PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Study of the orientation of thiourea adsorbed on aluminum oxide by tunneling spectroscopy. I. Determination of partial charges from molecular electrostatic potential calculations for thiourea and urea

C. D. Crowder, G. P. Alldredge, and H. W. White

Department of Physics and Astronomy, University of Missouri—Columbia, Columbia, Missouri 65211

(Received 24 September 1984)

Ab initio electrostatic molecular potentials for urea [$CO(NH_2)_2$] and thiourea [$CS(NH_2)_2$] have been calculated with use of restricted Hartree-Fock theory. A nonlinear least-squares regression package was used to fit atomic partial charges to the potentials. Calculations were made with use of several different basis sets with and without polarization functions. Basis-set scaling factors calculated for each atom showed that the potential-derived (PD) charges were much more reliable than the Mullikan values. The effects of a vibrational mode on the calculated partial charges were also evaluated. Dipole moments were calculated with use of various basis sets and compared with observed values. The potential was also fitted by splitting the static charge determined for each atomic site into two portions. The core-charge portion was forced to follow the nuclear motion, whereas the valence-charge portion was allowed to float in a direction such that the best fit to the potential was obtained. This latter procedure provided reproductions of the calculated quantum-mechanical electrostatic potentials which were determined to be sufficiently accurate for electron-tunneling-intensity calculations. Comparison of experimental and calculated tunneling intensities for thiourea are presented in the following paper.

I. INTRODUCTION

Many of the theoretical models used in inelastic electron-tunneling spectroscopy (IETS) require the assignment of partial atomic charges for molecules of interest. In the past, Mullikan population analyses have been used to determine these atomic charges: however, recent articles by Momany[1] and Cox and Williams[2] have shown that Mullikan charge distributions depend strongly on the basis set used in the calculations. Since theoretical tunneling intensities are very sensitive to the choice of partial atomic charges, we have used Momany's[1] method to determine net atomic charges for urea [$CO(NH_2)_2$] and thiourea [$CS(NH_2)_2$].

Momany calculated the quantum-mechanical electrostatic potential (QMEP) of formamide, methanol, and formic acid using a self-consistent field molecular orbital (SCF-MO) approach. Momany determined partial atomic charges by fitting the electrostatic potential resulting from atom-centered point charges to the QMEP for each molecule. Cox and Williams[2] extended Momany's work to several simple molecules using a variety of basis sets. In this work, Mullikan (M) charges and potential-derived (PD) atomic charges are compared for different basis sets, and the fits of the M and PD charges to the QMEP are examined for urea and thiourea.

It is commonly assumed in tunneling calculations that the partial charge located on an atom site remains constant during a vibrational excitation of the molecule. In Sec. IV of this paper this assumption is evaluated; it is found that the PD charges vary significantly from one mode to another. In an effort to develop a technique which is tractable for tunneling calculations, the effects of splitting the net atomic charges into two parts were explored. One point charge represented the positive core of each atom and a second point charge represented the valence electron cloud. We call this approach the "floating-valence" model and find that it gives a significantly better fit to the QMEP of the molecules studied than does the use of single partial charges located at each atom site. It also allows the electrostatic potential of a vibrating molecule to be described in terms of two charges on each atom and their displacements during a vibrational excitation. Comparison of experimental and theoretical tunneling intensities for thiourea are presented in the following paper.[3] While this work was motivated by IETS studies, the techniques developed have a wide range of applications.

II. PARTIAL CHARGE DETERMINATIONS

Momany calculated *ab initio* molecular electrostatic potentials using atomic orbital basis sets. The effective partial charge located at each atom site was then determined by fitting the resultant classical Coulomb potential to the *ab initio* values while maintaining molecular neutrality. The PD charges obtained differed significantly from those obtained from population analysis and semiempirical methods.

We calculated *ab initio* electrostatic potentials using self-consistent restricted Hartree-Fock theory, as implemented by Quantum Chemistry Program Exchange (QCPE) No. 437 (GAUSSIAN 80).[4] The QMEP acting on a unit positive test charge located at a position $\mathbf{r}$ due to the presence of a neighboring molecule is given by

$$V(\mathbf{r})=\sum_A \frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|}-\sum_{\mu,\nu} P_{\mu\nu}\int \frac{\phi_\mu\phi_\nu}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' , \quad (1)$$

where Z_A is the nuclear charge of atom A, $\mathbf{R}_A$ is the position of atom A, $\sum_A$ indicates the sum over all nuclei, ϕ_μ is an atomic orbital, $P_{\mu\nu}$ is an SCF-MO density matrix element, and $\sum_{\mu,\nu}$ indicates sums over all the electrons in the molecule.

