

## Electronic Compressibility and Polarizability: Origins of a Correlation

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Recently, two new chemical concepts have been introduced, namely, the atomic compressibility  $\beta' = r^4/Z_{\text{eff}}$  and the corresponding group (molecular) compressibility  $G\beta' = \sum_{i=1}^N n_i \beta'_i$ . Here,  $r$  is the radius of the atom,  $Z_{\text{eff}}$  is the effective nuclear charge,  $n$  is the number of atoms of a given element  $i$ , and  $N$  is the total number of different elements in the molecule. The physical meaning of these two compressibility parameters is examined briefly in this work. A fundamental difficulty with the derivation of the primary relationship  $\beta' = r^4/Z_{\text{eff}}$  is pointed out. We have investigated the origins of an observed linear variation of  $G\beta'$  with molecular polarizability  $\alpha'_{\text{mol}}$  for a series of predominantly organic molecules. We show that a linear correlation is to be expected for a plot of  $G\beta'$  vs  $\alpha'_{\text{mol}}$  if certain conditions are satisfied for all members of a given set of molecules. In particular, if the average value of  $r/Z_{\text{eff}}$  for the constituent atoms is similar for each molecule in the series, then a linear variation is to be expected for  $G\beta'$  vs  $\alpha'_{\text{mol}}$ .

### Introduction

The successful introduction of a new concept into Chemistry can be an extensive and eventful process; it may require years of “negotiation” in the literature to approach any universal agreement on the definition or meaning of a novel parameter. The history of the electronegativity concept illustrates this fact.<sup>1</sup> Nonetheless, it is imperative that newly introduced ideas be analyzed critically, and that this be done as soon as possible after they have been presented. In that way, lingering questions may be identified and answered early, and the usefulness of a new idea explored in solving old problems and tackling new ones.

A new property termed “atomic compressibility” has been defined recently.<sup>2,3</sup> For a spherical atom with volume

$$V = 4\pi r^3/3 \quad (1)$$

where  $r$  is the radius of the atom, the atomic compressibility is<sup>2</sup>

$$\beta = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (2)$$

The form of the above expression is identical to that for the isothermal compressibility of a material on the macroscopic scale. The partial derivative in brackets is a measure of the rate of change of volume with respect to some applied pressure,  $P$ , at constant temperature  $T$ .

For the atomic compressibility,  $P$  has been defined as the ratio of the attractive Coulomb force

$$F = \frac{Z_{\text{eff}} e^2}{4\pi \epsilon_0 r^2} \quad (3)$$

exerted on an electron with unit charge  $e$  at some distance  $r$  from the nucleus, and  $A (=4\pi r^2)$  the surface area of the spherical atom. So, for a given atom

$$P = F/A = \frac{Z_{\text{eff}} e^2}{16\pi^2 \epsilon_0 r^4} \quad (4)$$

where  $Z_{\text{eff}}e$  is the nuclear charge<sup>4,5</sup> that is seen by the electron and  $\epsilon_0$  is the vacuum permittivity.

By eqs 1, 2 and 4, Noorizadeh and Parhizgar derived the following expression for the atomic compressibility:<sup>2</sup>

$$\beta = \left( \frac{12\pi^2 \epsilon_0}{e^2} \right) \frac{r^4}{Z_{\text{eff}}} \quad (5)$$

A molecular or group compressibility

$$G\beta = \sum_{i=1}^N n_i \beta_i \quad (6)$$

has been defined in that work as well, on the basis of the assumption that  $\beta$  is an additive atomic property.  $n$  is the number of atoms of a given element  $i$ , and  $N$  the total number of different elements in the molecule.

Having introduced  $\beta$  and  $G\beta$ , the authors investigated the relationship between them and certain other atomic and molecular properties. An attempt to demonstrate a linear relationship between  $\beta$  and atomic properties such as electronegativity<sup>1,5–7</sup> and chemical hardness<sup>8</sup> proved unsuccessful.<sup>2</sup> On the molecular side, they identified a surprisingly good correlation between  $G\beta$  numbers and the molecular polarizabilities  $\alpha_{\text{mol}}$  of a group of forty (mainly organic) molecules.

It is the purpose of the present contribution to briefly consider the physical meaning of the newly defined atomic and group compressibility. Additionally, the relationship between atomic polarizability  $\alpha_{\text{atom}}$  and  $\beta$  (and molecular polarizability  $\alpha_{\text{mol}}$  and  $G\beta$ ) has been examined. We find that the definition of  $\beta$  itself may explain the failure to observe a linear correlation between it and  $\alpha$  or other atomic properties related to  $\alpha$ . We demonstrate that, although the observed correlation between  $\alpha_{\text{mol}}$  and  $G\beta$  is quite remarkable, it does not necessarily imply a general linear relationship between  $\alpha_{\text{mol}}$  and  $G\beta$  for all molecules. The

observed correlation is not at all fortuitous but represents a case in which particular conditions are satisfied for most of the molecules in the series. Before considering these relationships, however, let us revisit the definitions summarized above to better understand the meaning of  $\beta$  as a physical property of the atom.

### What is $\beta$ ?

Built into the definition of  $P$  (see eq 4)<sup>2</sup> is an assumption that the local Coulomb force  $F$  acts somehow on the entire surface of the atom. Yet,  $F$ , as defined in eq 3, describes a two-body attractive interaction involving the shielded nucleus and an electron located at some point on the surface of the spherical atom of radius  $r$ . Hence, any pressure exerted on the atom due to this force is localized, and not spread over the entire atomic surface. We find, therefore, no apparent justification for the form of the pressure term  $P (=F/4\pi r^2)$  based on which the compressibility concept has been proposed. In the absence of any further clarification of the nature of  $F$ , it is not obvious how  $P$  should be interpreted, or what characteristic of the atom  $\beta$  in fact represents.

The above criticism notwithstanding, we accept in the following the proposed forms of  $\beta$  and  $G\beta$ . We propose to analyze the interesting relationships highlighted in ref 2 between compressibility and polarizability in atoms and molecules.

### A Relationship Examined: Polarizability and Compressibility

In ref 2, the atomic and molecular compressibility have been accepted a priori as a measure of a system's tendency to undergo volume changes in an external electric field. Following from that interpretation, Noorizadeh and Parhizgar envisioned a linear correlation between  $\beta$  (and  $G\beta$ ) and a number of other properties, including the atomic (and molecular) polarizabilities,  $\alpha_{\text{atom}}$  (and  $\alpha_{\text{mol}}$ ). We will examine the relationship between polarizability and compressibility in some detail presently. In preparation to do so, let us clarify first the terms we plan to use.

