*J. Am. Chem. Soc.* **1995,** *117,* 4379–4386

# Polarized Vacuum Ultraviolet Spectra of Crystalline Glycoluril: A Urea Dimerlike Molecule

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*Received September 6, 1994*®

**Abstract:** Polarized ultraviolet reflection spectra of the *a*, *b*, and *c* crystal axes from the (010) and (100) faces of single crystals of glycoluril have been measured between 370 and 140 nm. Corresponding absorption spectra are obtained through Kramers–Kronig analysis of the reflection data. Four transitions are observed for the $C_{2v}$ molecule as follows: transition I at 54 500 cm$^{-1}$, (183 nm), $f = 0.26$, $B_2$ symmetry; II at 60 300 cm$^{-1}$ (166 nm), $f = 0.49$, $B_1$ symmetry; IV at 64 300 cm$^{-1}$ (156 nm), $f = \sim 0.12$, *A*1 symmetry; III at 66 100 cm$^{-1}$ (151 nm), $f = \sim 0.24$, $B_2$ symmetry. These assignments are in close agreement with the results of an Independent Systems calculation in which glycoluril is treated as a urea dimer-like molecule, and the previous assignments for urea by Campbell and Clark (*J. Am. Chem. Soc.* **1989**, *111*, 8131) are assumed. The results of calculations using the method of intermediate neglect of differential overlap configuration interaction (INDO/S-CI) and employing a modified parameterization are in satisfactory agreement with the experimental energies, oscillator strengths, and excited state symmetries for both urea and glycoluril.

## Introduction

Glycoluril, tetrahydroimidazo[4,5-*d*] imidazole-2,5-(1*H*,3*H*)-dione, is a urea dimer-like molecule in which two urea moieties are connected through a bridging ethylenic group (Figure 1). This substance has been used as a slow release fertilizer,[1,2] and its molecular structure and ground state electronic properties have been studied extensively as a biotin analog.[3] Of particular interest in the present work is the fact that glycoluril is composed of two symmetrically disposed urea linkages and therefore is of value in regard to understanding the electronic structure of the basic urea chromophore. Furthermore, it represents another simple molecular system (involving C, N, and O atoms) for which theoretical electronic structure calculations can be tailored. Generally there are few spectroscopic assignments available for such molecules. Since their spectra for the most part appear in the vacuum ultraviolet and since they are not volatile materials, VUV spectra of solid state samples are called for. Because few experiments of this sort have been carried through, it is not surprising that available experimental information is limited.

Owing to the dimer-like quality of glycoluril its electronic spectrum is expected to be directly related to and derivable from that of the urea molecule. Two papers on the electronic structure of urea including a semiempirical study by Rosa and Simpson in 1964[4] and an ab initio study by Elbert and Davidson in 1974[5] have been published. However in spite of the fundamental nature of the urea chromophore, no other theoretical studies of the urea electronic spectrum have been published to our knowledge. A fairly recent experimental study of the polarized electronic spectrum of crystalline urea presented results that differ substantially from those of both theoretical calculations. Three strong absorption bands were observed in the 56 000 and 65 000 cm$^{-1}$ region in spectra taken from the (110) face of tetragonal urea: I, 56 000 cm$^{-1}$, $f = 0.21$, $B_2$ symmetry; II 62 000 cm$^{-1}$, $f = 0.23$, $A_1$ symmetry; and III, 65 000 cm$^{-1}$, $f = 0.09$, $B_2$ symmetry.[6] Their assignments were supported by additional polarized spectra taken from crystals of a urea–hexadecane adduct reported in the same study. Further, they found that effects of exciton mixing on the urea crystal spectra are of minor importance, and therefore the experimental assignments were particularly clearcut.

The molecular and crystal structures of glycoluril have recently been determined.[3,7] The molecule has two equivalent planes (dihedral angle 124.1°) containing urea moieties and hence exhibits $C_{2v}$ symmetry.[7] The axis convention used in this paper is consistent with the one used in the earlier paper on urea.[6] The 2-fold axis is chosen as *z*, and the direction normal to the reflection plane passing through the carbonyl groups is chosen as *y* (see Figure 1). The symmetry axes of the glycoluril molecule (*x*, *y*, and *z*) coincide exactly with the crystallographic axes (*c*, *a*, and *b* respectively) of the orthorhombic crystal. This unusual situation greatly simplifies interpretation of the crystal spectra.

In this paper we report polarized ultraviolet absorption spectra of single crystals of glycoluril. The absorption curves are obtained from experimental reflection spectra through Kramers–Kronig analysis. Our aim is to measure the oscillator strengths and excited state symmetries of the transitions in the accessible wavelength range (to 140 nm) of the spectrum of glycoluril and then to relate these results to those of urea. Two theoretical schemes are considered here. The Independent Systems (or molecular exciton) approach in which glycoluril is considered to be a urea dimer is applied first. Second, semiempirical MO calculations for both urea and glycoluril are carried through. The results of these latter calculations are compared to the experimental results and the Independent Systems predictions for the dimer model of glycoluril.

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® Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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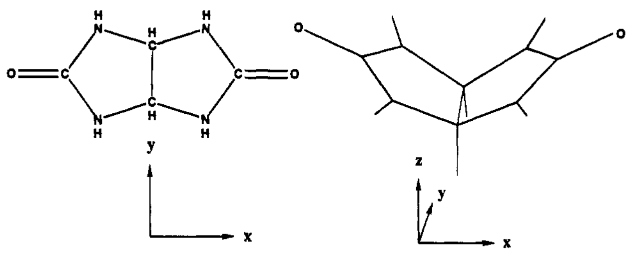

**Figure 1.** Structure of glycoluril and molecular coordinate system.

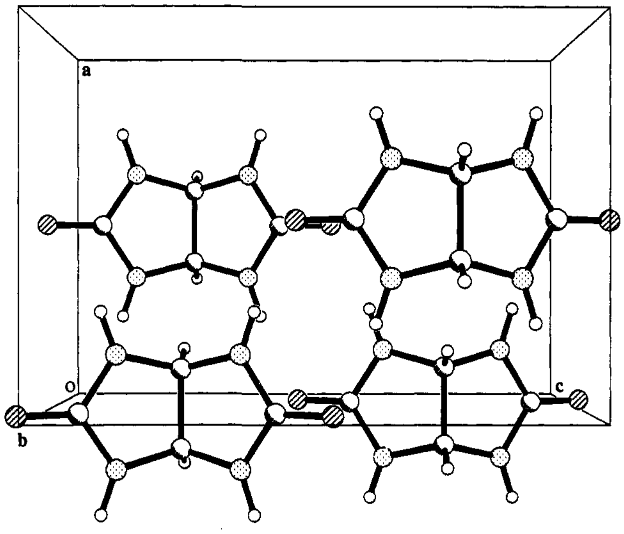

**Figure 2.** The four molecules of the unit cell of crystalline glycoluril. The molecular symmetry axes coincide exactly with the unit cell axes.

