assumptions about the separation of overlapping bands.

except for the intensities of  $\nu_5$  and  $\nu_6$ , where the error is about 50%. It would certainly seem desirable to remeasure the intensities using the improved techniques and instrumentation of recent years, to recalculate the normal coordinates using the frequencies of HDCO, and to treat the combined data with a statistical error analysis.<sup>10</sup> However, it seems worthwhile examining the old data in terms of the CNDO calculation partly in hope that this report will stimulate interest in new experimental work.

## CALCULATIONS AND RESULTS

The Cartesian coordinate system, the symmetry coordinates, and the geometry of formaldehyde used here are identical to those chosen by Hisatsune and Eggers.<sup>9</sup> This coordinate system, with schematic diagrams illustrating the symmetry coordinates S<sub>4</sub>, S<sub>5</sub>, and S<sub>6</sub> and the corresponding rotational corrections, are shown in Fig. 1. The dipole moment sign convention used in this paper is opposite to the one used by Hisatsune and Eggers, to facilitate comparison of these results with other molecules for which CNDO results have been reported in the literature. Calculations of the total dipole moment and of the dipole derivatives were made as described previously,<sup>1-5</sup> using an IBM 360-65 computer with the Segal CNDO program from QCPE.<sup>11</sup> The theoretically calculated equilibrium dipole moment of formaldehyde is +1.94 D (with the O atom at the negative end of the dipole), in reasonable agreement with the experimental value<sup>12</sup> of 2.33 D. The signs and magnitudes of the rotational corrections  $v_{0j}$  to  $\partial p_x/\partial S_4$ ,  $\partial p_x/\partial S_5$ , and  $\partial p_x/\partial S_6$  used in this analysis are all shown in Fig. 1.

The experimental sets of dipole moment derivatives with respect to the symmetry coordinates  $\partial p/\partial S_j$  of formaldehyde, calculated from the intensity data and normal coordinates of Hisatsune and Eggers<sup>9</sup> for all possible sign combinations of the  $\partial p/\partial Q_i$ 's, are presented in Table I. The experimental values listed in this table have been calculated with the assumption that  $\nu_1$  and  $\nu_4$  each contribute 50% of the intensity of the overlapped band ( $\nu_1, \nu_4$ ) and that  $\nu_5$  contributes 60% of the ( $\nu_5, \nu_6$ ) overlapped band. Although it appears from the band shape reported by Hisatsune and Eggers<sup>9</sup> that  $\nu_1$  and  $\nu_4$  are of about equal intensity and that  $\nu_5$  is slightly stronger than  $\nu_6$ , they considered that the fractional contribution of  $\nu_1$  could range from 30% to 70% of the total ( $\nu_1, \nu_4$ ) band intensity; and similarly for  $\nu_5$  in the ( $\nu_5, \nu_6$ ) band. The corresponding range in  $\partial p/\partial S_j$  values spanned by these different assumptions about the overlapped bands is indicated in Table I by the uncertainties in the experimental values. The values we have calculated by the CNDO method are also listed there for comparison. Comparison of the calculated results with the possible experimental results leads us to prefer the experimental values shown in boldface in the table.

TABLE II. The transformation equations relating the dipole moment derivatives with respect to internal coordinates to those with respect to symmetry coordinates.

$A_1$ symmetry species	$B_1$ symmetry species	$B_2$ symmetry species
$\partial p_x/\partial S_1 = (1/\sqrt{2})\partial p/\partial r_{CH}$	$\partial p_x/\partial S_4 = (\sqrt{3}/\sqrt{2})\partial p/\partial r_{CH}$	$\partial p_y/\partial S_6 = \partial p/\partial \gamma$
$\partial p_x/\partial S_2 = -\partial p/\partial r_{CO}$	$\partial p_x/\partial S_5 = -(1/\sqrt{2})\partial p/\partial \alpha$	
$\partial p_x/\partial S_3 = (1/\sqrt{2})(\partial p/\partial \alpha)^a$		

<sup>a</sup> This coefficient of  $1/\sqrt{2}$  differs from the one given by Hisatune and Eggers (9/8)<sup>1/2</sup>. This coefficient should be the same as the one relating  $\partial p/\partial S_{4a}$  of  $BF_3$  to  $\partial p/\partial \alpha$ .<sup>2</sup>

