emissions between 77 and 295 K, in contrast to the small red shifts observed for the  $\pi - \pi^*$  emissions of analogous Rh(III) complexes. This type of nuclear barrier may be sufficiently important in ortho-metalated Ir(III) complexes to prohibit thermal equilibration of their close-lying MLCT excited states even though the electronic coupling of these states is promoted by their Ir-C bonds. In fact, these same Ir-C bonds may, through trans effects, be responsible for distortions which give rise to barriers. The nature of the nuclear distortions in which these barriers originate is presently under investigation.

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**Registry No.** bpy, 366-18-7; phen, 66-71-7; [Ir(ppy)<sub>2</sub>(bpy)][PF<sub>6</sub>], 106294-60-4; [Ir(bzq)<sub>2</sub>(phen)][PF<sub>6</sub>], 106294-61-5; [Rh(ppy)<sub>2</sub>(bpy)]-[ClO<sub>4</sub>], 106251-21-2; [Rh(bzq)<sub>2</sub>(phen)][ClO<sub>4</sub>], 106251-23-4; [Rh-(ppy)<sub>2</sub>Cl]<sub>2</sub>, 33915-80-9; [Rh(bzq)<sub>2</sub>Cl]<sub>2</sub>, 33915-76-3; [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub>, 92220-65-0; [Ir(bzq)<sub>2</sub>Cl]<sub>2</sub>, 52352-02-0; [Ir(ppy)<sub>3</sub>], 94928-86-6.

# Solid-State Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Studies of Alkaline Earth Metasilicates

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We have obtained high-field (11.7 T, 67.8 MHz) <sup>17</sup>O nuclear magnetic resonance (NMR) spectra of a series of alkaline earth metasilicates (clinoenstatite, MgSiO<sub>3</sub>; diopside, CaMgSi<sub>2</sub>O<sub>6</sub>; pseudowollastonite,  $\alpha$ -CaSiO<sub>3</sub>; strontium metasilicate,  $\alpha$ -SrSiO<sub>3</sub>; and barium metasilicate, BaSiO<sub>3</sub>). Values of the nuclear quadrupole coupling constants ( $e^2 qQ/h$ ), electric field gradient tensor asymmetry parameters ( $\eta$ ), and isotropic chemical shifts ( $\delta_i$ ) have been deduced for all the types of oxygen sites encountered. The  $e^2 q Q/h$  values for the nonbridging oxygens (Si-O-M, M = divalent cation) are in the range 1.6-3.2 MHz and increase with increasing cation electronegativity, the asymmetry parameters vary from 0 to 0.1, and the isotropic chemical shifts become more deshielded with increasing cation radius. The total range of isotropic chemical shifts for the nonbridging oxygens is 127 ppm. For the bridging oxygens (Si-O-Si) in the metasilicates, the  $e^2qQ/h$  values are in the range from 3.7 to 5.1 MHz and the asymmetry parameters vary from 0.2 to 0.4. The isotropic chemical shifts again become more deshielded with increasing cation radius, the total range of isotropic chemical shifts being 25 ppm. The chemical shifts for both bridging and nonbridging oxygens in metasilicates indicate that deshielding may be correlated with the presence of large cations, as found previously for <sup>17</sup>O NMR spectra of the group IIA (2) and group IIB (12) oxides.

# Introduction

Oxygen is a major constituent of all silicates and of many organic polymers, so <sup>17</sup>O solid-state nuclear magnetic resonance (NMR) spectroscopy should have considerable potential for investigating the structures of such materials.<sup>1-3</sup> In this paper, we present the first comprehensive report of the solid-state <sup>17</sup>O NMR spectra of a series of alkaline earth metasilicates (diopside, CaMgSi<sub>2</sub>O<sub>6</sub>; clinoenstatite, MgSiO<sub>3</sub>; pseudowollastonite,  $\alpha$ -Ca-SiO<sub>3</sub>; strontium metasilicate,  $\alpha$ -SrSiO<sub>3</sub>; and barium metasilicate, BaSiO<sub>3</sub>), using high-field (11.7 T, 67.8 MHz and 8.45 T, 48.8 MHz) NMR of <sup>17</sup>O labeled materials.