## Experimental Section

Glycoluril was purchased from Aldrich and was used without further purification. Crystals were grown by the slow cooling of filtered, hot, aqueous solutions. Typical crystals had dimensions of about 2 × 10.5 mm and were elongated along the *a* axis. Many faces were present on the crystals. Glycoluril crystallizes in two different structures (labeled A and B in ref 3), but only A form crystals were observed in the present work. Miller indices were determined through morphologic examination by measuring interfacial angles and were consistent with the (010) face being predominant and showing excellent cleavage.[7]

Reflection spectra were measured between 370 and 140 nm from freshly cleaved *ac* surfaces (010) and from artificially prepared *bc* faces (100). Each crystal face yields two spectra that are individually polarized parallel to the two unit cell axes of that face. However, the *c*-axis polarized spectrum from both faces is the same. The two instruments used for the reflection measurements and the procedures employed in the Kramers–Kronig transformation have been described previously.[6,8]

The polished *bc* face was prepared using an ultramicrotome. A crystal of suitable size was epoxied to one end of a brass rod that was mounted in the specimen holder of the microtome (LKB Model 4802A). The arcs of the specimen holder were adjusted so that the *a* axis was oriented close to perpendicular to the diamond knife blade of the microtome. Initial coarse cuts were made on the crystal using the mechanical feed of the microtome. After some initial strokes, final adjustment of the orientation of the face was made by examining the angles the polished face made with the natural boundaries. On occasion the specimen holder was dismounted, and the crystal was examined microscopically to confirm the correct orientation of the face being created. When it was determined that the desired face was parallel to the knife blade and of a size suitable for reflection measurement, the crystal face was polished by advancing the crystal using the thermal feed of the ultramicrotome. The feed rate of typically 200 Å per stroke was applied, and the face was polished for about 30 min. The polished face thus prepared was highly reflective and free of optical imperfections.

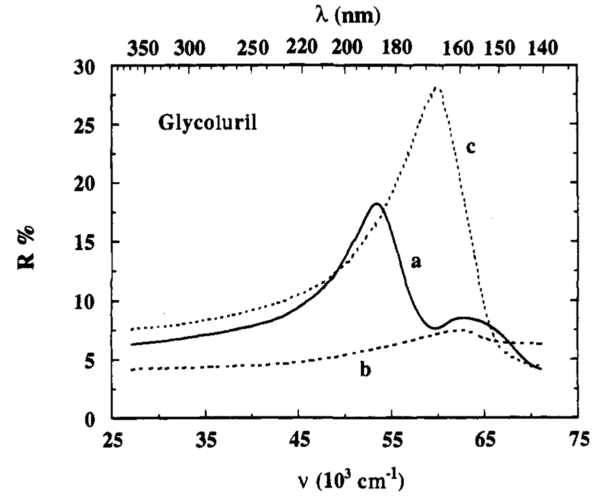

**Figure 3.** Reflection spectra of glycoluril for light polarized along the *a* (solid line) and *c* (dotted line) axes of the (010) face and the *c* (again the dotted line) and *b* (dashed line) axes of the (100) face.

## Crystal Structure

The crystal structure of glycoluril is orthorhombic (space group *Cmcm*) with four molecules per cell.[7] The molecules occupy *m*2*m* symmetry sites. These sites are $(0, \bar{y}, {}^3/_4)$, $(0, y, {}^1/_4)$, $({}^1/_2, {}^1/_2 - y, {}^3/_4)$, $({}^1/_2, {}^1/_2 + y, {}^1/_4)$. The disposition of glycoluril molecules in the crystal is particularly convenient for spectroscopic interpretations and assignments. The structure is shown in projection onto the (010) face in Figure 2. The molecular symmetry axes exactly coincide with the crystallographic axes. For unit cell faces, this situation implies that each molecular transition will appear polarized uniquely and fully along but one of the crystallographic axes. There will be no partial projection along any other unit cell axis. In addition, for crystal states accessible from these crystal planes, there can be no crystal field induced mixing between states of different molecular symmetry. Any absorption band observed polarized along any one of these three axes must correspond to a unique transition of the glycoluril molecule. Bands along the *a* axis represent *y* polarized transitions with B2 excited state symmetry; bands observed along the *b* and *c* crystal axes are derived from *z* and *x* polarized transitions with corresponding A1 and B1 excited state symmetries.

## Spectra and Assignments

The reflection spectra polarized along the *a*, *b*, and *c* axes are shown in Figure 3. Since the spectrum obtained polarized along the *c*-axis of the cleaved *ac* plane was essentially identical with that obtained from the polished *bc* face, we conclude that no observable disordering occurred from the polishing procedure. The absorption spectra obtained from the Kramers–Kronig transformations of the reflection spectra along the three individual crystal axes are shown in Figure 4. The transformation procedure requires extrapolation of each measured reflection spectrum both to higher and lower frequency. These assumed "trial" regions are adjusted in a systematic way until the transformed spectrum shows essentially zero calculated absorption throughout the known transparent spectral region. Using this criterion for transformation it is found that a variety of trial region extensions can lead to equally acceptable absorption curves. However, the variation between such a family of

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[8] Zaloudek, F.; Novros, J. S.; Clark, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 7344.