The atomic or molecular polarizability  $\alpha$  is, in the simplest terms,<sup>9</sup> a constant of proportionality linking the applied electric field  $\vec{E}$  and the induced dipole moment  $\vec{\mu}$ .

$$\vec{\mu} = \alpha \vec{E} \quad (7)$$

Nevertheless, atomic and molecular polarizabilities are commonly presented in the form of polarizability volumes

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0} \quad (8)$$

so called because they have the dimensions of volume. Expressing the quantity in this form is convenient because there is generally a direct correlation between the volume of atomic (and molecular) systems and their polarizabilities.<sup>10,11</sup> To discuss the relationship between the polarizability and compressibility, we will define an analogous scaling of the atomic compressibility

$$\beta' = \frac{\beta}{e^2/12\pi^2\epsilon_0} = \frac{r^4}{Z_{\text{eff}}} \quad (9)$$

Note, though, that all we have done in defining  $\alpha'$  and  $\beta'$  is to simplify  $\alpha$  and  $\beta$  by factoring out a constant in each case. Otherwise, nothing new has been done. In fact, the compressibility numbers given in ref 2 are equal to  $\beta'$ ; we have followed the lead of Noorizadeh and Parhizgar in factoring out the

**TABLE 1: Covalent Radii  $r$ , Effective Nuclear Charges  $Z_{\text{eff}}$ , Atomic Polarizabilities  $\alpha'$ , and Computed Compressibility Coefficients for Main Group and First Row Transition Metal Atoms**

atom	$r/\text{\AA}^a$	$Z_{\text{eff}}^a$	$\alpha'/\text{\AA}^3 b$	$r^3/\text{\AA}^3$	$(r/Z_{\text{eff}})/\text{\AA}$	$(\beta' = r^4/Z_{\text{eff}})/\text{\AA}^4$
H	0.498	1.00	0.666793	0.124	0.498	0.062
Li	1.225	0.95	24.3	1.838	1.3	2.4
Be	0.889	1.60	5.60	0.703	0.556	0.390
B	0.781	2.25	3.03	0.476	0.347	0.165
C	0.771	2.90	1.76	0.458	0.266	0.122
N	0.741	3.55	1.10	0.407	0.209	0.085
O	0.74	4.20	0.802	0.405	0.176	0.071
F	0.721	4.86	0.557	0.375	0.148	0.056
Na	1.572	1.85	24.11	3.885	0.850	3.30
Mg	1.363	2.50	10.6	2.532	0.545	1.38
Al	1.248	3.15	6.8	1.944	0.396	0.770
Si	1.173	3.80	5.38	1.614	0.309	0.498
P	1.013	4.45	3.63	1.040	0.228	0.237
S	1.041	5.10	2.90	1.128	0.204	0.230
Cl	0.994	5.75	2.18	0.982	0.173	0.170
K	2.025	1.85	43.4	8.304	1.10	9.09
Ca	1.737	2.50	25.0	5.241	0.695	3.64
Ga	1.245	4.65	8.12	1.930	0.268	0.517
Ge	1.223	5.30	6.07	1.829	0.231	0.422
As	1.211	5.95	4.13	1.776	0.204	0.361
Se	1.172	6.60	3.77	1.610	0.178	0.286
Br	1.142	7.25	3.05	1.489	0.158	0.235
Rb	2.195	1.85	47.3	10.576	1.186	12.5
Sr	1.915	2.50	27.6	7.023	0.766	5.38
In	1.497	4.65	10.2	3.355	0.322	1.08
Sn	1.399	5.30	7.7	2.738	0.264	0.723
Sb	1.41	5.95	6.6	2.803	0.237	0.664
Te	1.37	6.60	5.5	2.571	0.208	0.534
I	1.344	7.25	4.7	2.428	0.185	0.450
Sc	1.439	2.65	17.8	2.980	0.543	1.62
Ti	1.324	2.80	14.6	5.387	0.626	3.37
V	1.224	2.95	12.4	2.888	0.483	1.39
Cr	1.172	3.10	11.6	2.554	0.441	1.13
Mn	1.168	3.25	9.4	2.538	0.420	1.07
Fe	1.165	3.40	8.4	1.581	0.343	0.542
Co	1.157	3.55	7.5	1.549	0.326	0.505
Ni	1.149	3.70	6.8	1.517	0.311	0.471
Cu	1.173	3.85	6.1	1.614	0.305	0.492
Zn	1.249	4.00	5.6	1.948	0.312	0.608

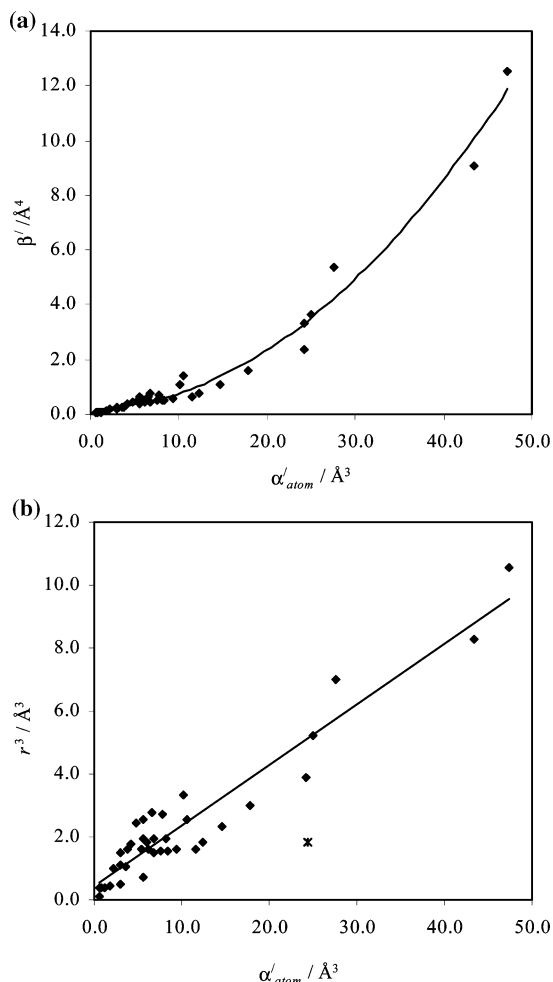
<sup>a</sup> Reference 2; the original sources are refs 5 and 13. The relatively large  $r$  ( $=0.498$ ) for H in ref 2 appears to have been taken from elsewhere; no data are available in refs 5 and 13 for this element. The radii data for the elements from Ti to Mn were taken directly from ref 13. <sup>b</sup> Reference 12.  $\alpha'$  ( $\text{\AA}^3$ ) =  $0.148184\alpha'$  ( $a_0^3$ ).

constant. Hereafter, we will refer to  $\alpha'$  and  $\beta'$  as simply polarizability and compressibility, respectively.