#### **Experimental Section**

Synthetic Aspects. All the silicates were synthesized by using  $Si^{17}O_2$  (prepared from the hydrolysis of  $SiCl_4$  with 40 atom % H<sub>2</sub><sup>[17</sup>O] (vide infra), obtained from Cambridge Isotope Laboratories, Cambridge, MA) and high-purity metal carbonates,  $MCO_3$  (M = Ca, Sr, or Ba), or MgO. Oxygen-17-enriched SiO<sub>2</sub> was synthesized by dissolving 3.40 g of SiCl<sub>4</sub> in 30 mL of anhydrous diethyl ether under an N2 atmosphere and then syringing in 1.3 mL of 40 atom % H<sub>2</sub>[<sup>17</sup>O] to cause hydrolysis of the SiCl<sub>4</sub>, basically as outlined by Bray et al.<sup>2</sup> A 1.43-g yield of enriched silica gel was thus obtained. The silica gel was then fired either at 1500 °C for about 15 min or at 350 °C for about 24 h to drive off volatile impurities. X-ray diffraction analyses indicated the SiO<sub>2</sub> to be amorphous after the 350 °C calcination or in the form of low cristobalite after the high-temperature calcination. Alkaline-earth-containing silicate glasses were then prepared with 99.999% metal carbonates (or MgO) and <sup>17</sup>O-enriched silica. Each glass was melted at about 50 °C above its liquidus and then quenched and ground to a fine powder. The process was repeated three times. To minimize loss of <sup>17</sup>O to the atmosphere, the enriched glasses were fused for only about 20 min each time. Crystalline metasilicates were finally obtained by crystallization of the isochemical glass at temperatures some 50-100 °C below the solidus. Purities were verified by means of powder X-ray diffraction.

Spectroscopic Aspects. Oxygen-17 NMR spectra were recorded at 67.8 and 48.8 MHz with "home-built" spectrometers. These consist of 11.7-T, 52-mm-bore or 8.45-T, 89-mm-bore superconducting solenoids (Oxford Instruments, Osney Mead, U.K.), Nicolet (Madison, WI) Model 1280 data acquisition systems, Amplifier Research (Souderton, PA) Model 200L amplifiers (for radio-frequency pulse generation), and "home-built" static (solenoidal) and "magic-angle"<sup>4</sup> sample-spinning (MASS) probes. The solution 90° pulse widths were in the range of 15–20  $\mu$ s, and 5-7  $\mu$ s pulses were used for data acquisition on the solid samples (where only the 1/2, -1/2 transition is observed, for both bridging and nonbridging oxygens). Typical recycle times of 30-120 s were used, based on preliminary recycle time dependencies of the <sup>17</sup>O NMR spectra. The spectra were simulated as described elsewhere.<sup>5</sup> All the chemical shifts are quoted with respect to the <sup>17</sup>O NMR signal of external tap water at 25 °C, with high-fre-

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Figure 1. <sup>17</sup>O NMR spectra (11.7 T) and spectral simulations of crystalline diopside (CaMgSi<sub>2</sub>O<sub>6</sub>): (A) static, 200 scans, recycle time 120 s; (B) 75° VASS at 3.4 kHz, 200 scans, recycle time 60 s; (C) MASS at 5.2 kHz, 100 scans, recycle time 60 s; (D) expansion of center band of (C); (E) simulation of (D) with individual spectral components, two nonbridging oxygens and one bridging oxygen.

quency, low-field, paramagnetic, deshielded values being denoted as positive (IUPAC  $\delta$  scale).