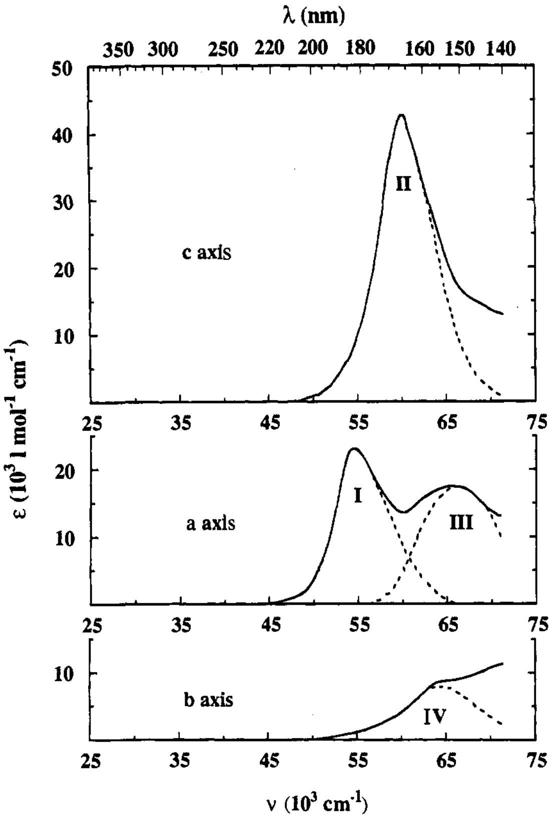

**Figure 4.** Absorption spectra for light polarized along the *c* (top), *a* (middle), and *b* (bottom) crystal axes obtained from Kramers–Kronig transformations of the corresponding reflection spectra. The dashed bands represent reasonable resolutions into components. The Roman numerals identify individual transitions.

calculated absorption curves throughout the experimentally measured region is inconsequential (once the criterion is met) irrespective of the particular shape or detail put into the trial region extensions.

**Table 1.** Crystal Spectral Data for Glycoluril from Experiments

| | *a*-axis | | *b*-axis | | *c*-axis | |
|---|---|---|---|---|---|---|
| | $f$ | $\nu$ (cm$^{-1}$) | $f$ | $\nu$ (cm$^{-1}$) | $f$ | $\nu$ (cm$^{-1}$) |
| I | 0.77 | 54 500 | | | | |
| II | | | | | 1.48 | 60 300 |
| III | ~0.72 | 66 100 | | | | |
| IV | | | ~0.37 | 64 300 | | |

**Table 2.** Correlation between Urea and Glycoluril

| | urea[a] | glycoluril |
|---|---|---|
| symmetry axes | $x'$ | $x, z$ |
| | $y'$ | $y$ |
| | $z'$ | $z, x$ |
| state symmetries | A$_1'$ | A$_1$, B$_1$ |
| | A$_2'$ | A$_2$, B$_2$ |
| | B$_1'$ | A$_1$, B$_1$ |
| | B$_2'$ | A$_2$, B$_2$ |

[a] Axes chosen as in ref 6.

Individual absorption bands were resolved while paying attention to the requirement for plausible band shapes. Since each transition of glycoluril will appear only along a single axis, the total number of spectral features along the three unit cell axes equals the number of observable transitions. The *a*-axis spectrum shows two strong bands (54 and 66 kK) which we label I and III, respectively. The *c*-axis spectrum exhibits a single strong band at 60 kK, and we label this band II. The spectrum along the *b*-axis is relatively weak and displays a single distinct feature at about 64 kK on a generally rising absorption background. The low energy tail of the latter feature extending to about 50 kK is unusually long and yields an unappealing, unsymmetrical bandshape. Nevertheless, lacking any evidence that there are multiple bands present we treat this absorption region of the *b*-axis spectrum as representing a fourth glycoluril electronic transition, IV (*vide infra*). The above Roman numeral designations have been chosen to facilitate comparison with the prior urea assignments. The band resolutions are displayed in Figure 4, and pertinent numerical values for the crystal spectra are listed in Table 1. The oscillator strengths have been evaluated with the formula, $f = 4.32 \times 10^{-9} \int \epsilon \, d\nu$, where $\epsilon$ is the decadic molar extinction coefficient (cm M)$^{-1}$ and $\nu$ is in wavenumbers. The values shown represent one-dimensional oscillator strengths. For comparison to oscillator strengths obtained from solution spectra, the numbers must be randomized by dividing by three. The results derived from the crystal data are summarized using the latter three-dimensional oscillator strengths as follows: transition I at 54 500 cm$^{-1}$ (183 nm), $f = 0.26$, $B_2$ symmetry; II at 60 300 cm$^{-1}$ (166 nm), $f = 0.49$, $B_1$ symmetry; III at 66 100 cm$^{-1}$ (151 nm), $f = \sim 0.24$, $B_2$ symmetry; IV at 64 300 cm$^{-1}$ (156 nm), $f = \sim 0.12$, $A_1$ symmetry.

## Calculations and Discussion

The purpose of this section is to relate the assignments made here for glycoluril to those previously reported for urea and to compare results of semiempirical molecular orbital calculations done on both systems. Since the two urea chromophores of glycoluril are separated by hydrocarbon bridging, the molecule is an appealing candidate for treatment as a dimer molecule. It is expected therefore that each transition of the glycoluril can be related to some parent urea transition. Both urea and glycoluril possess $C_{2v}$ symmetry, but only the $y$-axis designations are similar in the two compounds. In order to minimize confusion about symmetry labels and axes designations a correlation between these items in going from urea to glycoluril is presented in Table 2. To keep the designations distinct we will employ primes on quantities representing urea. In keeping with the dimer viewpoint for glycoluril we note that a $B_2'$ excited state of urea (allowed, $y'$-polarized) will yield both a $y$-polarized $B_2$ excited state and a forbidden $A_2$ excited state of glycoluril. On the other hand, a urea transition polarized along the $z'$ axis will produce two allowed transitions in glycoluril. These two transitions will be polarized individually along the $x$ and $z$ axes of glycoluril and have $B_1$ and $A_1$ symmetries respectively, and their relative intensities will be related to the dihedral angle found for glycoluril (124.1°). An $x'$-polarized urea transition will behave similarly to a $z'$-polarized urea transition.