The  $\partial p/\partial S_j$  values can be transformed to  $\partial p/\partial r_k$  (derivatives with respect to the internal coordinates) using the equations listed in Table II. These latter derivatives represent the change in the total dipole moment of the molecule as one bond or angle coordinate is distorted. The derivatives  $\partial p/r_{CH}$ ,  $\partial p/\partial r_{CO}$ ,  $\partial p/\partial \alpha$ , and  $\partial p/\partial \gamma$  are equal to the bond moment parameters  $(\partial \mu/\partial r)_{CH}$ ,  $(\partial \mu/\partial r)_{CO}$ , and  $\mu_{CH}$  (both  $\partial p/\partial \alpha$  and  $\partial p/\partial \gamma$ ), if the bond-moment hypothesis is applicable; that is if the dipole changes ( $\Delta p$ ) are simple vector sums of bond dipole changes ( $\Delta \mu_i$ ) that are independent of bond coordinates  $r_j \neq r_i$ . If this assumption were valid, then with the convention we have employed for the sign of the dipole moment a positive value of  $\partial p/\partial \alpha (= \mu_{CH})$  would indicate a CH bond dipole polarity of  $^-C-H^+$ . Similarly, a positive value for  $\partial p/\partial r_{CO} [= (\partial \mu/\partial r)_{CO}]$  or  $\partial p/\partial r_{CH} [= (\partial \mu/\partial r)_{CH}]$  would indicate that the oxygen (or hydrogen) end of the bond dipole becomes more positively charged as the C-O (or C-H) length is increased. The derivatives in terms of internal coordinates, derived from the values in Table I using the relations in Table II, are presented in Table III.

### A<sub>1</sub> Symmetry Species

Now let us consider the results in Tables I and III in some detail, beginning with those for the  $A_1$  symmetry species. The values of  $\partial p/\partial S_j$  calculated by the CNDO method agree exceptionally well in magnitude and sign for this species with the experimental dipole moment derivatives from the  $(-+++)$  sign combination ( $\partial p/\partial Q_1$  negative,  $\partial p/\partial Q_2$  and  $\partial p/\partial Q_3$  both positive) although the experimental values from the  $(-+-)$  set may not be so far from the calculated values that they can be safely ignored. Referring to Table III we see that only these two possible sets of results give negative values both for  $\partial p/\partial r_{CH}$  and for  $\partial p/\partial r_{CO}$ . One might expect  $\partial p/\partial r_{CH}$  to be negative since previous calculations of this derivative, (particularly for ethylene<sup>6</sup> and benzene<sup>7</sup>) have found it to be negative. A negative value of  $\partial p/\partial r_{CO}$  for formaldehyde is expected also because of the negative sign found for the corresponding derivative in  $F_2CO$ .<sup>1</sup> The preferred  $(-+++)$  sign choice in the  $A_1$  class

of formaldehyde leads to an experimental value (Table III) of  $\partial p/\partial r_{CO}$  of  $-3.6$  D/Å, very similar to the value of  $-4.1$  D/Å reported for this derivative in  $F_2CO$ .<sup>13,1</sup> The experimental value of the derivative for the CH bending motion  $\partial p/\partial \alpha$  is found to be small and negative for the preferred  $(-+++)$  sign choice, in excellent agreement with the value calculated by the CNDO method. This result ( $\partial p/\partial \alpha$  small and negative) may seem surprising since this derivative is calculated to be positive for other molecules with  $\pi$  electron systems such as  $C_6H_6$ ,<sup>7</sup>  $C_2H_4$ ,<sup>3,4</sup>  $C_2H_2$ ,<sup>3,4</sup> and HCN.<sup>5</sup> If the bond moment hypothesis is applicable, we conclude that the very small CH bond dipole has a  $^+C-H^-$  polarity for formaldehyde, in contrast with the polarity found for the other molecules. The alternative  $(-+-)$  set leads to a  $\partial p/\partial \alpha$  value of  $-0.60$  D/rad, also corresponding to a negative bond moment, an order of magnitude larger than the calculated value. Since the  $(-+++)$  sign combination leads to experimental values for the derivatives that are in better agreement with the derivatives calculated from the CNDO method, and because the magnitude for  $\partial p/\partial r_{CO}$  from this set is intuitively more agreeable than is that from the  $(-+-)$  set, we believe the  $(-+++)$  sign choice for the  $\partial p/\partial Q_i$ 's is to be preferred and we shall use the experimental values from that set of results in subsequent comparisons with the other derivatives.

