Table V. Eigenvalues of the Vibrational Wave Function[a]

j	Eigenvalues, cm^{-1} e_{j1}	e_{j3}	e_{j3}^{D}
0	334.0	838.1	684.3
1	980.3	1124.9	768.3
2	1579.4	2384.6	1672.8
3	2117.2	3636.0	2330.1
4	2589.8	5184.3	3255.5
5	3042.1	6924.0	4295.6

[a] e_{j1} is the value corresponding to the potential V_1. e_{j3} and e_{j3}^{D} are the eigenvalues corresponding to the double-minimum potential V_3 of $N_2H_7^+$ and V_3^D of the deuterated complex $[H_3D\text{–}D\cdots NH_3]^+$, respectively. All values are with respect to the minima of corresponding curves.

such a double-well potential;[27, 28] the depth of the minima is not great enough, however, to allow for more than one such pair of levels (ν_3 = 0, 1, with a splitting of 283 cm^{-1}). The next allowed transitions in the infrared region are $0 \rightarrow 3$ and $1 \rightarrow 2$, respectively, the latter of which is slightly less probable (especially at low temperatures) because of the lower population of the first excited level relative to that of the ground state. The calculated frequencies are 2798 and 1260 cm^{-1} respectively for $N_2H_7^+$ and 1646 and 904 cm^{-1} for the deuterated species. The larger of these values for $N_2H_7^+$ is quite consistent with the absorption band for ν_3 found in the infrared spectrum of concentrated solutions of ammonium salts in liquid ammonia and also in solid $NH_4Cl\cdot(NH_3)_3$ in the range[6] of 2400–3200 cm^{-1}. The second absorption band corresponding to the $\nu_3 = 1 \rightarrow 2$ transition should become prominent at higher temperatures in the 1000–1500-cm^{-1} region of the spectrum, not far from the characteristic ammonia inversion frequency (also an antisymmetric vibration).

Finally, in evaluating these results it should be emphasized that the barrier to proton transfer in the preceding vibrational analysis (for constant R_{NN}) is almost twice as large as it is when the effect of simultaneous NN contraction is given explicit consideration. Inclusion of cross-terms in the description of the two-dimensional potential for the nuclear motion can thus be expected to lead to a general decrease in the spacing of the vibrational energy levels associated with the proton transfer, but the actual quantitative effects of such a perturbation have not yet been determined.[29]

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(27) R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, **36**, 1980 (1962).

(28) J. Brickmann and H. Zimmermann, *ibid.*, **50**, 1608 (1969).

(29) NOTE ADDED IN PROOF. After the present paper was submitted, it came to our attention that similar study of the proton transfer between NH_4^+ and NH_3 was carried out by J. J. Delpuech, G. Serratrice, A. Strich, and A. Veillard, *Chem. Commun.*, results submitted for publication.

Properties of Atoms in Molecules.
IV. Atomic Charges in Some Linear Polyatomic Molecules

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Abstract: Atomic charges have been calculated for a number of linear polyatomic molecules, using a recently proposed method which involves integrating the molecular electronic density over regions associated with the individual atoms. The results correlate well with the experimentally observed properties of the molecules; for example, the atomic charges computed for SCN$^-$ and OCN$^-$ show detailed agreement with the nucleophilic behavior of these ions. For SCN$^-$, OCN$^-$, SCO, and OCO, the quantities of valence electronic charge in various portions of the molecules, such as the internuclear regions, are also presented, in order to permit a comparative analysis of their electronic structures.

A new definition of atomic charge, based directly upon the total electronic density distribution in a molecule, has recently been proposed.[1] It involves partitioning the space of the molecule into regions associated with the individual atoms, and then integrating the molecular electronic density function over each of these regions. This method has been applied to a group of diatomic and a few polyatomic molecules, and the calculated charges were shown to be in good agreement with the physical and chemical properties of the molecules.[1,2]

Results

Atomic charges have now been computed for some additional linear polyatomic molecules, and also for two molecular ions, OCN$^-$ and SCN$^-$. The ions were treated in the same manner as the molecules; the atomic

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(1) P. Politzer and R. R. Harris, *J. Amer. Chem. Soc.*, **92**, 6451 (1970).

(2) P. Politzer, *Theor. Chim. Acta*, **23**, 203 (1971).

regions were established by reference to the superposed neutral O, C, and N (or S, C, and N) atoms. In all cases, extended-basis-set self-consistent-field wave functions were used for both the molecules[3] and the free atoms,[3,4] the wave functions chosen for the latter being those most consistent with the molecular functions. The results are presented in Table I. In order to facilitate comparisons, the charges calculated earlier for acetylene and for fluoroacetylene are also included in the table.