#### **Results and Discussion**

The crystalline alkaline earth metasilicates (especially the pyroxenes and cyclosilicates) have the general formula  $M_1M_2Si_2O_6$ , where  $M_1$  and  $M_2$  are alkaline earths, and  $M_1$  may equal M<sub>2</sub>. These metasilicates are either comprised of infinite, single chains of SiO<sub>4</sub> tetrahedra containing two bridging oxygens (Q<sup>2</sup> units, in silicate nomenclature) or, for the pseudowollastonite polytype, as the cyclic trimer,  $Si_3O_9$ , as illustrated:



For chain silicates, the chains of silicate tetrahedra are parallel to one of the crystallographic axes and can be visualized as being held together by the divalent cations. Within each chain, each  $[SiO_4]$  tetrahedron shares two oxygens with adjacent tetrahedra (bridging oxygens, Si-O-Si) and also contains two crystallographically different oxygens that are coordinated to the divalent cations (nonbridging oxygens, Si-O-M). The bridging oxygens are also coordinated to either one or two divalent cations. The alkaline earth metal cations are in six- to eightfold coordination with oxygen. A typical mineralogical example of such a silicate is diopside,  $CaMgSi_2O_6$ , the crystal structure of which is well established.<sup>6,7</sup> Three crystallographically distinct oxygen sites exist, two nonbridging and one bridging. We have recently shown that <sup>17</sup>O MASS NMR is able to clearly separate all three sites,<sup>1,3</sup> and we shall briefly describe these (and related) results as an introduction to the <sup>17</sup>O NMR of metasilicates.

TABLE I: Oxygen-17 Nuclear Quadrupole Coupling Constants, Asymmetry Parameters, and Isotropic Chemical Shifts for the Alkaline Earth Metasilicates<sup>a</sup>

system	oxygen type	$e^2 q Q/h$ , MHz	η	$\delta_{i}$
MgSiO <sub>3</sub>	O <sub>nb</sub>	(3.2)	(0.0)	(60)
	Onb	(3.2)	(0.0)	(42)
	Obr	(5.1)	(0.3)	(62)
CaMgSi <sub>2</sub> O <sub>6</sub>	Onb	2.7 (2.9)	0.0 (0.0)	84 (86)
	Onb	2.7 (3.0)	0.1 (0.1)	63 (64)
	Obr	4.4 (4.5)	0.3 (0.2)	69 (71)
$\alpha$ -CaSiO <sub>3</sub>	Onb	2.1	0.1	94
	Onb	2.3	0.1	91
	Obr	3.8	0.2	75
$\alpha$ -SrSiO <sub>3</sub>	Onb	2.1	0.1	108
	Onb	2.2	0.1	105
	Obr	4.1	0.4	80
BaSiO <sub>3</sub>	Onb	2.1	0.1	169
	Onb	1.6	0.1	159
	Obr	3.7	0.4	87

<sup>a</sup> All parameters are derived from spectral simulations of 67.8-MHz (11.7-T) <sup>17</sup>O NMR spectra, except for the values derived from the static spectra of diopside and clinoenstatite, which were obtained at 48.8 MHz (8.45 T). Values in parentheses indicate that the sample was static. All other values are taken from MASS NMR spectra. Errors are typically  $\pm 0.2$  MHz  $(e^2 q Q/h)$ ,  $\pm 0.1$  ( $\eta$ ), and  $\pm 2$  ( $\delta_i$ ).

We show in Figure 1 the 11.7-T <sup>17</sup>O NMR spectra of an enriched sample of crystalline diopside, CaMgSi<sub>2</sub>O<sub>6</sub>. At this field, the static spectrum is quite broad and featureless (Figure 1A) and does not lead to a ready identification of the various nonequivalent oxygen sites. Similarly, the 75° variable-angle sample-spinning (VASS)<sup>5</sup> spectrum provides relatively little readily interpretable information (Figure 1B). However, the (54.7°) "magic-angle" sample-spinning (MASS)<sup>4</sup> spectrum (Figure 1C) clearly shows two well-resolved peaks, having "fine" structure, as described previously.<sup>3</sup> In Figure 1D we show an expansion of this spectrum, together with its computer simulation (Figure 1E); values for the nuclear quadrupole coupling constant  $(e^2qQ/h)$ , electric field gradient tensor asymmetry parameter  $(\eta)$ , and isotropic chemical shift  $(\delta_i)$  for each type of oxygen are given in Table I. As discussed previously, we assign the two high-frequency "doublets" (with  $e^2 q Q/h$  values of ~2.7 MHz) to the two nonbridging oxygen sites and the lower frequency "doublet" (with  $e^2 qQ/h$  of 4.4 MHz) to the single bridging oxygen site. This is in accord with the empirical relationship observed between the magnitude of the nuclear quadrupolar coupling constant and the ionicity of the cation-oxygen bond.<sup>1,8</sup> Qualitatively, nonbridging oxygens coordinated to the divalent cations may be considered to be of a more ionic nature than bridging oxygens, resulting in less p-orbital contribution to the electric field gradient and consequently smaller values of the quadrupole coupling constant.