### $\beta'$ and $\alpha'_{\text{atom}}$

As was mentioned above, the authors in ref 2 probed unsuccessfully for a linear relationship between  $\beta'$  and properties such as atomic softness ( $\sigma_{\text{atom}}$ ), hardness ( $\eta_{\text{atom}}$ ), and electronegativity ( $\chi_{\text{atom}}$ ).<sup>2</sup> Nonetheless, a linear correlation was found between  $\beta'$  and  $\alpha'$  for a limited class of atoms: H, C, N, O, F, S, Cl, Br, I.<sup>2</sup>

In the present work, we have extended this list of atoms and examined the relationship between the  $\beta'$  and  $\alpha'$  for a group of 39 elements spanning the main group and the first transition metal series (see Table 1). Shown in Figure 1a is a plot of  $\beta'$  vs  $\alpha'$  for those elements. The atomic polarizabilities,<sup>12</sup> and the  $Z_{\text{eff}}$  and  $r$  numbers<sup>2,5,13</sup> used to compute  $\beta'$ , are listed in Table 1. A quadratic fit of these data (Figure 1a) gives a correlation coefficient of 0.990, with the absolute deviation increasing as the polarizability of the atom increases. The relationship between



**Figure 1.** (a)  $\beta'$  vs  $\alpha'_{\text{atom}}$  for the main group and first row transition elements listed in Table 1. For the quadratic fit,  $y = 0.005x^2 + 0.005x + 0.198$ ;  $R = 0.990$ . (b)  $r^3$  vs  $\alpha'_{\text{atom}}$  for the main group and first row transition elements listed in Table 1. For the fit shown,  $y = 0.194x + 0.427$ ;  $R = 0.952$ . Li (indicated by (\*)) shows a significant deviation and has been ignored in deriving the best-fit line.

$\beta'$  and  $\alpha'$  for this larger set of atoms could hardly be described as linear.

The failure to find a linear correlation is, in fact, not surprising and may be rationalized by initially comparing the dimensions of  $\alpha'$  and  $\beta'$ . Recall that  $\alpha'$  has the dimensions of volume and, for a spherical atom, may be taken to be proportional to  $V (=4\pi r^3/3)$ .<sup>11</sup> Hence

$$\alpha' \propto r^3 \quad (10)$$

(see Figure 1b) whereas, by eq 9,  $\beta'$  ( $=r^4/Z_{\text{eff}}$ ) has a significantly perturbed  $r^4$  dependence; perturbed, because  $Z_{\text{eff}}$  (see Table 1) varies significantly across the periodic table.

Let us tolerate, for a brief moment, however, the supposition that  $Z_{\text{eff}}$  at a distance  $r$  away from the nucleus is the same for all atoms. On that premise, we expect, on the basis of (9) and (10) above, a relationship of the form  $\beta' \propto \alpha'^{4/3}$ —and not  $\beta' \propto \alpha'$ . Now, let us incorporate the dependence of  $\beta'$  on  $Z_{\text{eff}}$ , as well. This step moves us away from anticipating any simple systematic relationship between  $\alpha'$  and  $\beta'$ —linear or otherwise. As shown in Table 1, the value of  $Z_{\text{eff}}$  can vary significantly from atom to atom. Furthermore,  $Z_{\text{eff}}$  does not necessarily exhibit an ordered dependence on  $r$  for a given groups of atoms, e.g.,  $r_{\text{Li}} (1.225 \text{ \AA}) \approx r_{\text{Ge}} (1.223 \text{ \AA})$  whereas  $Z_{\text{eff(Li)}} (0.95) \ll Z_{\text{eff(Ge)}} (5.30)$ . The dependence of  $\beta'$  on  $Z_{\text{eff}}$  leaves us, therefore, with

no fool-proof way of predicting the nature the relationship between  $\alpha'$  and  $\beta'$  for a large group of atoms. In particular, a linear relationship is only guaranteed if, coincidentally,  $r/Z_{\text{eff}}$  is constant for all atoms in the group such that  $\beta' \propto r^3$  and, by (10),  $\beta' \propto \alpha'$ !

As mentioned earlier,  $\beta'$  showed a linear variation with  $\alpha'$  for the elements H, C, N, O, F, S, Cl, Br, and I, with a correlation coefficient  $R = 0.983$ .<sup>2,14</sup> Interestingly, a check of the data used in ref 2<sup>15</sup> (see Table 1 and ref 14) reveals that, if we exclude hydrogen, the atoms have an average value for  $r/Z_{\text{eff}}$  of  $0.19 \pm 0.04 \text{ \AA}$ , so that the criterion  $r/Z_{\text{eff}} = \text{constant}$  is satisfied roughly for the remaining eight elements. Hence, a plot of  $\beta' = (r/Z_{\text{eff}})r^3$  vs  $\alpha'$  gives a reasonable linear variation, with an intercept in the vicinity of the origin. For hydrogen,  $r/Z_{\text{eff}}$  is  $0.49 \text{ \AA}$  (Table 1; footnote a), which is much larger than the average value for the other elements. It is easily shown, however, that because  $r^3$  (and hence  $\beta'$ ) is quite small for hydrogen, the H ( $\alpha'$ ,  $\beta'$ ) coordinates lie close to the origin, so that including H in the set does not disrupt the linear correlation. It is for those reasons that a linear variation is found for that select group of elements. The particular condition  $r/Z_{\text{eff}} \approx \text{constant}$  is not satisfied, however, for the larger set of elements considered in this work (Table 1). Indeed, a linear relationship between  $\beta'$  and  $\alpha'$  would be unlikely for any arbitrary slice of the periodic table. For the elements we have studied (Figure 1a) a quadratic function seems to provide the best fit for  $\beta'$  vs  $\alpha'$ .