### B<sub>1</sub> Symmetry Species

The value of  $\partial p_x/\partial S_4$  calculated by the CNDO method agrees very well with the experimental derivatives from either one of sign choice sets  $(--)$  or  $(-+)$ . On the other hand, the calculated value of  $\partial p_x/\partial S_5$  is not in close agreement with any of the possible experimental values. It does have the same algebraic sign as the derivative from the  $(-+)$  set of signs. The alternative  $(--)$  sign choice leads to a value of  $\partial p/\partial \alpha$  in the  $B_1$  species (Table III) that is positive and much larger than the other value found for this derivative from the  $A_1$  classes or for  $\partial p/\partial \gamma$  from the  $B_2$  class. Since the values of  $\partial p/\partial \gamma$  found for the out-of-plane bends in  $C_6H_6$ ,<sup>7</sup>  $C_6F_6$ ,<sup>7</sup>  $C_2H_4$ ,<sup>3,4</sup>  $BF_3$ ,<sup>2</sup> and  $F_2CO$ <sup>1</sup> are all more positive than are the

TABLE III. Comparison of CNDO-calculated dipole moment derivatives with respect to internal coordinates with the corresponding experimental values for H<sub>2</sub>CO. (Units are D/Å for  $\partial p/\partial r_i$ ; D/rad for  $\partial p/\partial \alpha$  and  $\partial p/\partial \gamma$ .)

A <sub>1</sub> symmetry species			B <sub>1</sub> symmetry species			B <sub>2</sub> symmetry species		
Experimental	$\partial p/\partial r_{CH}$	$\partial p/\partial r_{CO}$	Experimental	$\partial p/\partial r_{CH}$	$\partial p/\partial \alpha$	Experimental	$\partial p/\partial \alpha$	$\partial p/\partial \gamma$
- + - <sup>a</sup>	-1.26	-1.87	+ +	+1.10	+0.06	+	+0.43 ± 0.07	
+ + -	+2.06	-1.25	- -	-0.90	+0.91	-	+0.03	
- + +	-1.22 ± 0.37	-3.55 ± 0.08	+ -	+0.98	+1.04	CNDO	+0.26	
+ + +	+2.13	-2.93	- +	-0.79 ± 0.33	-0.07 ± 0.14			
CNDO	-0.80	-3.45	CNDO	-0.98	-0.80			

<sup>a</sup> See Table I, Footnote b.

values of  $\partial p/\partial \alpha$  from the corresponding in-plane bends, we do not believe that the reverse order for CH<sub>2</sub>O implied by the (—) sign above is likely. It is noteworthy that the preferred sign choice (—+) is the only one (of all the sets for the B<sub>1</sub> class) that, invoking the bond moment hypothesis, leads to a CH bond moment polarity of +C—H<sup>-</sup> in agreement with the polarity found for this bond moment in the A<sub>1</sub> symmetry species. Secondly, the magnitudes of the experimental values of  $\partial p/\partial r_{CH}$  and  $\partial p/\partial \alpha$  from this preferred sign choice (—+) in the B<sub>1</sub> symmetry species agree very closely with the experimental values from the preferred sign set in the A<sub>1</sub> symmetry species. Thus, we conclude that the (—+) set is the preferred experimental set, even though the value of  $\partial p_x/\partial S_5$  predicted by the CNDO method is much more positive than is the experimental value.