For comparative purposes, we show in Figure 2B the static <sup>17</sup>O NMR spectrum of diopside obtained at a lower field (8.45 T). In this case, a better resolved second-order quadrupole powder pattern is obtained, due presumably to a reduction in chemical shift anisotropy broadening (which is proportional to the applied field) and increased second-order effect (which is inversely proportional to the applied field). It is now possible to obtain quadrupole interaction parameters from the static experimental spectrum, although the values of  $e^2 q Q/h$  are somewhat greater and suggest a small contribution from chemical shift anisotropy and/or dipole-dipole interaction in the static case. Thus, the MASS-derived values are thought to be the most accurate ones, in all of the cases we have studied.

We show in Figure 2C-J 11.7-T <sup>17</sup>O MASS and 8.45-T static NMR spectra of a series of metasilicates. As with diopside,<sup>6,7</sup> each metasilicate contains a 2:1 ratio of nonbridging to bridging oxygens. However, in the case of MgSiO<sub>3</sub>,  $\alpha$ -CaSiO<sub>3</sub>, and  $\alpha$ -SrSiO<sub>3</sub>, X-ray structural analysis indicates that further crystallographic nonequivalencies exist, resulting from the stacking

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Figure 2. Oxygen-17 11.7-T MASS and 8.45-T static NMR spectra of a series of crystalline alkaline earth metasilicates: (A) CaMgSi<sub>2</sub>O<sub>6</sub>, MASS at 5.2 kHz, 100 scans; (B) CaMgSi<sub>2</sub>O<sub>6</sub>, static, 1460 scans; (C) MgSiO<sub>3</sub>, MASS at 4.9 kHz, 1400 scans; (D) MgSiO<sub>3</sub>, static, 2580 scans; (E)  $\alpha$ -CaSiO<sub>3</sub>, MASS at 5.4 kHz, 2000 scans; (F)  $\alpha$ -CaSiO<sub>3</sub>, static, 2500 scans; (G)  $\alpha$ -SrSiO<sub>3</sub>, MASS at 4.9 kHz, 560 scans; (H)  $\alpha$ -SrSiO<sub>3</sub>, static, 1770 scans; (I) BaSiO<sub>3</sub>, MASS at 4.9 kHz, 1080 scans; (J) BaSiO<sub>3</sub>, static, 1000 scans. Typical recycle times were 30-120 s. Values of between 50- and 300-Hz exponential line broadening were used.

pattern. As a result, there are in fact six distinct oxygen sites for MgSiO<sub>3</sub> (four nonbridging, two bridging),<sup>9</sup> eighteen for  $\alpha$ -CaSiO<sub>3</sub> (twelve nonbridging, six bridging),<sup>10</sup> and ten for  $\alpha$ -SrSiO<sub>3</sub> (twelve nonbridging oxygens in six different sites, six bridging oxygens in four different sites).<sup>11</sup> However, the magnitude of any "crystallographic nonequivalences" in the <sup>17</sup>O NMR results is apparently very small (although a small splitting of the <sup>29</sup>Si spectrum of enstatite has been observed<sup>12</sup>). Consequently, we have limited our spectral simulations to a three-site model in all cases, on the grounds that any distribution of quadrupolar coupling constants and chemical shifts resulting from the presence of crystallographic nonequivalence is less than the magnitude of the uncertainties involved in measuring these parameters.