Table I. Calculated Net Atomic Charges

Molecule	Net atomic charges[a]				
HCCH[b]	+0.14	−0.14	−0.14	+0.14	
FCCH[b]	−0.05	+0.09	−0.19	+0.15	
ClCCH	+0.03	−0.02	−0.15	+0.15	
HCN	+0.18	0.00	−0.18		
FCN	−0.02	+0.23	−0.21		
ClCN	+0.08	+0.10	−0.19		
NCCN	−0.10	+0.10	+0.10	−0.10	
NCCCH	−0.16	+0.09	−0.05	−0.06	+0.18
SCN^-	−0.55	+0.03	−0.47		
OCN^-	−0.49	+0.13	−0.64		
SCO	−0.14	+0.34	−0.20		
OCO	−0.23	+0.46	−0.23		
NNO	−0.08	+0.33	−0.25		

[a] The charges are presented in the same order as the atoms in the molecular formula in column 1. [b] The results for HCCH and FCCH are taken from ref 1.

Discussion

(1) Haloacetylenes and Cyanogen Halides. In part I of this series, the near-zero charge obtained for the fluorine in HC_2F was discussed at some length.[1] It was pointed out that this result is consistent with the chemical behavior of the chloro-, bromo-, and iodoacetylenes, which indicates that the halogen atoms in these molecules are positively charged. Thus, the charge of +0.03 which has now been obtained for the chlorine in HC_2Cl is in agreement with both the experimental data and the previously calculated fluorine charge.

The charges computed for the atoms X in the molecules XCN (X = H, F, Cl) are very close to the corresponding values for the acetylene derivatives, HC_2X. This is perhaps not surprising, in view of the marked similarity in the properties of a given C–X bond in the two sets of molecules (Table II), indicating its relative insensitivity to the nature of the remainder of the molecule.[5–7] Again, no significant negative charge is found associated with either of the halogen atoms in FCN and ClCN, and again this result is supported by a considerable amount of experimental evidence, ranging from infrared studies to gaseous phase ion–molecule reactions.[8–13]

Table II. Experimentally Determined Bond Properties

Bond	Molecule	Bond length,[a] Å	Force constant, mdyn/Å
H–C	HCCH	1.058	5.85[b]
H–C	HCN	1.063	5.70[c]
F–C	FCCH	1.279	8.64,[d] 8.8[e]
F–C	FCN	1.262	8.41,[f] 8.70[g]
Cl–C	ClCCH	1.637	5.4[e]
Cl–C	ClCN	1.631	4.97[f]

[a] All bond lengths except that for HCCH are from ref 18; the HCCH value is from "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ., Suppl.*, No. 18 (1965). [b] B. L. Crawford and S. R. Brinkley, *J. Chem. Phys.*, 9, 69 (1941). [c] Reference 29. [d] J. K. Brown and J. K. Tyler, *Proc. Chem. Soc.*, 13 (1961). [e] Reference 10. [f] Reference 6. [g] E. E. Aynsley and R. Little, *Spectrochim. Acta*, **18**, 667(1962).

The near-zero charges which have been obtained for the halogen atoms in these haloacetylenes and cyanogen halides can be rationalized by invoking important contributions from resonance structures of the forms $X^+{=}C{=}C^-{-}H$ and $X^+{=}C{=}N^-$. Indeed, the electronic structures of these molecules have sometimes been described in terms of the contributions of various resonance forms.[14,15] Such descriptions should be used cautiously, however, especially when questions of bond strengths are at issue; resonance structures can be quite misleading.[16]

A certain amount of information about the electronic distribution in a molecule can be obtained from nuclear quadrupole coupling constants.[14,17] On the basis of the measured ^{14}N coupling constants in the three triatomic molecules FCN, ClCN, and HCN (−2.67, −3.63, and −4.58 Mc/sec, respectively[18]), it can be anticipated that the nitrogen atom should become increasingly negative in the order HCN < ClCN < FCN.[17,18] It is gratifying to note that the computed charges show the same trend (Table I).

