Structural Classification of AB_2 Molecules and A_3 Clusters from Valence Electron Orbital Radii

Wanda Andreoni, Giulia Galli,[(a)] and Mario Tosi[(a)]
Institut de Physique Expérimentale, Ecole Polytechnique Féderale de Lausanne, CH 1015 Lausanne, Switzerland

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We show that *a priori* atomic parameters (valence-orbital radii) allow classifications of molecular shapes for a large number of *sp*-bonded AB_2 compounds with the number of valence electrons $N \leqslant 16$, in parallel with classifications of crystal structures in the solid phase. Triatomic A_3 clusters with $N \leqslant 15$ are structurally classified with the same scheme.

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The problem of molecular shapes has acquired renewed interest especially in view of recent progress in the preparation and structure determination of small atomic aggregates.[1] One of the primary questions is to understand whether and why a given AB_2 molecule or A_3 cluster will adopt a linear or a bent shape in its ground state. In this Letter we propose a new way of looking at this question, which appeals to progress made recently in structural classifications of solids through simple *a priori* parameters of the atomic constituents.[2] Such structural parameters are simple linear combinations of *s*- and *p*-orbital (either pseudopotential or nodal) radii derived from *ab initio* calculations for atomic electron states. Here we show that it is possible to predict the equilibrium shape of atomic aggregates in the molecular state by use of the *same* parameters which classify them in the solid phase.[2] In particular, we present for the first time successful structural plots for all the *sp*-bonded AB_2 and A_3 molecular species known so far.

We recall that the Mulliken-Walsh rules for molecular shapes[3] identify the number N of valence electrons in the molecule as a relevant parameter. In particular, for the equilibrium shapes of *sp*-bonded nonhydride AB_2 molecules, they indicate $N=16$ as a dividing line between linear ($N<16$) and bent ($N>16$) shapes. However, a large number of bent molecules with $N \leq 16$ are now known, and this suggests the need for more sophisticated criteria. Considering first the double-octet (DO) molecules with $N=16$, we examine the usefulness of the Zunger-Cohen coordinates[2] which successfully classify the crystal structures of a large number of AB solids. These are defined as $Y_{\mathrm{ZC}} = |R_\sigma^A - R_\sigma^B|$ and $X_{\mathrm{ZC}} = R_\pi^A + R_\pi^B$ where, for each element E, $R_\sigma^E = R_0^E + R_1^E$ and $R_\pi^E = |R_0^E - R_1^E|$. The R_l's ($l=0,1$) are the orbital pseudopotential radii, i.e., the classical turning points of *ab initio* hard-core pseudopotentials, and measure the size of core repulsion. We find that the single coordinate Y_{ZC} suffices to discriminate between bent and linear molecules, since all molecules with $Y_{\mathrm{ZC}} < 2.1$ are linear, with the only exception being BaI_2, which is bent[4] but has $Y_{\mathrm{ZC}} = 1.82$. For the DO AB_2 crystals, the ($Y_{\mathrm{ZC}}, X_{\mathrm{ZC}}$) plot is not appropriate. Instead, as Burdett, Price, and Price[2] have shown, a rather successful structure map can be obtained in terms of the two elemental ZC coordinates R_σ^A and R_σ^B. For the DO molecules, we find that this scheme also works nicely, with a dividing line

$$R_\sigma^A = 0.41 R_\sigma^B + 2.74,$$

which completely separates bent (above) from linear molecules (below). Actually, it is interesting to note that a similar plot based on Pauling's ionic radii[5] for the two elements works almost as well and fails only for mercury dihalides.

In searching further for parallelism between solids and molecules, we adopt here the coordinates used already by one of us[2] to classify successfully the structures of DO AB_2 solids. These are $Y = y_B - y_A$ and $X = x_A + x_B$, where for each element, $y_E = \frac{1}{4}(\mathcal{N}_0 + 3\mathcal{N}_1)$ and $x_E = \frac{1}{4}(3\mathcal{N}_0 - \mathcal{N}_1)$. The $\mathcal{N}_l$'s ($l=0,1$) are the nodal-orbital radii,[6] i.e., the outermost nodes of *s* and *p* valence wave functions, which measure the size of the core orthogonality hole in a straightforward way. In our scheme we have the simple result that all DO AB_2 molecules with $Y < -1.25$ are found to be bent, the value of X being immaterial. The individual y_E gives (in analogy with R_σ^E) a measure of the average core size, and increasingly negative values of Y correspond in a loose sense to increasing ionicity,[2,7] as can be seen, e.g., from the ordering of the various halides of each metal in Fig. 1. In the solid phase increasing ionicity is reflected in an increases of the coordination number.[2] Furthermore, there is an excellent correlation between the value of Y and the known apex angles of these molecules,[4,8,9] as shown in Fig. 1. This actually suggests a simple model for the free energy $F(\alpha, Y)$ of AB_2 molecules as a function of the bond angle and of the bond ionicity:

$$F(\alpha, Y) = F_{\pi/2} + a(Y - Y_c)(\alpha - \pi/2)^2 + b(\alpha - \pi/2)^4, \quad a, b > 0,$$

which has an equilibrium solution $\alpha = \pi/2$ for $Y > Y_c$ and $|\alpha - \pi/2| = (a/2b)^{1/2}(Y_c - Y)^{1/2}$ for $Y < Y_c$.

AB_2 molecules with $N < 16$ present a broad spectrum of apex angles, and their structural classification requires a full two-dimensional plot. In Figs. 2 and 3 we present two structural maps for all such AB_2 molecules known so

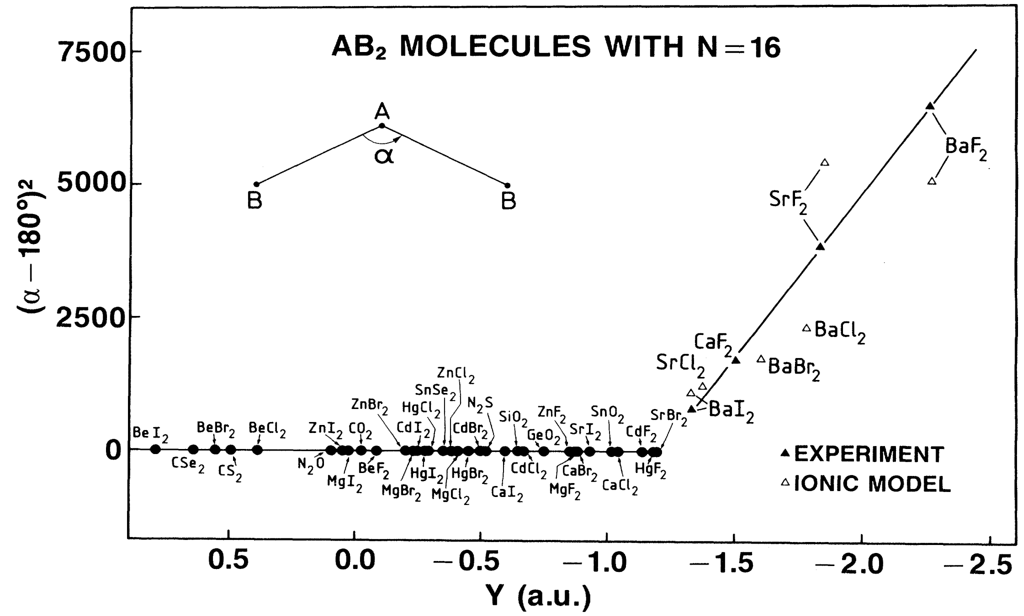

FIG. 1. Correlation between apex angle α and our coordinate Y for DO molecules. The results of an ionic model are from G. Galli and M. Tosi, Nuovo Cimento Soc. Ital. Fis. D 4, 431 (1984).