The <sup>17</sup>O MASS NMR spectrum of clinoenstatite (MgSiO<sub>3</sub>) is shown in Figure 2C and consists of a broad ( $\Delta \nu_{1/2} \simeq 35$  ppm) signal centered at ca. 50 ppm. At least four shoulders are noted, but a meaningful computer simulation is clearly very difficult. The static spectrum is shown in Figure 2D. As with diopside, this presents a set of well-resolved second-order powder patterns which are amenable to spectral simultation using only three sites. The results are consistent with the crystal structure in that there are three kinds of oxygen (one bridging, coordinated to one Mg; one nonbridging, bound to three Mg; one nonbridging, bound to two Mg).<sup>9</sup> The values for the quadrupole coupling constant, asymmetry parameter, and isotropic chemical shift obtained are given in Table I. However, as with diopside, the values for the quadrupole coupling constant derived from the static spectrum are susceptible to contributions from chemical shift anisotropy and dipolar broadening and must therefore be regarded as upper limiting values.

The next two compounds,  $\alpha$ -CaSiO<sub>3</sub> and  $\alpha$ -SrSiO<sub>3</sub>, have pseudowollastonite polytype, cyclosilicate structures.<sup>13</sup> This structure is characterized by layers, one of which is composed of rings of three  $SiO_4$  tetrahedra ( $Si_3O_9$ , see above inserted structure), the other being an octahedral layer. Within the ring, three silicons form a chain with three bridging oxygens, while the six nonbridging oxygens are bound to either two or three divalent cations. The bridging oxygens are also coordinated to either one or two divalent cations, which are themselves coordinated to eight oxygen atoms.<sup>10,11</sup> In the case of pseudowollastonite ( $\alpha$ -CaSiO<sub>3</sub>), the ratio among these four different oxygen types is 3:3:2:1, as follows: nonbridging oxygen bound to three Ca; nonbridging to two Ca; bridging coordinated to two Ca; and bridging to one Ca.<sup>10</sup> There are thus six nonbridging oxygens for every three bridging oxygens (2:1 ratio)

The <sup>17</sup>O MASS NMR spectrum of pseudowollastonite ( $\alpha$ -CaSiO<sub>3</sub>) is shown in Figure 2E, along with its static spectrum (Figure 2F). Both spectra may by complicated due to the presence of several quadrupole coupling constants and chemical shifts from the many apparently different oxygens. However,  $e^2qQ/h$ ,  $\eta$ , and  $\delta_i$  can nevertheless be derived from simulations of the MASS spectrum, as follows: the sharp, high-frequency feature is attributed to the twelve nonbridging oxygens, while the low-frequency powder pattern is assigned to the signal from the six bridging oxygens. These assignments are consistent with the integrated intensity ratio of ~2.2:1 and imply that "crystallograpohic" effects are small; i.e., the observed spectrum can be well simulated by using just two nonbridging and one bridging sites (Table I).

Both the <sup>17</sup>O MASS (Figure 2G) and static (Figure 2H) NMR spectra of strontium metasilicate ( $\alpha$ -SrSiO<sub>3</sub>) are similar to those of pseudowollastonite and are thus similarly assigned.  $\alpha$ -SrSiO<sub>3</sub> has three different types of oxygen: twelve nonbridging oxygens bound to three Sr; four bridging oxygens coordinated to two Sr; and two bridging oxygen bound to one Sr.<sup>11</sup> The <sup>17</sup>O MASS NMR spectrum is again, however, well simulated with just the 2:1 ratio of nonbridging to bridging oxygen sites by using the parameters given in Table I.

Finally, the <sup>17</sup>O MASS and static NMR spectra of barium metasilicate (BaSiO<sub>3</sub>) are shown in Figure 2, I and J, respectively. The compound synthesized is the high-temperature form.<sup>14</sup> It has a chain structure, with two nonbridging oxygens bound to three Ba and one bridging oxygen coordinated to two Ba.<sup>15</sup> The static spectrum is difficult to interpret, but the MASS NMR spectrum shows a sharp, high-frequency feature assigned to the two nonbridging oxygen. The values of  $e^2 qQ/h$ ,  $\eta$ , and  $\delta_i$  derived by computer simulation are shown in Table I.