### B<sub>2</sub> Symmetry Species

The value of  $\partial p_y/\partial S_6$  calculated from the CNDO method is almost midway between the two possible experimental values, so that additional information is needed to choose the most probable experimental value. However, the intensity perturbation of  $\nu_5$  and  $\nu_6$  by the Coriolis coupling first observed by Hisatsune and Eggers<sup>9</sup> has been interpreted as showing that  $\partial p_x/\partial Q_5$  and  $\partial p_y/\partial Q_6$  have the same relative signs.<sup>14</sup> Thus, if our preferred sign choice for the B<sub>1</sub> species (—+) is correct, then  $\partial p_y/\partial Q_6$  must be positive. The corresponding experimental value of  $\partial p/\partial \gamma$  in Table III has a sign opposite to that found for the corresponding derivative ( $\partial p/\partial \alpha$ ) in the A<sub>1</sub> and B<sub>1</sub> symmetry species. We note that the sign of  $\partial p/\partial \gamma$  (B<sub>2</sub>) is also predicted by the CNDO method to be positive and is opposite to that predicted for  $\partial p/\partial \alpha$  in the A<sub>1</sub> and B<sub>1</sub> classes.

On the other hand, it is possible that  $\partial p/\partial Q_6$  is negative, with a value of +0.03 D/rad for  $\partial p/\partial \gamma$ . Although this value is small and close to that found for  $\partial p/\partial \alpha$  in the A<sub>1</sub> species, the interpretation of the Coriolis coupling implies that the alternative (—) set of signs in the B<sub>1</sub> species may indeed be correct. However, we believe that the arguments against the (—) sign choice, presented above in the discussion of the B<sub>1</sub> species, are conclusive so that the preferred sign for  $\partial p/\partial Q_6$  here in the B<sub>2</sub> species is positive as indicated in Tables I and III.

### DISCUSSION

A summary of the preferred choices for the experimental values of the derivatives with respect to internal coordinates is presented in Table IV, together with the calculated values. The two different experimental values of the derivative with respect to the CH bond coordinate  $\partial p/\partial r_{CH}$  obtained from the A<sub>1</sub> and B<sub>1</sub> symmetry species, have similar values (within about 0.4 D/Å) in agreement with the prediction

by the CNDO calculations. The preferred experimental values of the corresponding two  $\partial p/\partial r_{CF}$  derivatives in  $F_2CO$  also were reported<sup>1</sup> to be close, within 0.1 D/Å. The values found experimentally for  $\partial p/\partial r_{CH}$  in formaldehyde appear to be about twice as large as the values of this derivative in ethylene<sup>6</sup> and benzene.<sup>7</sup>

The preferred experimental and CNDO-calculated values of  $\partial p/\partial r_{CO}$  for formaldehyde are compared in Table V with the corresponding values of this derivative from  $F_2CO$ ,<sup>1</sup>  $Cl_2CO$ ,<sup>8</sup> and  $Br_2CO$ .<sup>8</sup> Also included in this table are the values of  $\partial p/\partial r_{CS}$  for  $F_2CS$ <sup>15</sup> and  $Cl_2CS$ .<sup>15</sup> The apparently regular monotonic increase in the experimental magnitude of  $\partial p/\partial r_{CO}$  for the  $X_2CO$  as the X atoms are changed from H to F to Cl to Br is reflected in the corresponding increase of the CNDO-calculated derivatives for these molecules, although the rate of change is predicted by the CNDO method to be much greater than that observed experimentally. The relative experimental magnitudes of  $\partial p/\partial r_{CS}$  from  $F_2CS$  and  $Cl_2CS$  suggest a similar behavior for that derivative in the thiocarbonyl halides. Comparison with the two calculated derivatives indicates that the CNDO theory may underestimate the rate of change in this series. It is worth noting that the value of  $(\partial p/\partial r_{CO} - \partial p/\partial r_{CS})$  obtained from the experimental derivatives is the same for  $Cl_2CY$  as it is for  $F_2CY$ , in contrast with the CNDO prediction that this difference should increase from  $F_2CO$  to  $Cl_2CO$ .