**Independent Systems.** The simplest calculation for a dimer molecule follows the Independent Systems[9] or Intramolecular Exciton approach in which dimer wave functions are written as products of monomer functions:

$$\varphi_a^m \varphi_b^n$$

Here $a$ and $b$ refer to the two monomer units, and $m$ and $n$ serve to identify particular monomer electronic states. The product functions of interest here correspond to singly excited states in which either $m$ or $n$ corresponds to the ground state. Each such product function is degenerate with the corresponding product in which the excitation has been placed on the other member. If now the Hamiltonian includes the mutual Coulombic interactions of the two parts, and if at the same time electron exchange between the two parts is excluded, then one can solve for the energies and wave functions of the dimer by diagonalizing the secular equation:

**Table 3.** Results for Independent Systems Calculation for Glycoluril[a]

| | | | | glycoluril | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| urea model | | | | calculated | | | | experimental | | |
| | $f^b$ | pol | $\nu^c$ | | $f$ | pol | $\nu$ | $f$ | pol | $\nu$ |
| I′ | 0.21 | $y'$ | 53.9 | I | 0.40 | $y$ | 54.6 | 0.26 | $y$ | 54.5 |
| II′ | 0.23 | $z'$ | 61.8 | II | 0.35 | $x$ | 60.5 | 0.49 | $x$ | 60.3 |
| | | | | IV | 0.11 | $z$ | 63.1 | ~0.12 | $z$ | 64.3 |
| III′ | 0.09 | $y'$ | 64.6 | III | 0.21 | $y$ | 64.9 | ~0.24 | $y$ | 66.1 |

[a] The center of each urea moiety was taken at the carbon atom of the carbonyl group. The separation between these atoms is 3.8 Å. [b] Oscillator strengths for glycoluril reflect the fact that two urea moieties make up a single molecule. [c] The energies have been shifted slightly relative to the positions found in crystalline urea (ref 6). Frequencies in kiloKaiser ($10^3$ cm$^{-1}$).

$$|H_{ij} + E_{ii}\delta_{ij}| = 0$$

where $H_{ij} = \langle \varphi_a^i \varphi_b^0 | H | \varphi_a^0 \varphi_b^j \rangle$, the $E_{ii}$ represent transition energies and $\delta_{ij}$ is the Kronecker delta. The Hamiltonian, $H = H_a + H_b + V_{ab}$, is the sum of Hamiltonians for the independent moieties and the sum of all electrostatic interactions between the two parts, $V_{ab}$.

In the absence of accurate monomer wave functions the matrix elements can be evaluated by employing suitable approximations. If the separation between the monomer units is large enough, the integral can be approximated by writing the interaction, $V_{ab}$, as a multipole expansion and retaining the leading dipole–dipole term. The matrix elements $H_{ij}$ are then mathematically equivalent to the electrostatic interaction of the two corresponding electric transition dipoles situated on different monomer units. Although much less involved, the procedure used here has the identical context as the usual approach to the electronic spectra of molecular crystals. It is to the results of such calculations that we now turn.

The previous work with urea assigned three relatively strong absorption bands. These bands, labeled here as I′, II′, and III′, are polarized along the $y'$, $z'$, and $y'$ urea axes, respectively. When the three transitions are incorporated into an independent systems calculation for glycoluril, the calculated spectral values for the dimer compare favorably with the experimental results as shown in Table 3. It should be noted that the band positions have been shifted slightly relative to their positions observed in the urea crystal spectra. These adjustments provide a better general fit of the glycoluril band positions and may represent the effects of the replacement of the hydrogen atoms bonded to the urea nitrogen atoms with carbons in the assembly of the glycoluril molecule. Transitions I and III appear to be easily derived from the corresponding urea transitions I′ and III′. The bulk of the intensity derived from the parent urea transition II′ shows up along the $c$-axis of glycoluril and corresponds to the $x$-polarized transition II. The remainder of the calculated urea intensity (22%) appears as transition IV along the $b$-axis, is $z$-polarized, and is displaced to higher energy. The observed distribution of intensity is in reasonable agreement with that expected based on the glycoluril dihedral angle of 124.1°. The experimental energy difference between these two bands (termed the *dimer split* and measured between the band maxima of II and IV) is 4200 cm$^{-1}$. This value compares with the calculated value of 2600 cm$^{-1}$ (*vide infra*).

Except for the increase in intensity for II along the $c$-axis and the question regarding the red tail of IV along the $b$-axis, the agreement is generally good and supports the mutual assignments for both urea and glycoluril. In particular, these results support the notion that II and IV are in fact derived from the urea II′ transition.

**Table 4.** Final INDO/S-CI Results for Urea

| calculation[a] | | | | experiment[b] | | | |
|---|---|---|---|---|---|---|---|
| $\nu$c | $f$ | pol | orbital assignment[d] | | $\nu$ | $f$ | pol |
| 50.36 | 0.00 | ($f$) | $n\pi_4^*$ | | >48.0 | | |
| 57.66 | 0.17 | $y'$ | $\pi_3\pi_4^*$ | I′ | 56.0 | 0.21 | $y'$ |
| 61.36 | 0.28 | $z'$ | $\pi_2\pi_4^*$ | II′ | 62.0 | 0.23 | $z'$ |
| 65.67 | 0.08 | $y'$ | $n\sigma_2^*$ | III′ | 65.0 | 0.09 | $y'$ |
| 65.85 | 0.00 | $x'$ | $\pi_3\sigma_2^*$ | | | | |
| 67.97 | 0.04 | $x'$ | $\pi_2\sigma_2^*$ | | | | |
| 77.02 | 0.07 | $x'$ | $\pi_3\sigma_3^*$ | | | | |
| 80.07 | 0.00 | $x'$ | $\pi_2\sigma_3^*$ | | | | |
| 81.41 | 0.25 | $z'$ | $n\sigma_3^*$ | | | | |

[a] Using parameter set in which $\gamma$ and $\beta$ for both oxygen and nitrogen have been modified relative to standard values. See Figure 7 second panel from top. [b] Taken from ref 6. [c] Frequencies in kiloKaiser ($10^3$ cm$^{-1}$). [d] All configurations show CI coefficients >0.94.