The chemical shift trends apparent in Figure 2 may be rationalized in terms of the nature of the divalent cations present. Nonbridging oxygens are bound to one silicon and to either two or three metal cations; their chemical environment is thus greatly affected by the divalent cations present. On the other hand, the bridging oxygens are bound to two silicon sites and are only remotely coordinated to either one or two divalent cations.<sup>16</sup> Consequently, the chemical shift of the bridging oxygens is expected to be less sensitive to the nature of the divalent cation. As the size of the cation increases, from MgSiO<sub>3</sub> to BaSiO<sub>3</sub>, the chemical shifts of the nonbridging oxygens are greatly affected, going from 60 and 42 ppm for MgSiO<sub>3</sub> to 169 and 159 ppm for BaSiO<sub>3</sub>, while the chemical shift of the bridging oxygens remains much more constant (62 ppm for  $MgSiO_3$ , 87 ppm for  $BaSiO_3$ ). A similar deshielding effect was found for the <sup>17</sup>O MASS NMR spectra of the group IIA  $(2)^{22}$  oxides.<sup>17</sup> To obtain the relationships

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Figure 3. Plots of  $\ln \delta_i$  vs.  $\ln r_{av}$  (Å) for <sup>17</sup>O-labeled crystalline metasilicates. The data for the nonbridging oxygens are represented by circles, and the bridging oxygens are represented by triangles. Average ionic radii,  $r_{av}$ , were obtained from the Shannon effective ionic radii, with two Mg(6) = 0.86 Å for clinoenstatite, Mg(6) = 0.86 Å and Ca(8) = 1.26Å for diopside, seven Ca(8) = 1.26 Å for pseudowollastonite, three Sr(8) = 1.40 Å for  $\alpha$ -SrSiO<sub>3</sub>, and one Ba(8) = 1.56 Å for BaSiO<sub>3</sub>. The numbers in parentheses are the coordination numbers of the metal cations.

between the <sup>17</sup>O chemical shifts and ionic radii of the metal cations, we have plotted  $\ln \delta_i$  vs.  $\ln r_{av}$  (Å), where  $r_{av}$  is the average of the Shannon effective ionic radii,<sup>18</sup> after considering the coordination numbers of the cations. The plots shown in Figure 3 yield the following wholly empirical correlations

$$\frac{1}{2}(\ln \delta_{a} + \ln \delta_{b}) = 1.83 \ln r_{av} + 4.16$$
 (1)

$$\ln \delta_{\rm c} = 0.555 \ln r_{\rm av} + 4.20 \tag{2}$$

where  $\delta_a$  and  $\delta_b$  are the chemical shifts of the nonbridging oxygens and  $\delta_c$  is the chemical shift of the bridging oxygen. The correlation coefficients are 0.979 and 0.996, respectively. These results indicate that the chemical shifts of the nonbridging oxygens (the geometric mean,  $(\delta_a \delta_b)^{1/2}$  are approximately proportional to the square of the average cation radius, while those of the bridging oxygens are approximately proportional to the square root of the average cation radius, as follows:

$$(\delta_a \delta_b)^{1/2} = 64.1 r_{av}^{1.83} \qquad \delta_c = 66.7 r_{av}^{0.555}$$
(3)

Although these relationships are quite empirical, we believe that they may nonetheless be of use in testing structural models of amorphous solids, such as glasses.<sup>19</sup> For example, in a glassy phase of nominal composition MgBaSi<sub>2</sub>O<sub>6</sub>, the distribution of alkali metals might be tested by using eq 3.

A second interesting correlation can be found between the  $e^2 q Q/h$  values for nonbridging and bridging oxygen sites (correlation coefficient of 0.966), as shown in Figure 4A. We find

$$e^2 qQ/h$$
 (MHz, bridging) =  
1.02 $e^2 qQ/h$  (MHz, nonbridging) + 1.75 (4)

implying once again, we believe, a general decrease in covalence with the more electropositive-ion-containing systems (electronegativity: Mg > Ca > Sr > Ba).