(2) Cyanate and Thiocyanate Ions. The molecular ions OCN^- and SCN^- are of practical interest as nucleophilic reagents in organic reactions. It is encouraging to find that there is a marked correlation between the calculated atomic charges, as given in Table I, and the chemical behavior of these ions. Assuming for the moment that nucleophilicity can be related to atomic charge, then it would be expected that the nitrogen end of OCN^- will be distinctly more nucleophilic than the oxygen, since the former is significantly more negative; in SCN^-, on the other hand, the difference between the sulfur and nitrogen charges is much less, suggesting that the two ends of the ion should have roughly similar nucleophilic characters. These expectations are borne out by the experimental facts. Alkyl cyanates, ROCN, are very unstable and generally cannot be isolated, whereas alkyl isocyanates, RNCO, are stable mole-

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(3) A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions," International Business Machines Corp., San Jose, Calif., 1967.

(4) E. Clementi, "Tables of Atomic Wave Functions," International Business Machines Corp., San Jose, Calif., 1965.

(5) V. W. Weiss and W. H. Flygare, *J. Chem. Phys.*, **45**, 8 (1966).

(6) E. J. Williams and J. A. Ladd, *J. Mol. Struct.*, **2**, 57 (1968).

(7) G. A. Thomas, G. Jalsovszky, J. A. Ladd, and W. J. Orville-Thomas, *ibid.*, **8**, 1 (1971).

(8) F. Fairbrother, *J. Chem. Soc.*, 180 (1950).

(9) J. Sheridan, J. K. Tyler, E. E. Aynsley, R. E. Dodd, and R. Little, *Nature* (*London*), **185**, 96 (1960).

(10) G. R. Hunt and M. K. Wilson, *J. Chem. Phys.*, **34**, 1301 (1961).

(11) J. G. Dillard, J. L. Franklin, and W. A. Seitz, *ibid.*, **48**, 3828 (1968).

(12) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

(13) G. A. Thomas, J. A. Ladd, and W. J. Orville-Thomas, *J. Mol. Struct.*, **4**, 179 (1969).

(14) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(15) P. A. Casabella and P. J. Bray, *ibid.*, **28**, 1182 (1958).

(16) P. Politzer and R. R. Harris, *Tetrahedron*, **27**, 1567 (1971).

(17) The quadrupole coupling constant is related to the symmetry of the charge distribution around a nucleus; it is zero for a spherically symmetrical charge distribution. For further discussion, see, for example, ref 14; E. Scrocco, *Advan. Chem. Phys.*, **5**, 319 (1963); A. Colligiani, L. Guibe, P. J. Haigh, and E. A. C. Lucken, *Mol. Phys.*, **14**, 89 (1968).

(18) J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, **59**, 2661 (1963).

cules.[19,20] However, *both* thiocyanates, RSCN, and isothiocyanates, RNCS, are stable.[19,20] Since the nitrogen in OCN^- is considerably more negative than that in SCN^-, it is also to be anticipated that there will be instances when it will be possible to form some particular isocyanate, RNCO, but not the corresponding isothiocyanate, RNCS. Precisely such a situation, involving a dithiazolium cation, has recently been encountered.[21] It is not being proposed here that nucleophilicity can in general be related solely to atomic charge; other factors may well be involved.[22,23] But the atomic charge does appear to be a very useful tool for correlating and interpreting nucleophilic behavior.

(3) Comparisons: SCO *vs.* SCN^- and OCO *vs.* OCN^-. An interesting and enlightening comparison can be made of the pairs SCO, SCN^- and OCO, OCN^-. Since the two members of each pair have the same number of electrons, they may be viewed, for present purposes, as being related by a hypothetical transition, from SCO (or OCO) to SCN^- (or OCN^-), involving two steps. First, an oxygen nucleus is replaced by a nitrogen nucleus, and, second, the molecular electronic charge redistributes itself in response to the diminished force of attraction resulting from this decrease in nuclear charge from +8 to +7. This redistribution of electronic charge would be expected to lead to the SC- and OC- portions becoming more negative than they had been in the neutral SCO and OCO molecules. This does indeed happen, as is indicated by the atomic charges in Table I. The carbon atom becomes more negative by about 0.3 electron unit in both cases, the sulfur by 0.41, and the oxygen by 0.26 electron unit. The fact that the increase in negative charge on the oxygen, in the "transition" OCO → OCN^-, is smaller than that on the sulfur, for SCO → SCN^-, may seem surprising, since oxygen has a much higher electronegativity than sulfur.