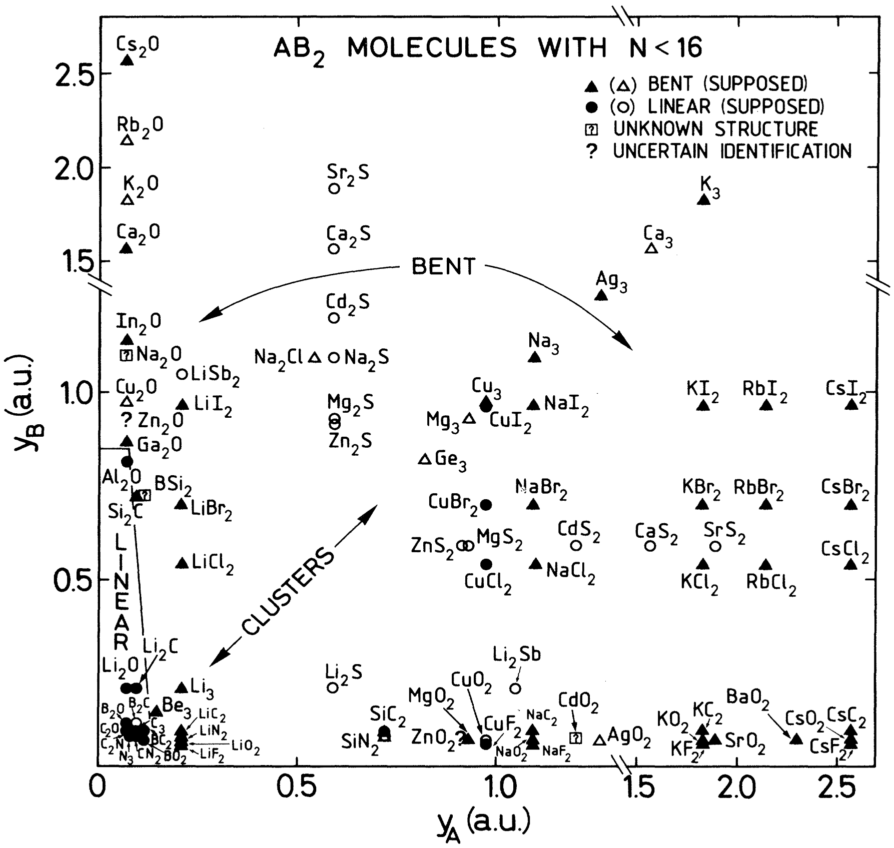

FIG. 2. Elemental-coordinates plot.

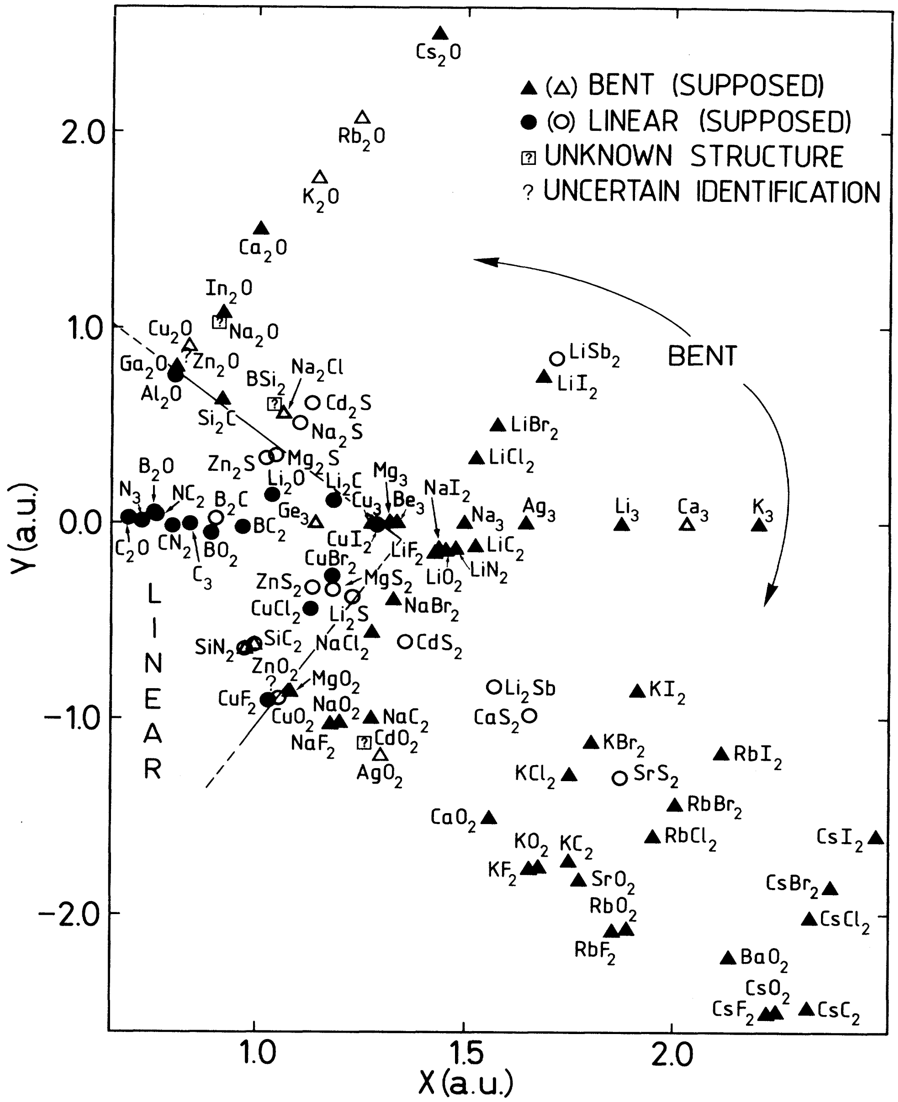

FIG. 3. Compound-coordinates plot for AB_2 molecules with $N < 16$.