As shown in Figure 4B, the observable  $e^2 qQ/h$  values for both nonbridging and bridging oxygens increase monotonically with the electronegativity (EN) of the alkaline earth metal(s) present. The plots yield the following correlations

$$e^2 q Q / h$$
 (MHz, bridging) = 3.134EN + 0.895

$$e^2 q Q / h$$
 (MHz, nonbridging) = 3.112EN - 0.882 (5)

with correlation coefficients of 0.948 and 0.996 for bridging and nonbridging oxygens, respectively. This immediately suggests



Figure 4. Correlation between bridging and nonbridging  $e^2 q Q/h$  values and cation electronegativities: (A) plot of  $e^2 q Q/h$  for bridging vs. nonbridging oxygens; (B) plots of  $e^2 q Q/h$  of the bridging and nonbridging oxygens vs. the electronegativity of the cation (or its average value). The data for the nonbridging oxygens are represented by circles, and the data for the bridging oxygens are represented by triangles. Modified Pauling electronegativity values<sup>20</sup> were used throughout.

application, for the nonbridging oxygens, of the correlation between  $e^2 q Q/h$  and average ionicity reported previously,<sup>8</sup> in order to predict  $e^2 q Q/h$  values.

Using Pauling electronegativities as modified by Allred<sup>20</sup> and adding data from Janes et al.<sup>21</sup> and that presented in this publication, we recalculated the correlation between  $e^2 q Q/h$  and average ionicity<sup>8</sup> using a total of 31 data points. We find

$$e^2 q Q / h (\text{MHz}) = -0.227 I (\%) + 15.07$$
 (6)

where I is the average of the ionic character and the correlation coefficient is 0.883. This correlation gives the following results: MgSiO<sub>3</sub>, 3.2 MHz (obsd), 2.3 MHz (calcd); CaMgSi<sub>2</sub>O<sub>6</sub>, 2.7 MHz (obsd), 1.7 MHz (calcd);  $\alpha$ -CaSiO<sub>3</sub>, 2.2 MHz (obsd), 1.3 MHz (calcd);  $\alpha$ -SrSiO<sub>3</sub>, 2.15 MHz (obsd), 1.1 MHz (calcd); BaSiO<sub>3</sub>, 1.85 MHz (obsd), 0.9 MHz (calcd).

These results indicate, as expected, a general reproduction of the trends in  $e^2 q Q/h$  vs. ionicity, but the actual magnitudes predicted are  $\sim 1$  MHz smaller than those observed experimentally. While this could be due, in part, to overestimation of the experimental values due to unresolved broadening from crystallographic nonequivalencies, further theoretical work aimed at predicting both nonbridging and bridging  $e^2 q Q/h$  values is doubtless in order.

#### Conclusions

The results we have presented above indicate that solid-state <sup>17</sup>O nuclear magnetic resonance spectroscopy can be used to

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<sup>(22)</sup> In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

determine, in many cases, the isotropic chemical shifts, nuclear quadrupole coupling constants, and electric field gradient tensor asymmetry parameters for each of the three main types of nonequivalent oxygen in alkaline earth metasilicates, for a total of nine pieces of information per silicate. These results are to be compared with the results of <sup>29</sup>Si NMR experiments, which can yield at best only three pieces of information, the individual components of the chemical shielding tensor. When higher field (or single crystal) data become available, it should also be possible to determine the overall breadth of the chemical shielding interaction for <sup>17</sup>O in silicates with some accuracy. Thus, <sup>17</sup>O NMR is likely to become a particularly powerful tool for investigating bonding in such systems. The results we have obtained to date show interesting correlations between isotropic chemical shift and cation radius, which may be useful in analyzing the structures of less well characterized systems (e.g., glasses), in addition to showing a very strong correlation between bridging and nonbridging <sup>17</sup>O  $e^2 q Q/h$  values and between bridging and nonbridging <sup>17</sup>O  $e^2 q Q/h$  values and the alkaline earth metal electronegativities.

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**Registry No.** <sup>17</sup>O, 13968-48-4; SrSiO<sub>3</sub>, 13451-00-8; BaSiO<sub>3</sub>, 13255-26-0; clinoenstatite, 14654-06-9; diopside, 14483-19-3; pseudowollastonite, 14567-52-3.