The situation can be studied in greater detail by determining the quantities of valence electronic charge contained in various regions within these molecules and molecular ions. In Table III are presented the results of integrating the valence electronic densities of SCO, SCN^-, OCO, and OCN^- over the regions defined by planes perpendicular to the molecule axes at the positions of the nuclei. It is noteworthy that the distribution of σ charge is nearly the same in SCO and SCN^-, and again in OCO and OCN^-; it is almost negligibly affected by the decrease in the positive charge of one nucleus. It is the π charge that undergoes the expected migration toward the SC- and OC- portions of the molecules. The net result, in each molecule, is primarily a decrease in π charge at one end and an increase at the other, with small increases also in the S–C and O–C internuclear regions. The increase in the neighborhood of the oxygen atom is significantly less than in the neighborhood of the sulfur, which is consistent with the calculated atomic charges.

Table III. Quantities of Valence Electronic Charge in Various Regions[a]

Molecule XCZ	Type of charge	Region			
		X	C	Z	
SCO	σ	1.65	2.29	2.23	1.82
	π	1.36	2.68	2.56	1.39
	Total	3.01	4.97	4.80	3.22
SCN^-	σ	1.69	2.30	2.19	1.83
	π	1.68	2.74	2.52	1.05
	Total	3.37	5.04	4.70	2.88
OCO	σ	1.82	2.18	2.18	1.82
	π	1.43	2.57	2.57	1.43
	Total	3.25	4.75	4.75	3.25
OCN^-	σ	1.83	2.21	2.15	1.82
	π	1.61	2.64	2.59	1.16
	Total	3.44	4.85	4.74	2.97
CO	σ		1.77	2.37	1.86
	π		0.29	2.41	1.30
	Total		2.06	4.78	3.16

[a] The data are given in electron units.

Although these results are the reverse of what would be expected from electronegativity considerations, this does not necessarily indicate any contradiction or anomaly. Electronegativity is as much a measure of an atom's hold on its own electrons as of the attraction which it exerts for the electrons of the other atoms in a molecule. In the cases being discussed, however, only the latter factor is involved, since the important point is the relative desires of the oxygen and the sulfur to accept additional electronic charge. Thus their electronegativities are not really relevant. It is perhaps more useful to consider the relative sizes of the oxygen and sulfur atoms. Because oxygen is very much smaller than sulfur,[24,25] an approaching electron should feel an anomalously large force of repulsion from the highly concentrated electronic charge of the oxygen, and the latter should accordingly have a lesser tendency to gain additional electronic charge.[26] This conclusion is supported by the values of the experimentally determined electron affinities of oxygen and sulfur, which are 1.465 and 2.07 eV, respectively.[27] Thus, by invoking this repulsive effect, it is possible to formulate a reasonable explanation for the greater increase of electronic charge in the neighborhood of the sulfur, as compared with the oxygen.

(4) Carbon Monoxide, Carbon Dioxide, and Carbonyl Sulfide. The data in Table III permit an interesting comparison of the carbon–oxygen bonds in CO, CO_2, and SCO.[28] Particularly noteworthy is the remarkable similarity in the total quantities of valence electronic charge in the C–O internuclear regions in these molecules: 4.78, 4.75, and 4.80 electron units, respectively. Of course the distribution of this charge between σ and π molecular orbitals is somewhat different in CO from what it is in CO_2 and SCO; a larger portion of the charge is in σ orbitals in the former case. This accounts

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[19] C. R. Noller, "Chemistry of Organic Compounds," 3rd ed, W. B. Saunders, Philadelphia, Pa., 1965.

[20] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968.

[21] J. E. Oliver, B. A. Bierl, and J. M. Ruth, *J. Org. Chem.*, 37, 131 (1972).

[22] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962.

[23] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

[24] R. T. Sanderson, "Chemical Periodicity," Reinhold New York, N. Y., 1960.

[25] C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966).

[26] A similar situation involving the halogens has been discussed in greater detail: P. Politzer, *J. Amer. Chem. Soc.*, **91**, 6235 (1969).

[27] B. L. Moiseiwitsch, *Advan. At. Mol. Phys.*, **1**, 61 (1965).

[28] The electronic structures of these molecules have previously been analyzed in terms of electronic density and density difference contour diagrams: M. J. Hazelrigg, Jr., and P. Politzer, *J. Phys. Chem.*, **73**, 1008 (1969).

for the greater strength of the C–O bond in CO than in CO_2 or SCO, since σ charge, being concentrated along the molecular axis, exerts a greater attractive force upon the two nuclei. Nevertheless, the near-equality of the total internuclear valence electronic charges emphasizes the artificiality of the characterization of these C–O bonds as "double" or "triple" bonds.

