dipeptides. The splitting in these two tripeptides is about 40% of that observed in the corresponding dipeptides. Lack of observed methylene splitting in the terminal glycyl residues of tripeptides and either glycyl residue in glycyl-L-leucylglycine is evidently due to their being out of a region of sufficient field gradient.

Temperature dependence of the extent of methylene splitting may in principle distinguish field from rotamer effects since all rotamers should be nearly equally populated at high temperatures, leaving only the averaged field effect to contribute to chemical shift nonequivalence. In the case of leucylglycine an increase in temperature from 25 to 120° reduced the methylene splitting by about 20%. Not even this degree of splitting may be ascribed to rotamer preferences about C–C single bonds because collapse of amide spectra has been observed at less than 100° owing to the onset of rapid rotation about the C–N bond. Because of the small energy differences between potential minima, a very wide temperature range would have to be studied in order to assess quantitatively the importance of rotamers about C–C single bonds. It does not seem possible to separate rotamer from field effects on the basis of the ionic strength dependence of $\Delta\nu$. We are unable to determine precisely the extent to which rotamer preferences due to nonbonded interactions contribute to chemical shift nonequivalence, which is due primarily to field effects in the compounds reported in this study.

Methylene or methyl group splitting has also been observed in many compounds that contain no charged groups. Chemical shift nonequivalence has been observed in the nitrogen substituents of uncharged amides with an asymmetric center in the carbonyl substituent.[22] The presence of an AB quartet of the methylene hydrogens of neopentyl O-methylmandelate[23] demonstrates that nonequivalence may occur across ester as well as amide bonds. Methyl group nonequivalence has been observed in several isopropyl esters.[24] In these compounds polar and aromatic groups may produce field gradients and nonequivalence as do charged and aromatic groups in peptides. The important role of solvent in contributing to the magnitude of chemical shift nonequivalence of solutes has been stressed. In cases where rotamer preferences appear unable to account for the results, greater magnitudes of methylene splitting are observed in media of lower dielectric constants.[25]

Two arguments suggest that the high-field resonance in the aminoacylglycine dipeptides is the one that would remain if the glycyl residue were stereoselectively deuterated so that the deuterium atom appears in the position of the side chain in an L,D or D,L dipeptide. Table II shows that the high-field α-CH hydrogen resonance of phenylalanylvalines occurs in the D,L diastereomer. In addition, selective deuteration of the methylene group in neopentyl O-methylmandelate such that the product might be considered analogous to a D,L compound results in retention of the high-field resonance.[23] Since both of these examples contain phenyl groups, the conclusion is valid for the compounds with nonaromatic side chains in Table I only if the additional effect of an aromatic group is simply to augment and not to reverse the sign of the chemical shift difference found with aliphatic groups.

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A New Evaluation of Platt's Model for Diatomic Hydrides[1]

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Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received January 30, 1967*

Abstract: Platt's model for diatomic hydrides has been reevaluated using Clementi's Roothaan–Hartree–Fock atomic wave functions. The diatomic hydrides from H_2 through HBr have been treated. The calculated equilibrium internuclear distances are in excellent agreement with experimental values for the united-atom model, $(Z + 1)^0 \rightarrow (ZH)^0$, but are too large for the separated-ion model, $(Z)^-, H^+ \rightarrow (ZH)^0$. The calculated force constants are also in better agreement with experiment for the united-atom model.

The united-atom model for diatomic hydrides has been the subject of a considerable literature since the initial formulation by Platt in 1950.[3–10] In the model one begins with a neutral atom of atomic number $Z + 1$. The wave function is assumed to have averaged spherical symmetry. A proton is removed from the nucleus and allowed to move out through the fixed

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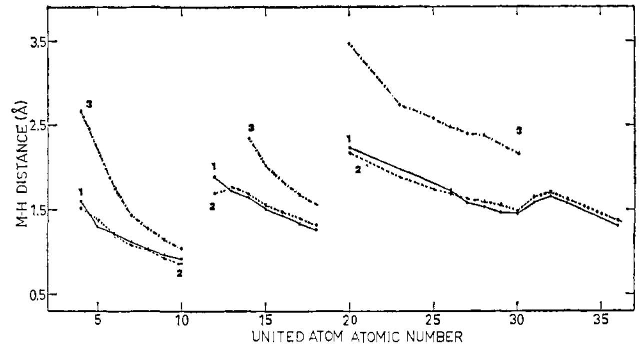

Figure 1. Comparison of experimental internuclear distances (1) with those calculated by the united-atom model (2) and by the separated-ion model (3).