At this point it is worth noting that the "experimental" value<sup>13</sup> of  $\partial p/\partial r_{CO}$  for  $F_2CO$  of  $-4.1$  D/Å, listed in Table V may, in fact, be in error. There is apparently still some confusion [even after publication of Ref. 1(b)] about the experimental values given by Hopper, Russell, and Overend<sup>13</sup> for  $F_2CO$ . In particular they have reversed in that paper the accepted<sup>16</sup> assignment of  $\nu_3$  and  $\nu_5$ . In a recent study McKean<sup>17</sup> has re-examined the evidence and concluded that the accepted assignment<sup>16</sup> is, in fact, correct. McKean<sup>17</sup> has recalculated the experimental derivatives<sup>13</sup> for  $F_2CO$  on the basis of the Overend-Scherer

TABLE V. Summary of experimental and CNDO values of  $\partial p/\partial r_{CO}$  and  $\partial p/\partial r_{CS}$  for  $X_2CO$  and  $X_2CS$  molecules (D/Å).<sup>a</sup>

	X	H	F	Cl	Br
$X_2CO$ (experimental)		-3.5	-4.1(-3.7) <sup>b</sup>	-4.7	-5.3
$X_2CO$ (CNDO)		-3.5	-5.4	-7.0	...
$X_2CS$ (experimental)		...	-3.1	-3.7	...
$X_2CS$ (CNDO)		...	-4.6	-4.9	...

<sup>a</sup> Data for  $H_2CO$  from Table IV; for  $F_2CO$ , data are from Ref. 1(b); for  $Cl_2CO$  and  $Br_2CO$  the experimental data are from Hopper, Russell, and Overend, Ref. 13; for  $F_2CS$  and  $Cl_2CS$  the experimental data are from Hopper, Russell, and Overend, Ref. 15. Calculated values for the latter four molecules are from Bruns, Ref. 8.

<sup>b</sup> Value for  $\partial p/\partial r_{CO}$  from new calculations made by McKean, Ref. 17.

assignment. Most derivatives do not change seriously in value, except for  $\partial p/\partial r_{CO}$ , which McKean now<sup>17</sup> finds to be  $-3.7$  D/Å, as indicated in Table V. [The value of  $\partial p/\partial r_{CF}(A_1)$  is also found by McKean<sup>17</sup> to be changed from  $-4.67$  to  $-5.30$  D/Å, in better agreement with the CNDO-calculated value of  $-5.53$  D/Å.] At this time, it is not entirely clear which value ( $-4.1$  or  $-3.7$  D/Å) is correct for  $\partial p/\partial r_{CO}$  from  $F_2CO$ , although it appears that the latter value may be correct. If so, then we must realize that the experimental values of  $\partial p/\partial r_{CO}$  for  $H_2CO$  and for  $F_2CO$  are nearly the same, in contrast with the CNDO-predicted increase from  $H_2CO$  to  $F_2CO$ .

Hopper, Russell, and Overend<sup>13</sup> correlated the  $\partial p/\partial r_{CO}$  value with the electronegativities of the substituent halogens in the halocarbons. However the range of uncertainties in these derivatives because of multiple experimental alternatives prevented them from assessing the validity of this correlation. Either set of results in Table V (with either  $-4.1$  or  $-3.7$  D/Å for  $\partial p/\partial r_{CO}$  from  $F_2CO$ ) certainly suggests that a simple relationship between  $\partial p/\partial r_{CO}$  and the electronegativities of the substituent X atoms in  $X_2CY$  does not exist. Instead it seems possible that the experimental values of  $\partial p/\partial r_{CO}$  may depend on the polarizability of the X atom, especially if  $-3.7$  D/Å is the correct experimental value for  $\partial p/\partial r_{CO}$  for  $F_2CO$ . It does seem unlikely, however, that the trend indicated by the CNDO calculations for  $\partial p/\partial r_{CO}$  as X changes from H to F to Cl to Br could be quite so badly exaggerated as these results indicate. We do expect the relative magnitudes of the CNDO derivatives to be useful to the experimentalist as a semiquantitative guide.

An analysis of the dipole moment derivatives into contributions<sup>3</sup> due to the displacement of equilibrium charges on the atoms ( $\partial p_1/\partial r_i$ ), to intramolecular charge transfer (the change in charge  $\partial p_2/\partial r_i$ ), and to  $sp$  polarization changes ( $\partial p_3/\partial r_i$ ) is presented in Table VI. Calculations of these contributions to the

TABLE IV. Summary showing the preferred experimental dipole derivatives of formaldehyde.<sup>a</sup> (Units are D/Å for  $\partial p/\partial r_i$ ; D/rad for  $\partial p/\partial \alpha$  and  $\partial p/\partial \gamma$ .)

