Testing the Validity of the Conventional Resonance Model for Protonated Carbonyl, Imine and Thiocarbonyl Compounds. An Ab Initio Valence Bond Study

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VB Procedure. In VB theory, the state wave function, Ψ, is expressed as a linear combination of VB structures, Φ_K, in Eq. 1,

$$\Psi = \sum_K C_K \Phi_K \qquad (1)$$

where the Φ_K are VB structures that correspond to all the modes of distributing the "active electrons" that participate in the interchanging bonds (here the π bonds), and the C_K are the corresponding structural coefficients.

The set of orbitals that are used to construct the Φ_K VB structures are divided into two subsets: the active orbitals that are treated at the VB level (here the π orbitals) and the remaining ones called "spectator orbitals". As each π-donating substituent brings one orbital and two π electrons into play, the numbers of active orbitals and active electrons amount, respectively, to 2 and 2 in the unsubstituted compounds, 3 and for in the mono-substituted ones, and 4 and 6 in the disubstituted ones. All the orbitals, spectator and active, are optimized in the calculation of the VB wave function, but the spectator orbitals take the form of doubly occupied molecular orbitals with fixed occupancy. On the other hand, the active orbitals are purely localized either on a single center (C, X) or on a single fragment (R), with occupancies determined by the considered VB structures.

In the VBSCF procedure, both the VB orbitals and structural coefficients are optimized simultaneously to minimize the total energy. As such, the VBSCF method takes care of the static electron correlation; however, it lacks dynamic correlation that is absolutely essential for obtaining quantitative accuracy. As a further improvement, the BOVB method that is used here improves the VBSCF method by allowing the orbitals to be different for different VB structures throughout the course of the orbital-optimization process. In this manner, the orbitals respond to the instantaneous fields of the individual VB structures rather than to an average field of all the structures. As such, the BOVB method accounts for part of the dynamic correlation, while leaving the wave function as compact as in VBSCF.

The weights of the VB structures are defined by the Coulson-Chirgwin formula,[1] Eq. 6, which is the equivalent of a Mulliken population analysis in VB theory.

$$W_K = C_K^2 + \sum_{L \neq K} C_K C_L \left\langle \Phi_K \middle| \Phi_L \right\rangle \qquad (2)$$

Nature of the π orbitals used in the VB structures. Unless otherwise specified, all the orbitals, spectator and active, are optimized in the calculation of the VB wave function, but the spectator orbitals take the form of doubly occupied molecular orbitals with fixed occupancy. On the other hand,

the active orbitals are purely localized either on a single center (C, X) or on a single fragment (R), with occupancies determined by the considered VB structures. The localized nature of the VB orbitals is illustrated in the following figure that represents the π orbitals in the covalent structure of protonated acetone (structure 1_P).
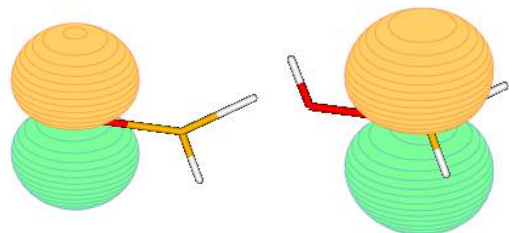

Figure 1. The optimised BOVB π orbitals of structure 1_P in protonated acetone.

As an exception, the π orbitals that are used to form the R-C and R'-C π bonds in 3P and 4P are of the GVB type. This means that the π bond is described as a unique and formally covalent VB structures that couples two orbitals, one mainly localized on C, the other mainly localized on R (or R'). During the optimization process, the orbital localized on C is allowed to delocalize on R, and vice-versa. The amount of delocalization is always small. As is well known in GVB theory, this slight delocalization allows to physically include both the covalent and ionic component of the bond, while dealing with a formally covalent singlet-coupling.

The PCM Solvation Model. In the framework of the standard Polarizable Continuum Model (PCM), the solute molecule is studied quantum mechanically and the interaction between solute and solvent is represented by an interaction potential, V_R, which is treated as a perturbation on the Hamiltonian of the solute molecule,

$$H^0\Psi^0 = E^0\Psi^0 \tag{3}$$

$$(H^0 + V_R)\Psi = E\Psi \tag{4}$$

where H^0 is the Hamiltonian of the solute molecule in vacuum, Ψ^0 and Ψ are the state wave functions of the solute in gas phase and in solution, respectively; E^0 and E are their corresponding respective energies. The interaction potential can be expressed as a sum of electrostatic, dispersion-repulsion and cavity components, as in Eq. 6.

$$V_R = V_{el} + V_{dr} + V_{cav} \tag{5}$$

The above three terms depend on the charge distribution of the solute and are calculated using a cavity defined through interlocking *van-der-Waals* spheres centered at atomic positions. The reaction field is represented through point charges located on the surface of the molecular cavity. The present calculations use the United Atom for Hartree-Fock Model (UAHF) to build the cavity, which

means that the spheres are located on heavy (that is, non-hydrogen) elements only. More details are given in the Gaussian user's manual.

Computational details.

All calculations have used the standard 6-31G(d) basis set, which is a bsis set of double-zeta quality with polarization functions on atoms other than hydrogen. The calculations using Density Functional Theory (DFT) have been done with the B3LYP hybrid functional. The geometry optimizations have been performed at the standard level of Møller-Plesset Many-Body Perturbation Theory to second order, referred to as MP2(full). All MP2 and B3LYP calculations have used the Gaussian 03 package.[2]

Gas phase *vs*. water phase π net charges from B3LYP calculations.

Table 1. π net charges at the X atom in protonated carbonyls, imines and thiocarbonyls.

X, R, R'	Gas Phase	Water phase
O, H, H	1.522	1.510
O, CH$_3$, H	1.584	1.569
O, CH$_3$, CH$_3$	1.626	1.608
O, SiH$_3$, H	1.558	1.548
O, OCH$_3$, H	1.674	1.676
O, SCH$_3$, H	1.685	1.664
O, NH$_2$, H	1.713	1.723
O, Cl, H	1.597	1.583
NH, H, H	1.409	1.377
NH, CH$_3$, H	1.458	1.425
NH, CH$_3$, CH$_3$	1.512	1.459
S, H, H	1.361	1.354
S, CH$_3$, H	1.460	1.454
S, CH$_3$, CH$_3$	1.525	1.512

(1) Chirgwin, H. B.; Coulson, C. A. *Proc. Roy. Soc. A. (London)* **1950**, *2*, 196.
(2) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.