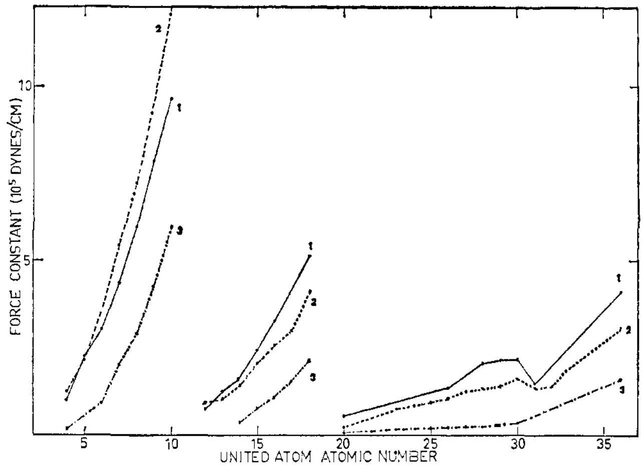

Figure 2. Comparison of experimental force constants (1) with those calculated by the united-atom model (2) and by the separated-ion model (3).

electron distribution. At any distance r from the nucleus it experiences a force

$$F_H = \frac{-Z + \int_0^r \Psi^*\Psi r^2 \, dr}{r^2} \tag{1}$$

where Ψ is the normalized radial function for the initial neutral atom of atomic number $Z + 1$. Zero force is achieved when the numerator on the right-hand side is zero. Thus r_e, the equilibrium internuclear distance, is determined by the relation

$$Z = \int_0^r \Psi^*\Psi r^2 \, dr \tag{2}$$

Differentiation of eq 1 gives

$$\frac{\partial F_H}{\partial r} = +\frac{2}{r^3}\left(Z - \int_0^r \Psi^*\Psi r^2 \, dr\right) + \frac{1}{r^2}\frac{\partial}{\partial r}\left(\int_0^r \Psi^*\Psi r^2 dr\right) \tag{3}$$

This derivative at the equilibrium distance $r = r_e$ gives the force constant k for M–H stretching. At $r = r_e$, the first term on the right is zero, so

$$k = \left(\frac{\partial F_H}{\partial r}\right)_{r=r_e} = \frac{1}{r_e^2}\frac{\partial}{\partial r}\int_0^{r_e} \Psi^*\Psi r^2 \, dr = (\Psi^*\Psi)_{r=r_e} \tag{4}$$

Thus, both the equilibrium internuclear distance and stretching force constant are obtainable from a knowledge of the united-atom wave function. Alternatively, one might begin with the separated-ion wave function for M$^-$ and bring the proton in through the fixed wave function until a point of zero force is reached. Since the model itself is not exact, the two procedures will not in general lead to the same values for r_e and k, even if the exact united-atom and separated-ion wave functions were employed.

It has been pointed out that Platt's model violates the quantum mechanical virial theorem, by requiring $\partial\Psi^*\Psi/\partial r$ to be zero.[5]

This deficiency can be remedied[7] by an appropriate scaling factor η_0, given by

$$\eta_0 = 1 - \frac{1}{U}\int_0^{\rho_0} \Psi^*\Psi r \, dr \tag{5}$$

where U is the united-atom potential energy, and ρ_0 is determined by the condition

$$Z = \int_0^{\rho_0} \Psi^*\Psi r^2 \, dr \tag{6}$$

The equilibrium internuclear distance is then given by $r_e = \rho_0/\eta_0$. The scaled force constant is given by the relationship

$$k = \eta_0^4\Psi^*\Psi(\eta_0 - \rho_0^2\Psi^*\Psi/U)^{-1} \tag{7}$$

In this expression it is assumed that the united-atom wave function satisfies the atomic virial theorem, which is in fact the case in the results presented here. Equation 7 approaches Platt's expression (eq 4) as $\eta_0 \rightarrow 1$. Equation 5 requires amendment for the separated-ion model; the correct expressions are given by Hall and Rees.[7]

Despite a perennial interest in Platt's model, and numerous considerations of its significance and limitations, it has not as yet been thoroughly tested in terms of an extensive set of accurate atomic and ionic wave functions. The recent appearance of such wave functions makes adequate testing feasible. We present herein the application of Platt's model for both united-atom and separated-ion wave functions to the extensive set of atomic and ionic wave functions of Clementi[11] for the elements He through Kr, both with and without scaling. In the following paper,[12] the model is extended to a consideration of the transition metal carbonyl hydrides.