It has been suggested that the electronic structure of a bond C–Z in a triatomic molecule X–C–Z is relatively little affected by the nature of the atom X.[6,29] Some support for this idea, at least in the case of CO_2 and SCO, is provided by the fact that the quantities of σ and π electronic charge in the CO portions of these two molecules are so very similar. There are, of course, certain differences in detail between the electronic structures of the C–O bonds in CO_2 and SCO.[28]

It has been noted[28] that there is no localized buildup of electronic charge to the outside of the sulfur atom in SCO; apparently the sulfur has nothing resembling a "lone pair," in marked contrast to the oxygen atoms in CO, CO_2, and SCO.[28] Another indication of this fact can now be obtained by computing the positions of the centers of the electronic charges associated with the sulfur and oxygen atoms in these molecules. It has been shown that the centers of charge of the covalently bonded atoms in a series of diatomic molecules are generally to the *outsides* of the atoms, rather than in the internuclear regions.[2,30] These results can, in most cases, be attributed to the effects of fairly localized molecular orbitals representing what may loosely be termed "lone pairs." The center of electronic charge of the sulfur atom in SCO, however, is only 0.01 au to the outside of the S–C internuclear region; the corresponding figures for the oxygen atoms in CO, SCO, and CO_2, on the other hand, are 0.06, 0.07, and 0.17 au, respectively. These indications that there is not associated with the sulfur in SCO any buildup of electronic charge which could be described as a lone pair are consistent with Bird and Townes' conclusion, based on the measured ^{33}S quadrupole coupling constant, that this sulfur atom is in an essentially unhybridized state.[31]

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(29) W. J. Orville-Thomas, "The Structure of Small Molecules," Elsevier, Amsterdam, 1966.

(30) P. Politzer and E. W. Stout, Jr., *Chem. Phys. Lett.*, **8**, 519 (1971).

(31) G. R. Bird and C. H. Townes, *Phys. Rev.*, **94**, 1203 (1954).

Molecular Orbital Studies on Hexagonal Ice

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Abstract: Molecular orbital calculations, based on the CNDO (complete neglect of differential overlap) approximation, are reported for hexagonal ice. The theoretical structural data are found to agree well with experiment. The difference between the bond angles for gas-phase and crystalline water molecules is interpreted in terms of the crystal polarization energy.

Although the most important manifestations of hydrogen bonding, such as the anomalous properties of certain solids and liquids, the conformation of proteins and solvation effects in some chemical reactions, involve semiinfinite aggregates of interacting molecules, theoretical investigations[1-6] of this effect have heretofore been largely limited to the study of dimers or trimers. These studies are clearly useful only in so far as the hydrogen-bonding interactions within these systems can be represented by the sum of pairwise potentials, and the long-range crystal or solvent interactions are negligible. In the present paper we consider these questions by departing from the traditional dimer approach to the study of hydrogen bonding, and consider instead the interactions within an infinite lattice of hydrogen-bonded molecules.

Hexagonal ice, the stable form of ice under ordinary conditions, was chosen as the subject for this study since it provides an intermediate step to the understanding of the properties of liquid water and its solutions. Thus, if the present investigation shows that molecular orbital theory adequately describes the intermolecular hydrogen-bonding interaction within the ice lattice, it would suggest that the present treatment could be usefully extended to the study of solvation in aqueous solution. Such a study would aid the understanding of, for example, the role of solvation molecules in organic chemical reactions.

The structure of hexagonal ice (ice-1h) has, of course, an intrinsic interest of its own. Although the main features of the lattice structure are fairly well understood, several questions concerning the observed small asymmetry of the oxygen sublattice (see below) remain to be resolved.[7,8] The structure of the water molecule

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(1) S. Bratoz, *Advan. Quant. Chem.*, **3**, 309 (1967).

(2) B. Pullman, *Theor. Chem. Acta*, **10**, 461 (1968).

(3) K. Morokuma and L. Pederson, *J. Chem. Phys.*, **48**, 3275 (1968).

(4) P. A. Kollman and L. C. Allen, *ibid.*, **52**, 5085 (1970).

(5) P. N. Noble and R. N. Kortzeborn, *ibid.*, **62**, 5375 (1970).

(6) D. Harkins, J. W. Moscowitz, and F. H. Stillinger, *Chem. Phys. Lett.*, **4**, 527 (1970).