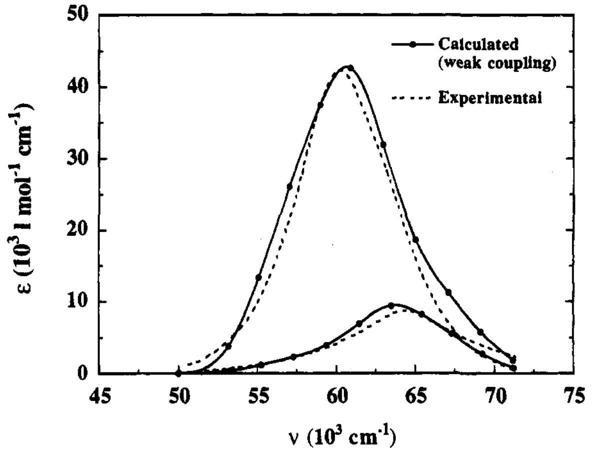

**Figure 5.** Band shape effects from the Independent Systems calculation. The dashed curves represent the resolutions obtained from the experimental spectra (see Figure 4). The solid lines represent the calculated band contours after breaking the parent urea transition into ten vibronic components (weak coupling). The solid curves were constructed by plotting calculated oscillator strength values, drawing a smooth curve through the points (cubic spline) and scaling to match the stronger experimental curve.

The asymmetric band shape of IV along the $b$-axis remains to be considered. The above dimer calculation was carried through in the strong coupling limit. For strong coupling the entire band envelope is used to evaluate a single transition moment dipole at an energy corresponding to the peak position of the band. An alternate weak coupling calculation can be carried through in which the input is obtained by artificially decomposing the parent urea transition into a sequence of vibronic components with individual transition moment magnitudes and energies. Presumably, this approach more faithfully represents the bandshapes found in real spectra. The results of such a calculation in which the urea II′ band is decomposed symmetrically into ten vibronic components is shown graphically in Figure 5. Interestingly, the resulting dimer intensity distributions closely resemble the band contours found in the crystal spectra. What happens of course is that intensity partially shifts from component to component toward lower energy for the $c$-polarized band and toward higher energy for the $b$-polarized band, and these shifts result in unsymmetrical band contours. The dimer split (measured between the apparent maxima) now, however, is about 3800 cm$^{-1}$ and is close to the experimental value. Similar band shape changes are commonly observed in crystal spectra and arise there from identical

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(9) Simpson, W. T. *Theories of Electrons in Molecules*; Prentice-Hall: Englewood Cliffs, NJ, 1962.

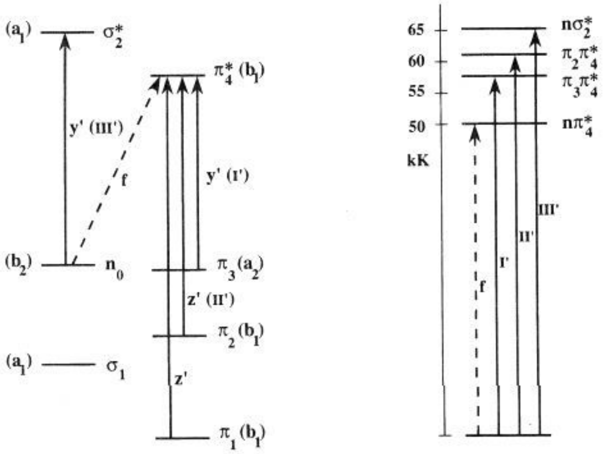

**Figure 6.** (left) Schematic orbital energy level diagram for the urea molecule. The polarizations are shown for several possible transitions. (right) Configuration energy level diagram for urea indicating the expected transitions. The energies shown represent the results of the "final" INDO/S calculation.

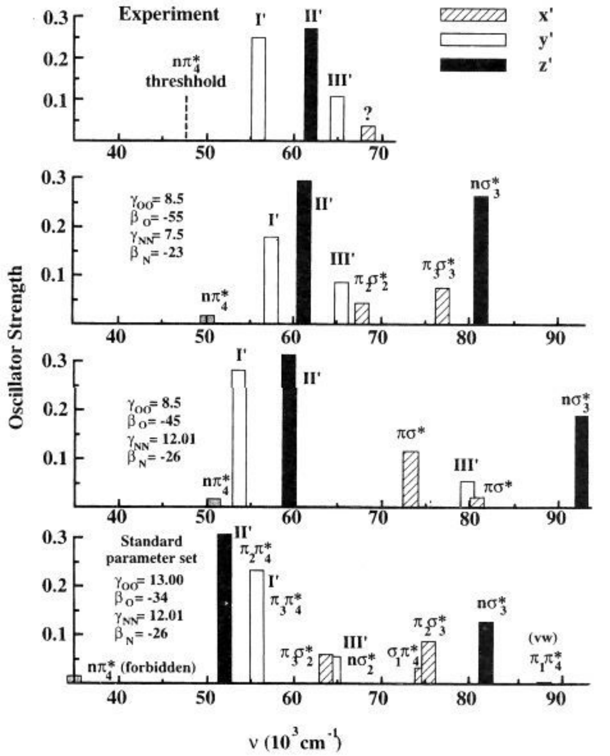

**Figure 7.** Schematic comparison of the predicted INDO/S spectra of urea. The bottom panel represents the results using the standard parameterization. The middle two panels show the results using different values for $\beta$ and $\gamma$ of the oxygen and nitrogen atoms. The particular values used are shown in each panel. The specific orbital assignments of transitions are indicated when the extent of configuration interaction leaves their identities clear. The upper panel represents the experimental spectrum taken from ref 6. The weak $x'$-polarized band at about 68 kK in the experimental spectrum is uncertain (see text). The n$\pi_4$* transition is symmetry forbidden and the calculated oscillator strength is zero.

considerations of internal intensity borrowing among the components of vibronic sequences.[10,11]

**Molecular Orbital Calculations for Urea.** The MO calculations for both urea and glycoluril molecules using a standard spectroscopic version of the intermediate neglect of differential overlap configuration interaction (INDO/S-CI) package[12,13] give some successes and some glaring failures. Since the failures found for the urea calculation showed up in a similar fashion in the glycoluril calculations, it was therefore decided to focus first on the possibility of modifying the parameterization of the calculation for urea itself.