Computation

The atomic and ionic wave functions employed in our calculations are the analytical Hartree–Fock functions developed by Clementi.[11] The total wave functions are expressed as sums of several Slater determinants which are in turn antisymmetrized products of one-electron spin orbitals. The orbital functions are obtained by solving the Roothaan–Hartree–Fock equations.[13] The orbitals which make up the Slater determinants are of the form

$$\vartheta_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha} C_{i\lambda p}$$

in which λ is a symmetry index (quantum number l)

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Table I. Observed Data for Diatomic Hydrides and Calculated Values Using the United-Atom and Separated-Ion Approximations

				United-atom approximation				Separated-ion approximation	
	Z^{a}	k, exptl^{b}	r_e, exptl^{c}	Scale factor	k^{b} (calcd unscaled)	k^{b} (calcd scaled)	r_e^{c} (calcd scaled)	k^{b} (calcd)	r_e^{c} (calcd)
HH	2	5.71	0.74^{e}	0.761	36.3	24.8	0.56		
HeH	3	...	...	0.805	1.36	0.73	1.01		
LiH	4	1.03	1.60	0.853	1.91	1.22	1.52	0.18	2.66
BeH	5	2.26	1.30^{e}	0.881	3.06	2.16	1.37		
BH(^{3}P)	6	3.04	1.23^{e}	0.900	4.75	3.56	1.22	0.93	1.75
BH(^{1}D)				0.900	4.54	3.37	1.23	0.72	1.82
BH(^{1}S)				0.899	4.05	3.00	1.26	0.91	1.77
CH(^{4}S)	7	4.37	1.12^{e}	0.913	7.03	5.44	1.09	2.04	1.43
CH(^{2}D)				0.913	6.55	5.07	1.11	1.70	1.48
CH(^{2}P)				0.913	6.25	4.84	1.12	1.50	1.52
NH(^{3}P)	8	5.98^{k}	1.04^{e}	0.923	9.05	7.23	1.03	2.92	1.28
NH(^{1}D)				0.923	8.80	7.0	1.01	2.73	1.30
NH(^{1}S)				0.923	8.28	6.62	1.02	2.35	1.33
OH	9	7.76	0.97^{e}	0.931	11.6	9.50	0.93	4.27	1.15
FH	10	9.66	0.92^{e}	0.937	14.6	12.1	0.86	5.97	1.04
NeH	11	...	...	0.943	1.29	1.08	1.21		
NaH	12	0.78	1.89^{e}	0.947	1.09	0.93	1.70		
MgH	13	1.27	1.73^{e}	0.952	1.24	1.07	1.77		
AlH(^{3}P)	14	1.61	1.65^{g}	0.946	1.70	1.45	1.69	0.40	2.35
AlH(^{1}S)					1.42	1.25	1.74	0.16	2.75
SiH	15	2.46^{k}	1.52^{e}	0.958	2.34	2.08	1.56	0.80	2.03
PH	16	3.26^{k}	1.44^{e}	0.961	2.89	2.59	1.48	1.12	1.85
SH	17		$1.35^{d,e}$	0.963	3.34	3.00	1.40	1.57	1.69
ClH	18	5.15	1.27^{e}	0.965	4.57	4.13	1.31	2.16	1.56
KH	20	0.56	2.24^{e}	0.969	0.27	0.24	2.18	0.09	3.47
TiH	23	...	...	0.973	0.85	0.79	1.89	0.19	2.75
VH	24	...	...	0.974	0.96	0.89	1.82		
CrH	25	...	...	0.975	1.05	0.98	1.75	0.22	2.59
MnH	26	1.38	1.73^{e}	0.976	1.19	1.09	1.70	0.25	2.48
FeH	27	...	$1.59^{d,j}$	0.977	1.34	1.26	1.62	0.27	2.41
CoH	28	2.09^{i}	1.54^{d}	0.977	1.42	1.33	1.59	0.28	2.38
NiH($4s^23d^9$)	29	2.17^{i}	1.47^{e}	0.978	1.52	1.43	1.55		
NiH($4s^13d^{10}$)				0.978	2.24	2.11	1.33	1.2	1.46
CuH	30	2.18	1.46^{e}	0.979	1.74	1.64	1.49	0.36	2.17
ZnH	31	1.50	1.59^{e}	0.980	1.44	1.36	1.65		
GaH	32	...	1.66^{f}	0.980	1.49	1.41	1.70	0.39	2.33
GeH	33	...	1.59^{h}	0.981	2.07	1.97	1.62		
BrH	36	4.12	1.41^{e}	0.982	3.25	3.09	1.47	1.64	1.72