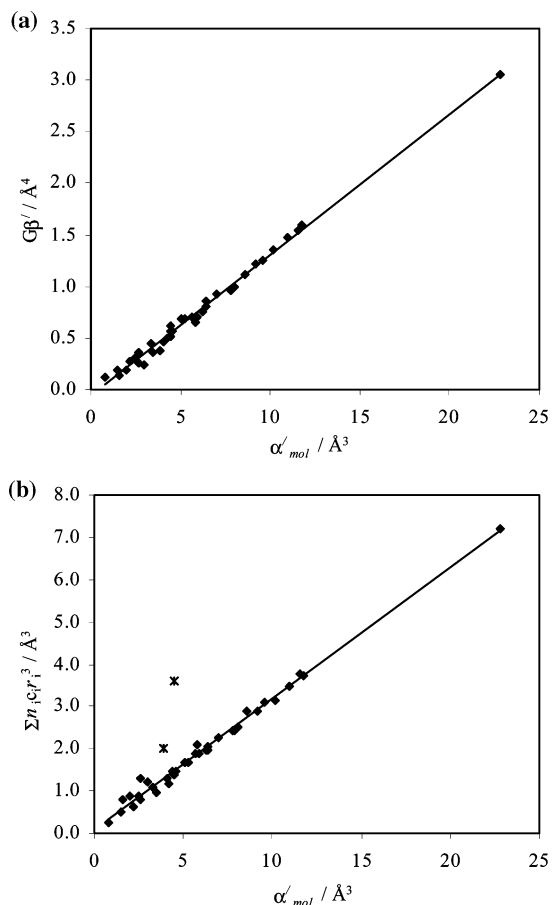
The above analysis enables us to explain the linear correlation found in ref 2 between  $\beta'$  and  $\alpha'$  for a small group of atoms, despite a failure to reproduce this relationship for the larger set of atoms (see Figure 1a). In general,  $\beta'$  is not proportional to  $\alpha'$ , and as found in ref 2, a search for a linear correspondence between  $\beta'$  and properties related to  $\alpha'$ , such as atomic softness ( $\sigma$ ) and electronegativity ( $\chi$ ), proves similarly unsuccessful. Incidentally, the variation of  $\alpha'$  with  $\sigma$  ( $=\eta^{-1}$ ) and  $\chi$  is very well described in the literature:<sup>16</sup>  $\sigma \propto \alpha'^{1/3}$ <sup>17–21</sup> and  $\chi \propto \alpha'^{-1/3}$ .<sup>22–24</sup> In the Appendix, we capitalize on the link between  $\sigma$  and  $\alpha'$  and examine in detail the relationship between softness and compressibility.

In the next section we turn to an intriguing question. A linear correlation between  $\beta'$  and  $\alpha'$  has not been found, and there is no evidence of a linear variation of  $\beta'$  with  $\sigma$ ,  $\eta$  or  $\chi$ . How, then, to explain the extremely good linear correlation observed between  $G\beta'$  and  $\alpha'_{\text{mol}}$ ?<sup>2</sup>

### $G\beta'$ and $\alpha'_{\text{mol}}$

In ref 2, a beautiful correlation has been found between the so-called group compressibility and molecular polarizability, with a correlation coefficient  $R = 0.997$ . A slight modification of that plot<sup>25</sup> is shown in Figure 2a (cf. Figure 1 in ref 2). The data set we have used is listed in Table 2; it is identical to that given in Table 1 of ref 2 except for a few minor corrections (see footnote to Table 2). At first glance, the correspondence between  $G\beta'$  and  $\alpha'_{\text{mol}}$  is somewhat startling. Particularly so because, as pointed out above, the meaning of the compressibility parameters has not been delineated fully in ref 2, and the analogous atomic properties  $\beta'$  and  $\alpha'_{\text{atom}}$  do not show a systematic linear dependence for a significant sample of the periodic table (Figure 1a).

We have pointed out already, however, that when  $r/Z_{\text{eff}}$  is nearly constant, a linear variation may be expected for  $\beta'$  vs  $\alpha'$ . In the following we explore the implications of this finding for molecules.



**Figure 2.** (a)  $G\beta'$  vs  $\alpha'_{\text{mol}}$  for molecules in Set 1 of Table 2. For the fit shown,  $y = 0.137x - 0.062$  with correlation coefficient  $R = 0.997$ . (b)  $\sum_{i=1}^N n_i c_i r_i^3$  vs  $\alpha'_{\text{mol}}$  for molecules in Set 1 of Table 2. For the fit shown,  $y = 0.310x + 0.082$  with correlation coefficient  $R = 0.995$ .  $\text{SF}_6$  and  $\text{SO}_2$  (indicated by (\*) in the figure) both show a significant deviation; see Table 2 for values. Both points have been ignored in deriving the best-fit line.

From eq 6,

$$G\beta' = n_1 \frac{r_1^4}{Z_{\text{eff},1}} + n_2 \frac{r_2^4}{Z_{\text{eff},2}} + n_3 \frac{r_3^4}{Z_{\text{eff},3}} + \dots + n_N \frac{r_N^4}{Z_{\text{eff},N}} \quad (11)$$

where  $n_i$  is the number of atoms of element  $i$  in the molecule.

Let us rewrite eq 11, however, in the form

$$G\beta' = \left( \frac{r}{Z_{\text{eff}}}_{\text{avg}} \right) [n_1 c_1 r_1^3 + n_2 c_2 r_2^3 + n_3 c_3 r_3^3 + \dots + n_N c_N r_N^3] \quad (12a)$$

$(r/Z_{\text{eff}})_{\text{avg}}$  being an average of the individual  $(r_i/Z_{\text{eff},i})$  values for all the atoms in a given molecule:  $(r/Z_{\text{eff}})_{\text{avg}} = (\sum_{i=1}^N n_i r_i / Z_{\text{eff},i}) / \sum_{i=1}^N n_i$ , and  $c_i = (r_i / Z_{\text{eff},i}) / (r / Z_{\text{eff}})_{\text{avg}}$ .