far.[8,9] These include both those whose shape seems well established from experiment or self-consistent-field configuration-interaction calculations (full symbols) and those for which suggestions have been made from ambiguous evidence or self-consistent-field calculations (open symbols). Some observations refer to molecules trapped in a matrix rather than in the free state, and a matrix dependence, as reported for SiN_2,[10] cannot be excluded. Both plots use coordinates constructed from nodal radii: the elemental-coordinate (y_A, y_B) scheme (Fig. 2) and the compound-coordinate (Y, X) scheme (Fig. 3), where $X = 2x_A + x_B$. X clearly gives more weight to the A component, relative to the choice $x_A + x_B$ made in our previous classification of DO solids; however, we have checked that the quality of the latter plot is unaltered by this change of coordinates. Indeed, the relative importance of the central atom in the compound-coordinate scheme (Fig. 3) is in agreement with well-known approaches to molecular shapes, such as the directed-valence approach.[5] Both our diagrams not only discriminate between linear and bent molecules, the only exceptions being open symbols, but also display a trend of the apex angle of bent species from the bottom right to the top left. This would correspond in an ionic picture to a shift from $A^+(B_2)^-$ (small angle) to $(B^+)_2A^-$ (large angle). Evidently, however, in Fig. 3 Y no longer correlates with an ionicity scale, and X is crucial. The most covalent species lie at $X < 1$, in accordance with the interpretation of X for solids as a measure of bond directionality.[7] The elemental-coordinate scheme does not yield a correct prediction for Cu dihalides for which one might expect an important role to be played by the d-atomic orbitals. We find the same difficulty with the scheme of Burdett, Price, and Price, which, when applied to these systems gives a plot very similar to Fig. 2. Further, we note that our plots for $N = 16$ and $N < 16$, though constructed with the same coordinates, cannot be superposed: This stresses again the relevance of N (the Mulliken-Walsh parameter).

Only some of the AB_2 compounds with $N < 16$ are known in the solid phase, the corresponding crystal structures being layer type (e.g., CsO_2), antifluorite (e.g., BaO_2), pyrite (e.g., MgO_2), cuprite (Cu_2O), CuF_2 type, and $CuCl_2$ type. Our coordinates, in both Figs. 2 and 3, appear to work except for $Cu(Cl_2,Br_2,I_2)$. It is very interesting that also A_3 clusters with $3 \leq N \leq 15$ fit into Figs. 2 and 3, which classify them with y_A and x_A, respectively. So far only a few have been studied carefully,[11] so that it is not possible to decide whether y_A or x_A is to be preferred.

Finally, we have examined the usefulness of the chemical scale χ proposed recently by Pettifor,[12] which also provides an elemental-coordinate scheme for the classification of crystal structures. For the DO molecules, we find again a critical line,

$$\chi_A = 0.52\chi_B - 0.83,$$

which nicely discriminates between bent (below) and linear (above) species. When applied to the molecules with $N < 16$, however, Pettifor's scheme fails for Li_2O, Li_2C, and Al_2O and again for copper dihalides. The difficulty we find with Pettifor's coordinates for the first-row elements is also apparent in his structural plot for the DO AB_2 solids where CdF_2, HgF_2, and Be dihalides are misplaced.[13] Overall it appears that Pettifor's one-parameter (χ) scheme, although it contains an adjustable constant for each element, is less successful than two-parameter (s and p radii) schemes which contain no adjustable elemental constants.

In conclusion, our results stress the role of the sizes of the orthogonalization holes in the atomic constituents for each angular momentum in determining the structure of atomic aggregates in both molecular and crystalline states. In particular, by condensing these orbital properties into suitable coordinates, we have been able to classify the known apex angles in triatomics with $N \leq 16$ and to give a picture for the molecules which is remarkably consistent with the structural classification of the corresponding solids. Furthermore, we have shown that an analysis of the sp-bonded AB_2 systems in molecular and crystalline phases provides a simple test for different structural classification parameters.[14] The ordering of elements according to Pettifor's semiempirical chemical scale passes this test with fair success, but near-perfect structural separation is achieved with the use of first-principles valence-orbital radii.

[a] Permanent address: International School for Advanced Study (Scuola Internazionale Superiore di Studi Avanzati), I-34100 Trieste, Italy.

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