For clarity we first give an orbital description of urea and make tentative assignments of the experimentally observed bands. As mentioned in the last section, urea displays three bands in the accessible VUV; these bands are labeled I′, II′, and III′ and have polarizations of $y'$, $z'$, and $y'$, respectively. Although the assignments shown are based on the final calculations, their general depiction here is useful for the convenience of later discussion. We would like to note that the number of simple molecules for which definite experimental assignments have been reported in the literature and upon which the parameterization of semiempirical procedures are based is scant. In fact the unambiguous assignment of the exited state symmetries of three transitions of urea puts this molecule in a class of its own for this type of heteroatom molecule.

There are six electrons distributed over four principal atomic centers in urea. Figure 6 (left) depicts schematically the four resulting molecular orbitals and the nearby n, $\sigma$, and $\sigma$* orbitals. The relative ordering shown is based on the final calculations (see second panel from the top of Figure 7); however, it is consistent with intuitive considerations also. Although there is considerable configuration interaction, the assignment of transitions based on this orbital description holds true qualitatively. According to the diagram there can be three $\pi\pi$* valence shell transitions. The lowest energy band will correspond to $\pi_3 \rightarrow \pi_4$* and will be $y'$ polarized. We assign band I′ to this transition. Both the remaining higher energy $\pi\pi$* transitions are predicted to be polarized along the $z'$ axis. Since but one such band (II′) appears in the experimental spectrum of urea, we conclude that this $z'$ polarized band must correspond to $\pi_2 \rightarrow \pi_4$*. The calculations give the third such transition, $\pi_1 \rightarrow \pi_4$*, to be $z'$ polarized and to occur above 82 000 cm$^{-1}$ (*i.e.*, beyond the experimental range) and to have a very low intensity ($f < 0.002$). The $y'$ polarized transition III′ must therefore not arise from the $\pi$ manifold. Rather, the final calculation predicts the n$\sigma_2$* transition to occur with about the observed intensity and energy as band III′. The right side of Figure 6 shows the state energy level diagram that results from the final INDO/S calculations.

For the convenience of the reader, we give here the principal atomic orbitals of the LCAOs most involved. The coefficients shown here were obtained from the final calculation using the adjusted parameters (*vide infra*):

$$\sigma_3{}^* = 0.332p_y(C) + 0.149p_y(O) - 0.383s(N_1) + 0.383s(N_2) + ...$$

$$\sigma_2{}^* = 0.484s(C) - 0.217p_z(C) - 0.414s(N_1) - 0.414s(N_2) + ...$$

$$\pi_4{}^* = 0.924p_x(C) - 0.429p_x(O) - 0.262p_x(N_1) - 0.262p_x(N_2) + ...$$

$$n = 0.920p_y(O) + 0.137p_y(N_1) - 0.137p_y(N_2) + ...$$

$$\pi_3 = -0.707p_x(N_1) + 0.707p_x(N_2) + ...$$

$$\pi_2 = 0.621p_x(O) - 0.554p_x(N_1) - 0.554p_x(N_2) + ...$$

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(10) Clark, L. B. *J. Am. Chem. Soc.* **1986**, *108*, 5109.
(11) Clark, L. B. *J. Phys. Chem.* **1990**, *94*, 2873.

$$\pi_1 = 0.566p_x(C) + 0.656p_x(O) + 0.353p_x(N_1) + 0.353p_x(N_2) + \ldots$$

$$\sigma_1 = 0.336p_z(C) - 0.409s(O) - 0.669p_z(O) - 0.285p_z(N_1) - 0.285p_z(N_2) + \ldots$$

Some details of the programs and calculational procedures can be found in a previous paper.[14] The structural data for urea are from a neutron diffraction study.[15] The standard SCI calculation[13,14] for urea (in this case all 12 occupied and 10 unoccupied orbitals are included) gives four transitions in the experimentally observed region: $\pi_3 \rightarrow \pi_4^*$ at 52 000 cm$^{-1}$, $f = 0.29$, polarized along the $z'$ axis; $\pi_2 \rightarrow \pi_4^*$ at 55 800 cm$^{-1}$, $f = 0.22$, polarized along the $y'$ axis; $\pi_3 \rightarrow \sigma_2^*$ transition at 63 700 cm$^{-1}$, $f = 0.045$, polarized along $x'$; and n → $\sigma_2^*$ transition at 64 700 cm$^{-1}$, $f = 0.044$ with $y'$ polarization. A forbidden n → $\pi_4^*$ transition is predicted to occur at 35 000 cm$^{-1}$. The bottom panel of Figure 7 shows these predictions schematically.

Although this calculation reasonably predicts the energies and intensities of the two $y'$-polarized transitions that are observed experimentally,[6] the $z'$-polarized transition is predicted to occur 10 000 cm$^{-1}$ below the experimental value and therefore to be in the wrong order. In addition, the predicted n → $\pi_4^*$ transition energy must be at least 13 000 cm$^{-1}$ in error relative to the minimum value (~48 000 cm$^{-1}$) suggested by Campbell and Clark.[6] Although it is possible to interchange the order of the first two calculated transitions by varying the interaction factors $f_\sigma$ and $f_\pi$,[12] the predicted energies and intensities then differ significantly from the experimental values. We have not been able to obtain a satisfactory fit of the experimental spectrum by simply changing the values $f_\sigma$ and $f_\pi$ in the INDO/S-CI program.