Equation (1) allows the molecular electrostatic potential at a point $\mathbf{r}$ to be determined. For comparative purposes the electrostatic potentials for both urea and thiourea were calculated using rectangular arrays of equally spaced points. Spatial axes for each molecule were oriented such that the plane of the molecule was the yz plane with the C=O or C=S bond directed along the positive z axis. The origin was chosen at the center of nuclear charge. For urea, a grid extending from -8 to 8 Bohr radii in the x (out-of-plane) direction, from -10 to 10 Bohr radii in the y and z directions, and with a cubic grid spacing of 2 Bohr radii (1.048 Å) provided an optimal balance between invariance of the fitted charges and efficient use of computer resources. Our grid spacing of 1.048 Å lies within the optimal range of 1.0 to 1.2 Å reported by Cox and Williams[2] in their calculations for similar molecules. For thiourea, where the C=S bond length is approximately 0.47 Å longer than the C=O bond length in urea, it was necessary to increase the size of the mesh from -10 to 10 Bohr radii in the x direction and from -12 to 12 Bohr radii in the y and z directions. A cubic grid spacing of 2 Bohr radii was retained for the thiourea calculations.

Since the molecular electrostatic potential is strongly positive near the atom centers, all fields points were excluded which were within the van der Waals radius of any atom. The radii used for the different atoms are as follows.

Atom	van der Waals Radii (Å)	Reference
S	1.85	5
O	1.40	5
C	1.70	6
N	1.50	5
H	1.20	6

The statistical analysis system (SAS) procedure NLIN,[7] a nonlinear least-squares regression package, was used to fit partial charges to the molecular electrostatic potential. Preliminary results showed the partial charge determinations to be strongly affected by the potential at field points which lay close to van der Waals radii of the atoms. In order to better fit the long-range potential, all field points which lay within 1 Å of the van der Waals shells were weighted by a factor of 0.25 in the fitting procedure. This weighting is consistent with Momany's[1] method; Cox and Williams[2] eliminated these marginally close field points from their calculations.

III. STATIC PARTIAL CHARGES FOR UREA AND THIOUREA

The QMEP for urea was calculated using the molecular structure determined by Worsham *et al.*[8] as shown in Fig. 1. The molecular geometry used for the thiourea calculations was determined by Kunchur and Truter[9] and is shown in Fig. 2. Both molecules are planar and have C_{2v} symmetry. The electrostatic potentials for both molecules were calculated using STO-3G, 4-31G, and 4-31G** basis sets.[4] We also used 6-31G and 6-31G** basis sets for urea. Equipotential contour plots were made for both molecules using a variety of basis sets, both in the plane of the molecule (yz plane) and perpendicular to the molecular plane (xz plane.) In all instances the carbon-chalcogen bond is directed along the positive z axis. The 4-31G** basis set results for urea are shown in Figs. 3(a) and 3(b), and the plots for thiourea are given in Figs. 4(a) and 4(b). All equipotential values in this paper are in kcal/mol and all distances are in Å.

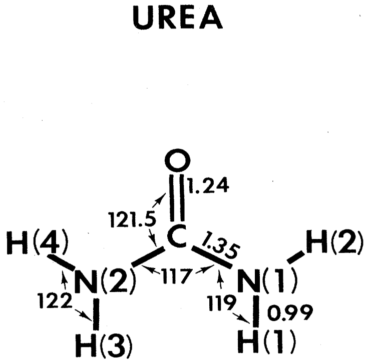

FIG. 1. Experimentally determined structure of urea. All distances are in angstroms, and all angles are in degrees.

PD charges for urea at equilibrium are given in Table I(a) for different basis sets. Table I(b) shows the Mullikan charges for these basis sets. Two important conclusions can be drawn from the information in these two tables. First, the PD charges calculated from 4-31G and 6-31G basis sets differ by less than 1%. Also, the difference between 4-31G** and 6-31G** PD values is less than 1%. Based on these comparisons, we chose not to use the more costly 6-31G basis set, with or without polarization functions, for thiourea calculations. Second, there is a large variation in Mullikan charges derived from different basis sets. The degree to which this basis-set dependence would affect calculated IETS intensities was estimated by determining the scaling factors between charges obtained for a particular atom using different basis sets. Both the STO-3G and 4-31G values for urea and thiourea were scaled to

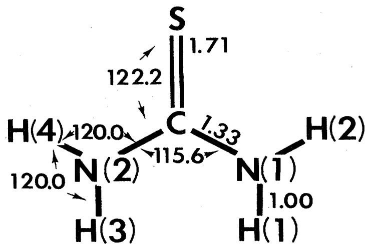

FIG. 2. Experimentally determined structure of thiourea. All distances are in angstroms, and all angles are in degrees.