If  $(r/Z_{\text{eff}})_{\text{avg}}$  turns out to be roughly constant for the vast majority of the molecules in a given set of molecules, then, by eq 12a

$$G\beta' \propto [n_1 c_1 r_1^3 + n_2 c_2 r_2^3 + n_3 c_3 r_3^3 + \dots + n_N c_N r_N^3] \quad (12b)$$

and, by (10), substituting for  $\alpha'_i$  into (12b) gives

$$G\beta' \propto [n_1 \alpha'_1 + n_2 \alpha'_2 + n_3 \alpha'_3 + \dots + n_N \alpha'_N] \quad (13)$$

To arrive at a relation connecting  $G\beta'$  and  $\alpha'_{\text{mol}}$ , it remains only to make contact between the right-hand side of (13) and

**TABLE 2: Experimental Molecular Polarizabilities and Computed Molecular Compressibility Coefficients**

molecule <sup>a</sup>	$\alpha'_{\text{mol}} / \text{\AA}^3$ <sup>b</sup>	$\sum_{i=1}^N n_i c_i r_i^3 / \text{\AA}^3$	$(r/Z_{\text{eff}})_{\text{avg}} / \text{\AA}$	$G\beta' / \text{\AA}^4$	
Set 1					
methane	CH <sub>4</sub>	2.620	0.815	0.45	0.368
ethane	C <sub>2</sub> H <sub>6</sub>	4.480	1.39	0.44	0.613
propane	C <sub>3</sub> H <sub>8</sub>	6.379	1.97	0.43	0.858
neopentane	C <sub>5</sub> H <sub>12</sub>	10.20	3.14	0.43	1.347
hexane	C <sub>6</sub> H <sub>14</sub>	11.80	3.72	0.43	1.592
cyclopentane	C <sub>5</sub> H <sub>10</sub>	9.143	2.91	0.42	1.224
cyclohexane	C <sub>6</sub> H <sub>12</sub>	11.00	3.49	0.42	1.469
dodecane	C <sub>12</sub> H <sub>26</sub>	22.80	7.21	0.42	3.061
dimethyl ether	C <sub>2</sub> H <sub>6</sub> O	5.240	1.67	0.41	0.684
ethylene oxide	C <sub>2</sub> H <sub>4</sub> O	4.429	1.45	0.39	0.561
sulfur dioxide	SO <sub>2</sub>	3.890	2.01	0.19	0.373
sulfur hexafluoride	SF <sub>6</sub>	4.471	3.61	0.16	0.564
ammonia	NH <sub>3</sub>	2.220	0.633	0.43	0.269
carbon dioxide	CO <sub>2</sub>	2.630	1.28	0.21	0.265
<i>p</i> -dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	8.601	2.91	0.39	1.122
nitrous oxide	N <sub>2</sub> O	2.999	1.22	0.20	0.241
ethyl cyanide	C <sub>3</sub> H <sub>5</sub> N	6.240	1.95	0.39	0.758
methyl cyanide	C <sub>2</sub> H <sub>3</sub> N	4.480	1.38	0.37	0.513
methyl dicyanide	C <sub>3</sub> H <sub>2</sub> N <sub>2</sub>	5.790	2.08	0.32	0.658
<i>tert</i> -butyl cyanide	C <sub>5</sub> H <sub>9</sub> N	9.591	3.11	0.40	1.248
isopropyl cyanide	C <sub>4</sub> H <sub>7</sub> N	8.049	2.53	0.40	1.003
methanol	CH <sub>4</sub> O	3.319	1.08	0.41	0.439
ethanol	C <sub>2</sub> H <sub>6</sub> O	5.080	1.67	0.41	0.684
propanol	C <sub>3</sub> H <sub>8</sub> O	6.971	2.25	0.41	0.929
2-propanol	C <sub>3</sub> H <sub>8</sub> O	6.971	2.25	0.41	0.929
cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	11.56	3.78	0.41	1.541
hydrogen	H <sub>2</sub>	0.790	0.247	0.50	0.123
oxygen	O <sub>2</sub>	1.600	0.810	0.18	0.143
carbon monoxide	CO	1.950	0.874	0.22	0.193
water	H <sub>2</sub> O	1.491	0.498	0.39	0.194
ethylene	C <sub>2</sub> H <sub>4</sub>	4.220	1.16	0.42	0.490
acetylene	C <sub>2</sub> H <sub>2</sub>	3.445	0.960	0.38	0.367
<i>N</i> -methylformamide	C <sub>2</sub> H <sub>5</sub> NO	5.910	1.87	0.38	0.708
acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	4.589	1.45	0.39	0.561
acetamide	C <sub>2</sub> H <sub>5</sub> NO	5.670	1.87	0.38	0.708
acetone	C <sub>3</sub> H <sub>6</sub> O	6.390	2.03	0.40	0.806
formaldehyde	CH <sub>2</sub> O	2.449	0.880	0.36	0.316
formamide	CH <sub>3</sub> NO	4.080	1.29	0.36	0.463
<i>N,N</i> -dimethylformamide	C <sub>3</sub> H <sub>7</sub> NO	7.809	2.45	0.39	0.952
<i>N</i> -methylacetamide	C <sub>3</sub> H <sub>7</sub> NO	7.820	2.45	0.39	0.952
Set 2					
fluoromethane	CH <sub>3</sub> F	2.620	0.948	0.38	0.362
chloromethane	CH <sub>3</sub> Cl	4.549	1.23	0.39	0.476
bromomethane	CH <sub>3</sub> Br	5.610	1.41	0.38	0.541
iodomethane	CH <sub>3</sub> I	7.590	1.94	0.39	0.743
difluoromethane	CH <sub>2</sub> F <sub>2</sub>	2.730	1.14	0.31	0.356
dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	6.819	1.82	0.32	0.584
dibromomethane	CH <sub>2</sub> Br <sub>2</sub>	8.681	2.26	0.32	0.714
diiodomethane	CH <sub>2</sub> I <sub>2</sub>	12.90	3.51	0.33	1.118
trifluoromethane	CHF <sub>3</sub>	2.810	1.45	0.24	0.350
trichloromethane	CHCl <sub>3</sub>	8.530	2.70	0.26	0.693
tribromomethane	CHBr <sub>3</sub>	11.84	3.59	0.25	0.887
triiodomethane	CHI <sub>3</sub>	18.04	5.81	0.26	1.494
tetrafluoromethane	CF <sub>4</sub>	2.921	2.00	0.17	0.801
tetrachloromethane	CCl <sub>4</sub>	10.51	4.18	0.19	0.344
trichlorofluoromethane	CFCl <sub>3</sub>	8.241	3.68	0.19	0.687

<sup>a</sup> The molecular formulas have been presented in a manner that is convenient for identifying the number of atoms of element  $i$  in the molecule,  $n_i$ . A more chemical representation is used in ref 15. <sup>b</sup> The polarizability data are from refs 2 and 15. The appropriate value for propanol (cf. refs 2 and 15) appears to be  $47.04 \text{ a}_0^3$  ( $=6.971 \text{ \AA}^3$ ). Isomers (such as propanol and 2-propanol) were treated separately in ref 2, and we have adopted a similar approach for comparison. Note, however, that by eqs 5 and 6, all isomers will have the same value for  $G\beta'$ , and  $(r/Z_{\text{eff}})_{\text{avg}}$ , as well.