[a] Atomic number of corresponding united atom. [b] In units of 10^5 dynes/cm. k is calculated from ω_e values[g] (*i.e.*, it is corrected for anharmonicity) except where noted. [c] In angstroms. [d] The equilibrium values given here are r_0 as defined in footnote *g*. The r_0 values differ very little from the r_e values. For example, r_e for NiH is 1.47 A, whereas r_0 is 1.49 A. [e] Data taken from Tables de Constantes et Données Numeriques, Vol. 4, B. Rosen, Ed., Hermann & Cie, Depositaires, Paris, 1951. [f] Value estimated by J. L. Margrave, *J. Phys. Chem.*, **58**, 258 (1954). [g] G. Herzberg, "Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950. [h] B. Kleman and E. Werhagen, *Arkiv Fysik*, **6**, 359 (1953). [i] Calculated from $\Delta G_{1/2}$ values as defined in footnote *g*. These values are uncorrected for anharmonicity in the vibrations. The correction is usually small and results in a 2% error at most in k. [j] There are two observed states. In the other, $r_0 = 1.48$ A. [k] The force constants are calculated from ω_e values which are not well known.

and α is the subspecies index which labels the individual members of the degenerate set transforming according to the λ representation. The subscript p refers to the pth basis function of symmetry λ. The χ's are Slater-type orbitals with integral quantum numbers

$$\chi_{p\lambda\alpha}(r,\upsilon,\varphi) = R_{\lambda p}(r)Y_{\lambda\alpha}(\upsilon,\varphi)$$

We are concerned with the radial part of the orbitals

$$R_{\lambda p} = [(2n_{\lambda p})!]^{-1/2}(2\zeta_{\lambda p})^{n_{\lambda p}+1/2}r^{n_{\lambda p}-1}\exp(-\zeta_{\lambda p}r) \quad (8)$$

The size of the basis set employed in obtaining each $\vartheta_{i\lambda\alpha}$ varies. In all cases, however, the resulting atomic wave functions are very good approximations to the Hartree–Fock limit and represent the most accurate extensive set of wave functions presently available.

The solutions to eq 2 or 6 and 5 are found by numerical integration of the appropriate expansions at various values for r. The values for k, from eq 2 or 7, are readily computed once η_0, ρ_0, and r_e are known (U is given by Clementi). The results for the binary hydrides are given in Table I for the united-atom and separated-ion models. (Scaling was not included in the separated-ion caculations because the scale factor is essentially unity in all cases.)

The internuclear M–H distances calculated by the two methods are compared with the experimental results in Figure 1.

Discussion

It is quite evident from Table I and Figure 1 that the united-atom model yields very good values for the internuclear distance. Discounting the results for the first two or three elements, to which the model can hardly be expected to apply, the error seldom exceeds 5%. This is a particularly pleasing result, since Platt was unable to obtain satisfactory values for r_e with the atomic wave functions available to him. It is also noteworthy that the united-atom model gives much better results for r_e than the separated-ion model. It has not been obvious until now that this would prove to be the case, and, in fact, arguments have been advanced[7] for the superiority of the latter model. The united-atom model is also clearly more successful in calculating the force constants (Figure 2). The general trend of force constant within each horizontal row is reproduced quite well. The errors in the calculated values for this observable are relatively much larger than for the internuclear distance. The reasons for this are perhaps most evident when the problem is viewed in terms of the Hellmann–Feynman theorem. The expectation value for internuclear distance is dependent on the equilibrium wave function, for which the Hartree–Fock atomic wave function for the neutral atom of $Z + 1$ nuclear charge is apparently a good approximation. The stretching-force constant, however, involves an expression of the form[8]