Correspondingly, the standard SCI calculation for glycoluril shows similar difficulties. Transitions I and III are adequately accounted for, but II and IV are predicted about 10 000 cm$^{-1}$ lower than their actual energies (see bottom panel of Figure 8). Here again the positions of the two nearly degenerate nπ* transitions are predicted far to the red of any observed (even very weak) absorption. Although the intensities of the strong transitions agree with the experimental values well enough, the energies of II and IV show the same sort of misordering as that found for urea. Again, we have not found it possible to match satisfactorily the experimental values for both the intensities and energies of all the various transitions by simply adjusting the interaction factors in the INDO/S-CI program. In our opinion, the general differences between theory and experiment are such as to render the calculated results of little value in the interpretation and assignment of experimental spectra.

Because the lower, originating molecular orbital of both the $\pi_3 \rightarrow \pi_4^*$ and the n → $\pi_4^*$ transitions of urea have large contribution coefficients from the atomic orbitals on oxygen, it seemed reasonable to investigate the effect of adjusting the oxygen parameters used in the calculations. Here the goal was to enhance the attraction of oxygen for electrons and thereby stabilize the two molecular orbitals in question relative to others. In this regard, we should note that the parameters for H, C, and N have been subject to more extensive testing than those for oxygen.[12,13] If the value of $\beta$ for oxygen is changed from the standard value of −34.0[12] to −56.0 eV (in fact Del Bene and Jaffé suggested −45.0 eV in their original parameter set),[16] the $z'$-polarized transition shifts to 61 100 cm$^{-1}$ with $f = 0.30$ and is slightly higher in energy than the first $y'$-polarized transition at 60 100 cm$^{-1}$ with $f = 0.17$. Now the order of transitions, their energies and intensities are all closer to the experimental results, but the predicted energy for the n → $\pi_4^*$ transition of 40 000 cm$^{-1}$ is still much too low. Because the values of $\beta$, $f_\sigma$, and $f_\pi$ are interrelated in their effect on the Fock matrix,[12] we do not expect to improve the results significantly by adjusting only these three parameters. Therefore, we propose to change the electron affinity of oxygen $A_O$ as well. In effect this change only alters $\gamma_{OO}$ by virtue of the simple relation ($\gamma_{OO} = I_O - A_O$) suggested by Pariser.[17,18] The reason for modifying electron affinity rather than ionization potential is twofold. First, the former is subject to more uncertainty (although as mentioned in the Appendix the latter is not very well-defined either). And second, by doing so we avoid certain complexities because the ionization potential appears at other places in the calculations as well.

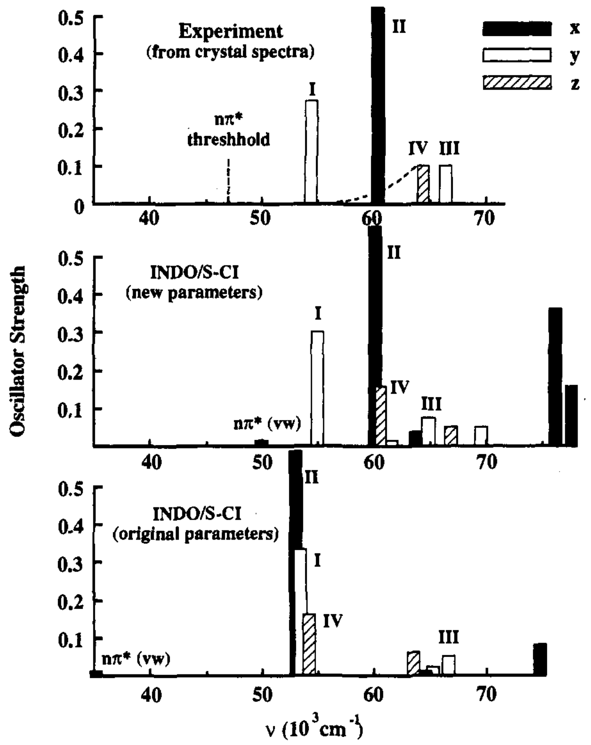

**Figure 8.** Schematic comparison of experimental and calculated glycoluril spectra. The experimental results are in the top panel. The middle panel represents the INDO/S calculation using the new parameter set for the oxygen and nitrogen atoms. The bottom panel shows the calculated results using the standard parameterization. The dashed line extending from IV in the top panel reflects the observed unusual bandshape of IV.

If we keep the $f_\sigma$ and $f_\pi$ values of 1.267 and 0.585 as suggested by Ridley and Zerner[12] but make oxygen more electron-attractive by increasing $A_O$ by 4.5 eV (equivalent to $\gamma_{OO}$ = 8.5 eV) and change $\beta_O$ to −45 eV, then not only are the first two ππ* transitions (I′, 53 900 cm$^{-1}$, $f = 0.27$, $y'$-polarization; II′, 59 600 cm$^{-1}$, $f = 0.31$, $z'$-polarization) ordered correctly and positioned near their experimental energies with the correct intensities, but the n → $\pi_4^*$ transition (50 900 cm$^{-1}$) is found effectively underneath the first ππ* transition (see second panel from the bottom in Figure 7). Although this calculation places the n → $\sigma_2^*$ transition too high in energy (79 900 cm$^{-1}$), there is a much better overall fit with the experimental data. It should be noted that $\beta_O$ = −45 eV is the

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original value proposed by Del Bene and Jaffé[16] in 1968. The value was then pegged at −30 eV by Jacques et al. in 1981[19] before settling at −34 eV in what we have referred to as "the standard parameter set". Finally, if the nitrogen parameters $\beta_N$ and $A_N$ are changed somewhat in addition, then a reasonable overall fit of the energies, oscillator strengths, and polarization directions of all the experimental bands of urea are obtained. In addition, the predicted position of the very weak $n \rightarrow \pi_4^*$ transition is found to be neatly tucked near the first strong absorption band and would not be observable experimentally. All the calculated results are summarized and compared with the experimental data in Figure 7.