the molecular polarizability. Now, we know that even for very small molecules the molecular polarizability is not a simple sum of atomic polarizabilities.<sup>26,27</sup> An additivity scheme, whereby  $\alpha'_{\text{mol}}$  is estimated by a sum of atomic contributions, seems to

gives reliable numbers only if the atomic polarizabilities are derived by reference to the appropriate valence state of the atom in the molecule.<sup>15,26,28,29</sup> The idealized additivity condition, i.e.,  $\alpha'_{\text{mol}} = \sum_{i=1}^N n_i \alpha'_i$ , needs not be invoked for the present argument, however. It is sufficient to employ a less stringent assumption, namely, that the sum of the atomic polarizability is directly proportional to the molecular polarizability, so that

$$\alpha'_{\text{mol}} \propto [n_1 \alpha'_1 + n_2 \alpha'_2 + n_3 \alpha'_3 \dots + n_N \alpha'_N] \quad (14)$$

which, by (13), gives

$$G\beta' \propto \alpha'_{\text{mol}} \quad (15)$$

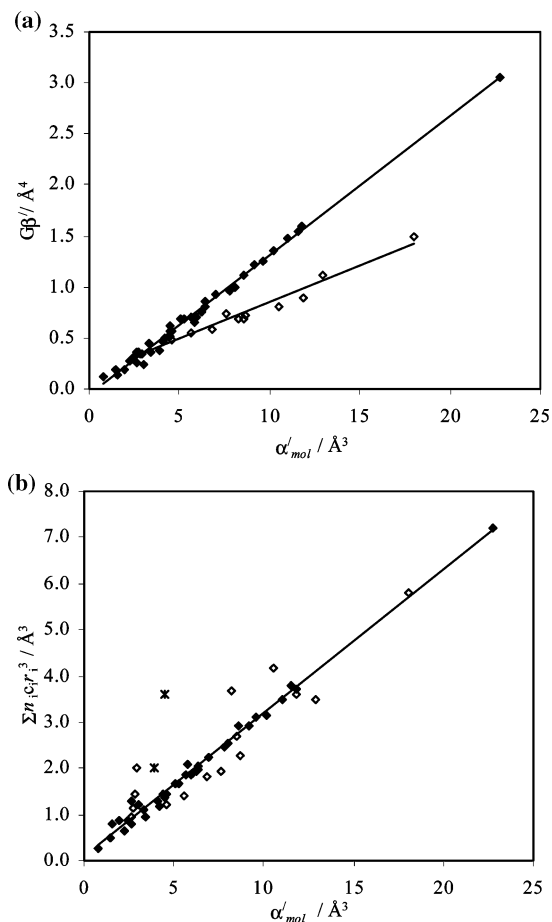
To sum up, we have suggested that the validity of (15) for the molecules discussed in ref 2 (Set 1 in Table 2) is due largely to  $(r/Z_{\text{eff}})_{\text{avg}}$  being roughly constant for most of those molecules. Hence, (15) appears to be a shrouded demonstration of a more recognizable relationship in chemistry— $\sum_{i=1}^N n_i \alpha'_i \propto \alpha'_{\text{mol}}$ —based on the concept of the additivity of atomic polarizability.<sup>15,26–30</sup>

We have tested the above analysis of the character of  $G\beta'$  by plotting the variation of  $\sum_{i=1}^N n_i c_i r_i^3$  with  $\alpha'_{\text{mol}}$  for the complete set of molecules considered in ref 2 (see Figure 2b). If the assumptions made in going from (12) to (15) are reasonable, we should find a linear relationship for  $\sum_{i=1}^N n_i c_i r_i^3$  vs  $\alpha'_{\text{mol}}$ , with a distribution similar to that of  $G\beta'$  vs  $\alpha'_{\text{mol}}$  (Figure 2a). For the plot of  $\sum_{i=1}^N n_i c_i r_i^3$  vs  $\alpha'_{\text{mol}}$  (Figure 2b), a linear correlation has indeed been found, with a correlation coefficient (0.995) and a distribution about the best fit line that is similar to what has been found for  $G\beta'$  vs  $\alpha'_{\text{mol}}$  (Figure 2a). Curiously, only sulfur dioxide and sulfur hexafluoride show significant deviations from the linear trend; for these two molecules,  $(r/Z_{\text{eff}})_{\text{avg}}$  is noticeably smaller than it is for most of the other molecules (see column 5, Table 2).

The universality of (15) has been checked briefly by preparing a second plot of  $G\beta'$  vs  $\alpha'_{\text{mol}}$  for a short series of halomethane molecules. For purposes of comparison, the halomethane data have been combined with the plot for the molecules of Set 1 that we have discussed earlier (see Figure 3a; cf. Figure 2a). The experimental molecular polarizabilities we used for the halomethanes have been taken from ref 15, as well.  $G\beta'$  has been computed, as before, using the values for  $r$  and  $Z_{\text{eff}}$  given in Table 1. A linear relationship between  $G\beta'$  and  $\alpha'_{\text{mol}}$  has been found for this new set of molecules, too. However, the slope of the trend line for the halomethanes is noticeably different from that established by the initial series of molecules.

The variation we observe for this second set of molecules has been rationalized as follows. When  $(r/Z_{\text{eff}})_{\text{avg}}$  is computed for a series of halomethanes  $\text{CH}_{4-m}\text{X}_m$ , for fixed  $m$ , the only change in element type from one molecule to the next is for the halides, X. Now, because  $r/Z_{\text{eff}}$  is similar for the halides (F, 0.15 Å; Cl, 0.17 Å; Br, 0.16 Å; I, 0.19 Å), the average value  $(r/Z_{\text{eff}})_{\text{avg}}$  will be almost constant for all molecules with the same  $m$ . Thus, we find (Set 2 in Table 2) that  $(r/Z_{\text{eff}})_{\text{avg}} \approx 0.38$  ( $m = 1$ ); 0.32 ( $m = 2$ ); 0.25 ( $m = 3$ ); 0.18 ( $m = 4$ ). One may expect, therefore, that a plot of  $G\beta'$  vs  $\alpha'_{\text{mol}}$  for the entire set of halomethanes (Table 2) should not give a straight line, because  $(r/Z_{\text{eff}})_{\text{avg}}$  shows a nonnegligible  $m$ -dependence.