# **Charge-Transfer Transitions of 2:1 Electron Donor–Acceptor Complexes**

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The theoretical formalism developed by Mulliken for the transition dipole moment of an electron donor-acceptor complex has been extended to the case of a 2:1 complex. Both symmetric (DAD) and asymmetric (DDA) complexes are considered. The theory provides a simple physical picture explaining optical data for two previously studied systems, p-xylene/bromanil and hexamethylbenzene/tetracyanoethylene. Numerical results for the 1:1 and 2:1 complexes of hexamethylbenzene with tetracyanoethylene (TCNE) are in good agreement with experiment, and support a model of a distorted D-A-D complex in the excited electronic state.

## I. Introduction

Multiwavelength linear regression of UV-visible absorption data has made it possible to resolve the charge-transfer (CT) spectra of 1:1 and 2:1 electron donor-acceptor (EDA) complexes.<sup>1-3</sup> This approach has provided new insight and raised some interesting questions concerning the structure and optical properties of 2:1 EDA complexes. For example, we have found that the optical spectrum of the 2:1 complex of *p*-xylene with bromanil is redshifted and broadened compared to that of the 1:1 complex.<sup>2</sup> The spectrum of the 2:1 complex of hexamethylbenzene (HMB) with tetracyanoethylene (TCNE), on the other hand, has been found to be nearly coincident with the spectrum of the 1:1 complex in both CCl<sub>4</sub><sup>1</sup> and cyclohexane<sup>3</sup> solutions. The ratio of the oscillator strength of the 2:1 complex to that of the 1:1 complex is approximately 5.0 for p-xylene/bromanil and 1.5 for HMB/TCNE. These differences are easily explained qualitatively if the structure of the 2:1 complex is DDA and DAD for p-xylene/bromanil and HMB/TCNE, respectively. The red shift of the DDA complex results from the resonance stabilization of the excited state, D<sup>+</sup>DA<sup>-</sup>  $\Rightarrow$  DD<sup>+</sup>A<sup>-</sup>. As explained previously,<sup>3</sup> the lack of red shift for the DAD complex is a result of the poor overlap of the two donor HOMO's, and thus a small value for the resonance integral connecting the two donor orbitals. It is shown in this work that the small value of this resonance integral leads to nearly degenerate symmetric and antisymmetric excited-state DAD wave functions, which can couple vibronically via a nontotally symmetric vibrational mode. Intuitively, the greater relative oscillator strength in the DDA complex derives from the contribution of the ionic state D<sup>+</sup>DA<sup>-</sup> to the excited state of the complex. That the second

donor molecule is, like the first, bound to the acceptor by charge-transfer forces in the conventional Mulliken sense is also evidenced by the greater line width of the optical spectrum of DDA compared to DA, as addition of the second donor results in an increase in the number of Franck–Condon active intermolecular modes.<sup>2</sup> In the symmetric EDA complex, however, there is no significant change in line width upon addition of the second donor molecule.<sup>3</sup> Thus the oscillator strength of DAD might be expected to be twice that of DA, whereas it is in fact increased by less than a factor of 2.

The purpose of this paper is to calculate the transition dipole moment,  $\mu_{ge}$ , of the symmetric (DAD) and asymmetric (DDA) 2:1 complexes, within the same formalism used by Mulliken<sup>4</sup> to derive  $\mu_{ge}$  for a 1:1 EDA complex. The square of the transition dipole moment is proportional to the oscillator strength or inte-grated absorbance. The calculation shows that the intuitive conclusions discussed above, concerning the ratio of the oscillator strength in the DDA/DA system, have a solid theoretical foundation. The transition dipole moment  $\mu_{ge}$  and excited-state dipole moment  $\mu_e$  of a DAD complex are also evaluated under two separate assumptions: In model A the complex is assumed to have a center of symmetry in both the ground and the excited states, and in model B the complex is considered to distort from  $D_{2h}$  to  $C_{2v}$  symmetry upon excitation. Numerical estimates of  $\mu_{ge}$  and  $\mu_{e}$  are compared in each case to experiment, leading to the conclusion that there is at least a small barrier separating the D<sup>+</sup>A<sup>-</sup>D and DA<sup>-</sup>D<sup>+</sup> excited states.

#### II. Theory

1. Overlap and Orientation Considerations in TCNE Complexes. In previous work, we considered the HOMO-LUMO overlap in the 1:1 and 2:1 complexes of HMB with TCNE.<sup>3</sup> X-ray

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