Class		$\partial p/\partial r_{CH}$	$\partial p/\partial r_{CO}$	$\partial p/\partial \alpha$	$\partial p/\partial \gamma$
$A_1$	Experimental	-1.22	-3.55	-0.13	...
	CNDO	-0.80	-3.45	-0.09	...
$B_1$	Experimental	-0.79	...	-0.07	...
	CNDO	-0.98	...	-0.80	...
$B_2$	Experimental	...	...	...	+0.43
	CNDO	...	...	...	+0.26

<sup>a</sup> Values selected from Table III.

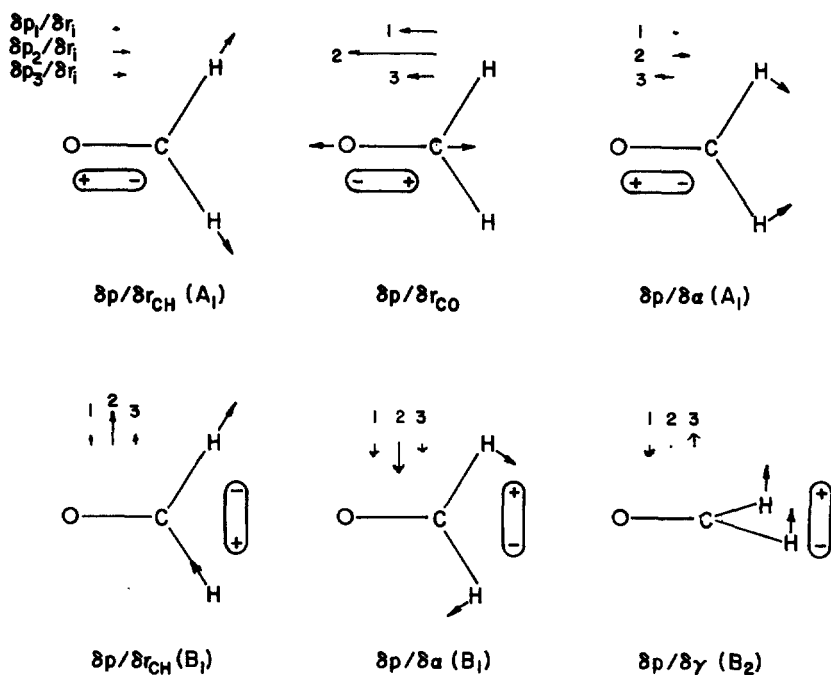


FIG. 2. Schematic representation of the contributions to  $\partial p/\partial r_k$  from the motion of the fixed equilibrium charge  $\partial p_1/\partial r_k$  (or 1), the change in charge  $\partial p_2/\partial r_k$  (or 2), and the  $sp$  hybridization term  $\partial p_3/\partial r_k$  (or 3).

derivatives with respect to the stretching coordinates of formaldehyde and also for the other molecules we have tested so far (C<sub>6</sub>H<sub>6</sub>,<sup>7</sup> C<sub>6</sub>F<sub>6</sub>,<sup>7</sup> C<sub>2</sub>H<sub>4</sub>,<sup>3,4</sup> BF<sub>3</sub>,<sup>2</sup> F<sub>2</sub>CO,<sup>1</sup> F<sub>2</sub>CS,<sup>8</sup> Cl<sub>2</sub>CO,<sup>8</sup> Cl<sub>2</sub>CS,<sup>8</sup> and N<sub>2</sub>O,<sup>5</sup> but not HCN<sup>5</sup> where there is an obvious disparity between the calculated and experimental signs for the stretching derivatives) have all predicted that each of these contributions is expected to be negative. This prediction of consistency in sign seems to us to be very pleasing.

Calculated contributions from each of these terms to  $\partial p/\partial r_k$  values are shown schematically in Fig. 2. For each stretching coordinate the intramolecular charge transfer results in the largest contribution to  $\partial p/\partial r_k$ . This contribution to  $\partial p/\partial r_k$  for stretching coordinates is shown in Fig. 2 to be reinforced by the contributions from equilibrium charge movements and changes in  $sp$  polarization.