It turns out, in fact, that if the four sets of halides ( $m = 1$ ,  $m = 2$ ,  $m = 3$  and  $m = 4$ ) are plotted separately, four reasonably well-defined lines are found; with slopes varying in the order ( $m = 1$ ) > ( $m = 2$ )  $\approx$  ( $m = 3$ ) > ( $m = 4$ ) (trichlorofluoromethane being combined with the two tetrahalides). The lines are sufficiently close, however, for us to be satisfied with a



**Figure 3.** (a)  $G\beta'$  vs  $\alpha'_{\text{mol}}$  for molecules in Sets 1 (shaded boxes) and 2 (unshaded boxes) of Table 2. For Set 2,  $y = 0.071x + 0.136$ , with correlation coefficient  $R = 0.986$ . (b)  $\sum_{i=1}^N n_i c_i r_i^3$  vs  $\alpha'_{\text{mol}}$  for molecules in Sets 1 (shaded boxes) and 2 (unshaded boxes) of Table 2 (cf. Figure 2b).

single line in Figure 3a for the entire set (unshaded boxes). Furthermore, the differences in the slopes of the individual lines are likely to be well within the margins of error associated with the experimental polarizabilities and atomic radii data used to construct the plot.

Let us turn our attention now, however, to a more significant difference in slopes: the difference in Figure 3a between the lines for Set 1 and Set 2. Why do the two sets of molecules follow separate linear trajectories for  $G\beta'$  vs  $\alpha'_{\text{mol}}$ ? Note that although  $(r/Z_{\text{eff}})_{\text{avg}}$  for halomethanes shows a noticeable  $m$ -dependence, the values are generally (for  $m = 2-4$ ) less than those for the molecules in Set 1 (Table 2). Therefore, because  $G\beta'$  vs  $\alpha'_{\text{mol}}$  gives a line with a slope that depends on  $(r/Z_{\text{eff}})_{\text{avg}}$ , (by (13) and (15)), a trend-line for the halomethane series would, indeed, be expected to have a somewhat smaller slope compared to that for the molecules in Set 1. The evident  $(r/Z_{\text{eff}})_{\text{avg}}$  dependence of the splitting shown in Figure 3a is, therefore, consistent with our basic analysis of why  $G\beta'$  varies linear with  $\alpha'_{\text{mol}}$ .

Finally, the validity of the assumption that  $\sum_{i=1}^N n_i c_i r_i^3 \propto \alpha'_{\text{mol}}$  has been evaluated for the halomethanes, as well. Figure 3b shows the distribution of the Set 2 halomethane data about the best fit line obtained earlier (Figure 2b) for Set 1 molecules. The general trend for the halomethane numbers compares closely with that of the Set 1 molecules although there is a relatively large average deviation from the Set 1 best-fit line (Figure 3b). The overall trend in both the Set 1 and Set 2 numbers does suggest, in fact, that the approximation

$\sum_{i=1}^N n_i c_i r_i^3 \propto \alpha'_{\text{mol}}$  is valid for the complete set of molecules listed in Table 2.

## Conclusion

The relationship between the newly introduced (atomic and molecular) compressibility<sup>2</sup> and (atomic and molecular) polarizability has been rationalized.

In particular, we find some evidence that the linear variation of a plot of the molecular compressibility against polarizability,  $G\beta'$  vs  $\alpha'_{\text{mol}}$ , for certain groups of molecules,<sup>2</sup> may be explained largely on the basis of a similarity in  $(r/Z_{\text{eff}})_{\text{avg}}$  for the relevant molecules. Here  $(r/Z_{\text{eff}})_{\text{avg}}$  is a simple average of  $r/Z_{\text{eff}}$  (the ratio of the atomic radius and effective nuclear charge) for the set of atoms comprising a given molecule. Where  $(r/Z_{\text{eff}})_{\text{avg}}$  is similar for the molecules in a given series, a linear variation is expected for  $G\beta'$  vs  $\alpha'_{\text{mol}}$ . Our analysis relies strongly on two key assumptions: first, that the atomic polarizability is proportional to the atomic volume<sup>11</sup> and, second, that the molecular polarizability is roughly proportional to the sum of the atomic polarizabilities.<sup>15,26–30</sup>

Although the atomic compressibility  $\beta'$ , as currently defined,<sup>2</sup> holds no apparent intuitive nor physical meaning, the phenomenological correlation between  $G\beta'$  and  $\alpha'_{\text{mol}}$  is of interest. It suggests a simple yet reliable route for approximating molecular polarizabilities.

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## Appendix

Empirical investigations have uncovered a cubic relationship between the polarizability ( $\alpha'$ ) and the global softness ( $\sigma$ ) of atomic species or similarly bonded molecules:<sup>17–20</sup>

$$\sigma \propto \alpha'^{(1/3)} \quad (\text{A.1})$$

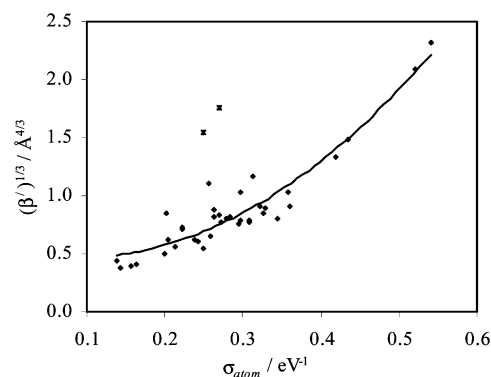
And a theoretical justification for this relationship was provided by Simón-Manso and Fuentealba<sup>21</sup> within the framework of density functional theory.<sup>16,31</sup>

Picking up on a suggestion by one of the referees, we have examined the relationship between  $\sigma$  and the newly defined compressibility parameters. By (A.1), one might anticipate a relationships between  $\sigma_{\text{atom}}$  and  $\beta'^{(1/3)}$  ( $\sigma_{\text{mol}}$  and  $G\beta'^{(1/3)}$ ) that is comparable to what has been found (in ref 2 and this work) for  $\alpha'_{\text{atom}}$  and  $\beta'$  ( $\alpha'_{\text{mol}}$  and  $G\beta'$ ). The results of our investigation of the softness vs compressibility relationship are summarized in the following.