The calculated spectrum fits the experimental spectrum so well that it is of interest to reexamine the original urea crystal spectra for any evidence of an $x'$-polarized transition ($\pi_2 \rightarrow \sigma_2^*$) in the vicinity of 65−70 kK. In fact there does appear to be a weak "feature" in the ⊥c spectrum of urea (110) near 68 kK,[6] and such a feature is consistent with the presence of such a transition. Although this evidence is not particularly compelling we note that the presence of a weak $x'$-polarized band near 68 kK actually improves the analysis of both the urea and urea–hexadecane spectra of the earlier work. Nevertheless, we have tentatively included such a band in the experimental spectrum for urea (top panel, Figure 7) and given it a question mark (?).

The new parameter scheme involving the oxygen atom (second panel from the bottom of Figure 7) is generally more successful than the original set for some other systems as well. For example, when the new oxygen parameters $\gamma_{OO} = 8.5$ eV and $\beta_O = -45$ eV (those of nitrogen remain unchanged) are substituted in a calculation on the glutarimide molecule, the positions of the two weak $n\pi^*$ transitions (experimentally found 39 600 and 44 800 cm$^{-1}$) are predicted to occur at 40 400 and 42 100 cm$^{-1}$. The calculated values using the original parameter set[14] are far to the red at 29 700 and 31 000 cm$^{-1}$. Calculations of other molecules containing the carbonyl group using these new oxygen parameters appear to give generally improved agreement. More details will be published elsewhere.[20]

**Molecular Orbital Calculations for Glycoluril.** When the modified values for oxygen and nitrogen are used (see second panel from the top of Figure 7) for glycoluril, the predicted spectrum is now in reasonable agreement with the experimental crystal spectra. The ordering of the transitions and their oscillator strengths seem generally to be correct (particularly for transitions I, II, and III). The two weak $n\pi^*$ transitions originally predicted to occur near 35 000 cm$^{-1}$ using the standard parameterization now are predicted to be near 48 000 cm$^{-1}$ and would be effectively buried under the red edge of the stronger bands. The results are presented graphically in Figure 8.

Ignoring the several weak bands predicted above 60 000 cm$^{-1}$ (middle panel of Figure 8) we see that only IV seems to be displaced significantly from its experimental peak position. As noted in an earlier section it is band IV that exhibits an unusually broad absorption contour in the crystal *b*-axis spectrum. The experimental peak position may not represent the vertical transition in this case. Further we note that the INDO/S calculation for the dimer split of the urea II′ band is 400 cm$^{-1}$ and is substantially less than the Independent Systems (strong coupling) value of 2600 cm$^{-1}$. The latter value is, of course, less than the actual difference between the peak positions (4000 cm$^{-1}$). These differences are not understood.

## Conclusion

The symmetry assignments of the four bands of the glycoluril molecule are fairly certain. That these four transitions are derived in a simple way from the three observed transitions of urea not only affirms the original urea assignments but in addition seems entirely reasonable. The Independent Systems approach in which glycoluril is treated as a urea dimer nicely links the spectrum of glycoluril to that of urea.

On the other hand, in order to obtain a "satisfactory" fit of the experimental glycoluril spectrum with that obtained from semiempirical MO methods, it is necessary to modify key parameters in the INDO/S program. When the parameters for the oxygen and nitrogen atoms are adjusted so that the predictions for the urea molecule match the experimental urea assignments, then the calculated results for glycoluril also come into alignment with the experimental spectrum.

Although the new set of parameter values are reasonably successful for another molecule or two, it is not clear just how general the new parameterization is. Further experimental and theoretical work is needed to reach a conclusion. The fact that the new parameterization brings the calculated results for a variety of transitions ($n\pi^*$, $\pi\pi^*$, $n\sigma^*$) in these multiheteroatom systems into alignment with experiment is, in our opinion, compelling evidence that some such adjustments are necessary for this calculational method *at least for the oxygen atom.* It is less evident, however, that the nitrogen parameters need to be adjusted. Nevertheless, it must be remembered that any such agreement is more or less useless unless it is general and not specific to one molecule or type of linkage.

Since the numbers used for ionization potentials and electron affinities are not clearly defined, and since these choices significantly affect the calculational outcomes, it would seem that the issue needs more careful consideration. What is needed in this regard are the unambiguous experimental assignments of transitions for a larger collection of molecules than is presently available. Further, it is important to have at hand the certain assignment of two, three, or more transitions for each of these systems. One finds too many literature assignments of the excited states of fundamental chromophores to be based simply on webs of speculation. The present work is a contribution toward the goal of acquiring sufficient experimental excited state information so that unequivocal judgments can be made regarding the efficacy of the semiempirical approach. In addition, such data provide appropriate targets for use in the refinement of ab initio methods.

**Acknowledgment.** This work was supported by a National Institutes of Health Grant GM38575. We also thank Prof. Michael Zerner in Gainesville and Prof. Patrik Callis in Bozeman for making available to us the original INDO/S (ZINDO) code.

## Appendix

Although ionization potentials and electron affinities play important roles in semiempirical molecular orbital calculations, somehow they appear to be not well-defined in the context of different types of the calculations. For example, in the original CNDO calculations, the "average" ionization potentials of 2*p*

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orbitals for C, N, and O are listed as 10.67, 13.19, and 15.85 eV, respectively,[21] and the electron affinities for the corresponding orbitals are 0.47, 1.36, and 2.37 eV, respectively.[22] These would give $\gamma$ values of 10.20, 11.83, and 13.51 eV, for C, N, and O, respectively. On the other hand, in the original CNDO/S calculations, a different set of $\gamma$ parameters are listed. They are 11.11, 12.01, and 13.00 eV for C, N, and O.[23] For C Pariser used a value of 10.53 eV,[17,18] which was obtained from the ionization potential of 11.22 and electron affinity of 0.69 of C according to Mulliken.[24] However, these values of $\gamma$ (particularly for O) are quite different from the set proposed by Ellis et al., i.e., 10.93, 11.88, and 15.13 eV for C, N, and O, respectively.[25] They are derived from the ionization potential of 11.27, 14.42, 18.53 eV and electron affinity of 0.34, 2.54, and 3.40 eV for C, N, and O, respectively, listed by Hinze and Jaffé.[26] Evidently no clear consensus has developed in this regard. And clearly these decisions do affect the calculational outcomes.

JA942939O