Perhaps the most interesting aspect of the calculations has been the prediction that the values of  $\partial p/\partial \alpha$  for the in-plane CH-bending coordinate should be opposite in sign from  $\partial p/\partial \gamma$  from the corresponding out-of-plane motion, in agreement with the result deduced experimentally by Mills *et al.*<sup>14</sup> (See the values of  $\partial p/\partial \alpha$  for the B<sub>1</sub> and  $\partial p/\partial \gamma$  for the B<sub>2</sub> species in Table IV.) The positive sign of  $\partial p/\partial \gamma$  for the out-of-plane motion can be attributed to effects due to changes in the  $sp$  polarization of the out-of-plane carbon  $p$  orbital. As the CH bonds bend along the positive  $y$  coordinate, the  $p_y$  orbital of carbon is polarized in the opposite direction, allowing a movement of negative charge in the negative  $y$  direction, which results in a positive contribution to the dipole

moment derivative. A similar rationalization has been used to explain the less negative out-of-plane CF bending derivative in F<sub>2</sub>CO.<sup>1</sup> The values presented in Table VI confirm this argument. Movement of the hydrogen atoms bearing an equilibrium charge of  $-0.0135e$  contributes  $-0.07$  D/rad to  $\partial p_1/\partial \alpha$  but polarization of the  $s$  and  $p_y$  orbitals on the carbon atom produces the major contribution of  $+0.33$  D/rad to this derivative and determines the positive sign of  $\partial p/\partial \alpha$ . The opposite directions of the dipole moment changes for these two effects are shown in Fig. 2 for  $\partial p/\partial \gamma$ .

TABLE VI. Analysis of the different contributions to the calculated derivatives of the dipole moment with respect to the internal coordinates.\*

Class	$\partial p_1/\partial r_i$	$\partial p_2/\partial r_i$	$\partial p_3/\partial r_i$	$\partial p/\partial r_i$	
A <sub>1</sub>	$r_i = r_{CH}$	-0.06	-0.41	-0.33	-0.80
	$r_i = r_{CO}$	-0.89	-1.89	-0.67	-3.45
	$r_i = \alpha$	-0.07	-0.43	+0.41	-0.09
B <sub>1</sub>	$r_i = r_{CH}$	-0.06	-0.70	-0.22	-0.98
	$r_i = \alpha$	-0.07	-0.62	-0.11	-0.80
B <sub>2</sub>	$r_i = \gamma$	-0.07	-0.00	+0.33	+0.26

\* These derivatives are the contributions to the total derivative  $\partial p/\partial r_i$ . Here  $\partial p_1/\partial r_i$  is the contribution from the movement of equilibrium charges;  $\partial p_2/\partial r_i$  is from changes in the charges on the atoms; and  $\partial p_3/\partial r_i$  is from changes in  $sp$  polarization of the orbitals. The units are D/Å for  $r_i = r_{CH}$  or  $r_{CO}$ , and D/rad for  $r_i = \alpha$  or  $\gamma$ .

Experimental out-of-plane derivatives have consistently been found to be more positive than the corresponding derivatives we have calculated by the CNDO method. As a result, we believe that the value of  $\partial p/\partial\gamma = +0.43$  D/rad is to be preferred, in comparison with the alternative experimental value of  $\partial p/\partial\gamma$  for the  $B_2$  symmetry species of formaldehyde. If so, then for benzene,<sup>7</sup> ethylene,<sup>3</sup> and formaldehyde the differences between the experimental magnitude and CNDO predictions are 0.27, 0.14, and 0.17 D/rad, respectively. The corresponding differences are much larger for halogen-containing compounds ( $F_2CO$ ,<sup>1</sup>  $BF_3$ ,<sup>2</sup>  $C_6F_6$ ,<sup>7</sup>  $Cl_2CO$ ,<sup>8</sup> and  $Cl_2CS$ ) where the experimental values are found to be more positive than the calculated values by 0.9 to 1.4 D/rad.