**Atomic Softness and Atomic Compressibility.** Shown in Figure A1 is a plot of  $\beta'^{(1/3)}$  vs  $\sigma_{\text{atom}}$  for all the atoms in Table 1 above. The atomic softness has been computed from the chemical hardness,  $\eta$ , data in ref 32:  $\sigma = 1/\eta$ , where  $\eta = (I - A)/2$ .<sup>8</sup>  $I$  is ionization energy, and  $A$  is the electron affinity of the atoms.

A variation similar to that observed between the atomic polarizability and the electronic compressibility (Figure 1a) is in fact found for  $\beta'^{(1/3)}$  vs  $\sigma_{\text{atom}}$  (Figure A1). The results of this brief analysis for atoms are, therefore, consistent with the proportionality between  $\sigma$  and  $\alpha'^{(1/3)}$ .

**Molecular Softness and Molecular Compressibility.** Molecular softnesses have been computed by the approximation



**Figure A1.**  $\beta'^{(1/3)}$  vs  $\sigma_{\text{atom}}$  for the main group and first row transition elements listed in Table 1. For a quadratic fit,  $y = 8.45x^2 - 1.44x + 0.524$ ;  $R = 0.946$ . Ca ( $\sigma = 0.25$  eV) and Sr ( $\sigma = 0.27$ ) (indicated by (\*)) show the most significant deviations.

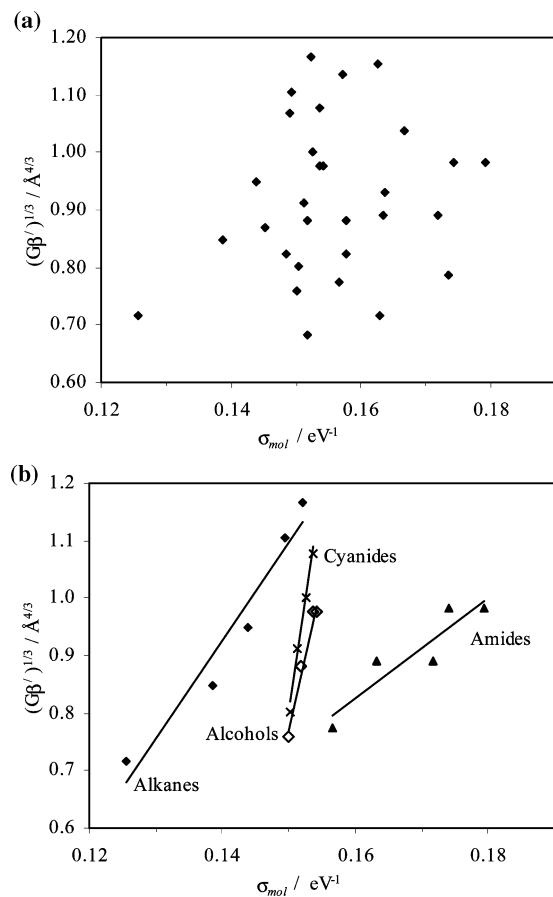
**TABLE A1:  $G\beta'^{(1/3)}$  and Global Softness Data for Organic Molecules**

no.	molecule	$G\beta'^{(1/3)}/\text{\AA}^{4/3}$	$\sigma_{\text{mol}}/\text{eV}^{-1}$	
			MP2	expt
1	methane	0.72	0.126	0.097
2	ethane	0.85	0.139	
3	propane	0.95	0.144	
4	neopentane	1.10	0.149	0.120
5	hexane	1.17	0.152	
6	cyclopentane	1.07	0.149	
7	cyclohexane	1.14	0.157	
8	dimethyl ether	0.88	0.158	0.125
9	ethylene oxide	0.82	0.148	
10	<i>p</i> -dioxane	1.04	0.167	
11	ethyl cyanide	0.91	0.151	
12	methyl cyanide	0.80	0.150	0.133
13	methyl dicyanide	0.87	0.145	
14	<i>tert</i> -butyl cyanide	1.08	0.154	
15	isopropyl cyanide	1.00	0.152	
16	methanol	0.76	0.150	
17	ethanol	0.88	0.152	
18	propanol	0.98	0.154	
19	2-propanol	0.98	0.154	
20	cyclohexanol	1.15	0.163	
21	ethylene	0.79	0.173	0.161
22	acetylene	0.72	0.163	0.143
23	<i>N</i> -methylformamide	0.89	0.172	
24	acetaldehyde	0.82	0.158	
25	acetamide	0.89	0.163	
26	acetone	0.93	0.164	0.179
27	formaldehyde	0.68	0.152	0.161
28	formamide	0.77	0.157	0.161
29	<i>N,N</i> -dimethylformamide	0.98	0.179	
30	<i>N</i> -methylacetamide	0.98	0.174	

$\sigma_{\text{mol}} = 2(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})^{-1}$ <sup>33</sup> for 30 of the organic molecules in Table 2. All our calculation have been performed at the MP2/6-311++G\*\* level using the GAUSSIAN 03 suite of programs.<sup>34</sup> Our results are summarized in Table A1 along with values computed with experimental  $I$  and  $A$  data from ref 32.

The relationship between  $G\beta'^{(1/3)}$  and  $\sigma_{\text{mol}}$  for the molecules in Table A1 appears to be quite random (Figure A2a). Upon closer inspection, however, we have observed a linear correlation between these two parameters for similarly bonded molecules. This is illustrated in Figure A2b in which the data for some alkanes, alcohols, cyanides, and amides have been replotted. In each of these short series of molecules, a reasonable linear correlation between  $\sigma_{\text{mol}}$  and the cube root of the molecular compressibility has been observed.

The data summarized in Figure A2b afford us two key conclusions: they (i) confirm the observation made by Simón-Manso and Fuentealba<sup>21</sup> of a good correlation between  $\sigma_{\text{mol}}$  and



**Figure A2.** (a)  $G\beta'$  ( $^{1/3}$ ) vs  $\sigma_{\text{mol}}$  for the molecules in Table A1. (b)  $G\beta'$  ( $^{1/3}$ ) vs  $\sigma_{\text{mol}}$  for selected molecules: aliphatic alkanes, cyanides, alcohols and amides (molecules no. 1–5; 11, 12, 14, 15; 16–19; and 23, 25, 28–30, respectively, in Table A1).

( $\alpha'_{\text{mol}}$ ) $^{1/3}$  (or  $\sigma_{\text{mol}}^3$  and  $\alpha'_{\text{mol}}$ ) for similarly bonded molecular systems and (ii) are consistent with the linear relationship described in ref 2 and the present work between  $G\beta'$  and  $\alpha'_{\text{mol}}$  (Figure 3a).

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