$$k = \frac{2Z}{r^3} + \int \Psi^*\Psi \frac{\partial^2 V_{\text{ne}}}{\partial r^2} d\tau + \int \frac{\partial(\Psi^*\Psi)}{\partial r} \frac{\partial V_{\text{ne}}}{\partial r} d\tau \tag{9}$$

where V_{ne} is the nuclear-electronic attraction operator, $V_{\text{ne}} = \Sigma_\alpha - 1/r_{\alpha\text{H}}$, where the sum is over all electrons. The last term in this equation is a measure of relaxation in the electron distribution accompanying nuclear motion. In the Platt model this term is assumed to be zero. Only a fortunate cancellation with another large term of opposite sign can yield a satisfactory value for k. Such a cancellation does apparently exist, but k is nevertheless not as accurately predicted as r_e.

Acknowledgment. Calculations were performed at the University of Illinois Digital Computer Laboratory.

Application of Platt's Model for Diatomic Hydrides to Metal Carbonyl Hydrides[1]

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Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received January 30, 1967*

Abstract: Platt's united-atom model for diatomic hydrides is extended to metal carbonyl hydrides. The equations are the same as for the diatomic case, except that a classical approximation is employed to take account of net charge which may be present on the CO groups. The model provides a simple picture for metal–hydrogen bonding and accounts nicely for the similarity in M–H stretching frequency with the corresponding diatomic metal hydride. The following values are estimated for equilibrium M–H distances: $Mn(CO)_5H$, 1.60 A; $Co(CO)_4H$, 1.40 A; $Fe(CO)_4H^-$, 1.40 A; $Cr(CO)_5H^-$, 1.50 A.

The transition metal carbonyl hydrides are an interesting and varied group of compounds.[2,3] The purpose of the present contribution is to consider the metal–hydrogen bond in terms of an extension of Platt's model for diatomic hydrides.[4,5]

The metal carbonyl hydrides can be considered to derive in principle from a parent metal carbonyl molecule or ion by abstraction of a proton from the nucleus of the central metal atom.[6] The abstracted proton is allowed to move out through an electronic environment which is forced to remain unchanged, except for relatively minor C–M–C bond angle changes. When the nuclear–electronic attractive forces on the proton equal the proton–nuclear repulsive forces, the proton comes to rest. Some examples of the process envisaged are

$$Fe(CO)_5 \longrightarrow Mn(CO)_5H$$
$$Mn(CO)_5^- \longrightarrow Cr(CO)_5H^-$$
$$Ni(CO)_4 \longrightarrow Co(CO)_4H$$
$$Co(CO)_4^- \longrightarrow Fe(CO)_4H^-$$

If it is assumed that the proton exerts a slight net repulsive effect on the CO groups, it may then be expected to occupy somewhat less space than the surrounding CO groups. Thus in $Mn(CO)_5H$ the axial-radial C–Mn–C angle is 97°;[7] the average CO–CO distance is only slightly less than in the parent $Fe(CO)_5$.

The carbonyl hydride formation described above is an isoelectronic process and may be considered in terms of the Hellmann–Feynman theorem. Employing the integral form of this theorem,[8] we label the parent carbonyl compounds as the X state and the carbonyl hydride in its equilibrium configuration as the Y state. Then the difference in energy, ΔW, exclusive of the change in nuclear energy, is given by

$$\begin{aligned} W &= \Delta V_{\text{nn}} + \frac{N}{S}\int \Psi_X H'(1) \Psi_Y \, d\tau \\ W &= \Delta V_{\text{nn}} + \frac{N}{S}\int \rho_{XY}(1) H'(1) \, d\tau(1) \end{aligned} \tag{1}$$

The first term on the right represents the difference in the classical nuclear–nuclear potential, $\Sigma_{jk}Z_jZ_k/r_{jk}$, where Z_j and Z_k are the charges on nuclei j and k, and r_{jk} is the internuclear distance. The normalized transi-

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