The analysis of the contributions to  $\partial p/\partial\gamma$  for these molecules, such as given in Table VI for formaldehyde, indicates one possible explanation for this apparently consistent underestimate for  $\partial p/\partial\gamma$  by the CNDO theory. The contribution to  $\partial p/\partial\gamma$  from the movement of equilibrium charge  $\partial p_1/\partial\gamma$  is exactly the same for in-plane and for out-of-plane bending derivatives for any one molecule. In view of the generally successful calculations of the in-plane bending derivatives (except for the in-plane  $B_1$  derivative of formaldehyde) for the molecules mentioned above and for the bond stretching derivatives (which also depend on the equilibrium charge) we conclude that  $\partial p_1/\partial\gamma$  is reasonably well estimated by the theory.

The well-known qualitative arguments relating the amount of  $s$  character in the carbon atomic orbitals to electronegativities of the X atoms in  $X_2CO$  suggested to us that  $\partial p_2/\partial\gamma$  might be expected to be different from zero. However, the value of  $\partial p_2/\partial\gamma$  is calculated consistently to be zero (or at least of very small magnitude) for all molecules mentioned above. These qualitative hybridization concepts suggest that the sign of  $\partial p_2/\partial\gamma$  may be expected to be negative (for the definitions of the coordinate systems chosen in these calculations). Hence, a nonzero contribution to the CNDO-calculated derivative from  $\partial p_2/\partial\gamma$  could increase the difference between the CNDO predictions and the experimental values for these molecules.

Since the geometrical change in the XCX angle of formaldehyde (where  $\gamma$  changes) is a second order effect compared with the change in  $\gamma$ , the carbon orbitals forming the CH bonds are actually expected to show only a small change in the amount of  $s$  character when  $\gamma$  changes; hence, the charges on the C and H atoms are expected to be affected only slightly.<sup>18</sup> In Table VI we see that  $\partial p_2/\partial\gamma$  is in fact calculated to be zero for formaldehyde.

Finally, we note that the out-of-plane derivatives  $\partial p/\partial\gamma$  are badly underestimated for  $F_2CO$ ,  $BF_3$ ,  $F_2CS$ ,  $Cl_2CO$ ,  $Cl_2CS$ , and  $C_6F_6$ , where  $sp$  polarization of orbitals on terminal F, Cl, O, or S atoms may occur. The polarization of these orbitals is opposite in direction

to that occurring on the multiply bonded central (carbon) atom in these molecules. These molecules (except for  $BF_3$ ) are expected to have occupied  $p\pi$  orbitals, but the polarization on the terminal atoms is expected to be in the same direction as would be the  $sp$  polarization of the orbitals on boron in  $BF_3$ , with a vacant  $p\pi$  orbital. In either case the  $sp$  polarizations for the orbitals on the terminal atoms result in negative contributions to the out-of-plane dipole moment derivative. Assuming that the theory successfully estimates the magnitude of the contribution to  $\partial p_3/\partial\gamma$  from  $sp$  polarization effects for the multiply bonded atoms, as indicated by the good agreement between CNDO-calculated and experimental out-of-plane derivatives for  $C_6H_6$ ,  $C_2H_4$ , and  $CH_2O$ , the increased disagreement between these derivatives for molecules where terminal  $sp$  polarization is possible suggests that the theory overestimates this effect for the terminal atoms.

Although the theory fails to predict the magnitude of  $\partial p_x/\partial S_6$  accurately, the general agreement for  $CH_2O$  between theory and experiment is quite good. These calculations illustrate that the predicted sign of the dipole moment derivative may be very sensitive to subtle electronic changes as described by molecular orbital theory. An electronic effect that may be important enough to determine the sign of a derivative for one symmetry class (e.g., the small equilibrium charge on the H atom determines the sign of  $\partial p/\partial\alpha$  for the  $A_1$  symmetry species) may be only of small importance for the corresponding derivative in a different symmetry species [e.g.,  $\partial p/\partial\alpha$  ( $B_1$ ) or  $\partial p/\partial\gamma$ ]. Hence, it is not surprising that experimental bond moments obtained by analyzing different vibrations of the same molecule have opposite signs, especially if these derivatives have small magnitudes, as they do in formaldehyde.

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