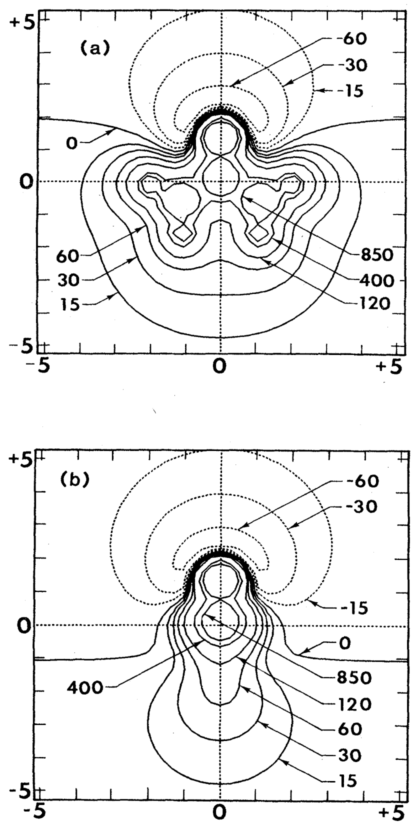

FIG. 3. Urea equipotential plot using the 4-31G** basis set: (a) *yz* plane, (b) *xz* plane. Potential values are in kcal/mol and distances are in angstroms.

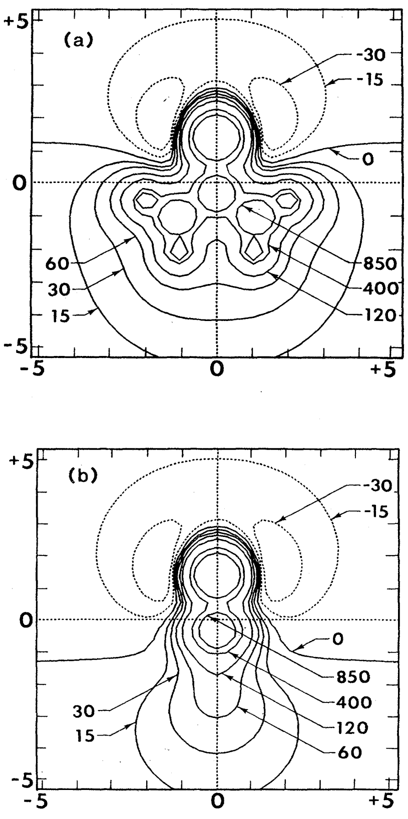

FIG. 4. Thiourea equipotential plot using the 4-31G** basis set: (a) *yz* plane, (b) *xz* plane. Potential values are in kcal/mol and distances are in angstroms.

the 4-31G** values. This procedure gave "basis-set scaling factors" for each atom. Relative intensities were used in the IETS calculations; thus, if the scaling factors were constant for all the atoms in a molecule, then the two basis sets would give equivalent results. These scaling factors are certainly not constant for the Mullikan charges for urea, as can be seen in Table II. The individual atomic scaling factors for the Mullikan STO-3G basis set deviate as much as 41% from the average value. The scaling factors for the 4-31G basis set vary as much as 20%. Table II also indicates that the PD charges for urea are less basis-set dependent than the Mullikan charges. The

TABLE I. Partial charges for urea: (a) PD and (b) Mullikan partial charges.

Atom	STO-3G	4-31G	6-31G	4-31G**	6-31G**
			(a) PD		
O	−0.537	−0.782	−0.788	−0.693	−0.695
C	0.928	1.279	1.284	1.068	1.073
N(1),N(2)	−0.875	−1.193	−1.200	−1.074	−1.085
H(1),H(3)	0.338	0.467	0.471	0.440	0.445
H(2),H(4)	0.342	0.478	0.481	0.477	0.451
			(b) Mullikan		
O	−0.346	−0.687	−0.644	−0.687	−0.672
C	0.418	1.022	0.975	0.932	0.936
N(1),N(2)	−0.459	−0.926	−0.934	−0.726	−0.766
H(1),H(3)	0.199	0.360	0.365	0.284	0.299
H(2),H(4)	0.224	0.398	0.404	0.320	0.335

TABLE II. Charge scaling factors for urea.

Atom	M STO-3G	M 4-31G	PD STO-3G	PD 4-31G
O	1.984	1.000	1.290	0.887
C	2.230	0.911	1.151	0.835
N(1),N(2)	1.582	0.784	1.227	0.900
H(1),H(3)	1.427	0.789	1.302	0.943
H(2),H(4)	1.429	0.804	1.307	0.935
Average scale factor	1.649	0.833	1.264	0.910
rms fit	0.313	0.074	0.053	0.086
Maximum deviation from average scale factor	0.682	0.167	0.113	0.075
Maximum percentage deviation from average	41%	20%	9%	8%

maximum deviations of the PD atomic scaling factors from the average values are only 9% and 8% for the STO-3G and 4-31G basis sets, respectively.

PD and Mullikan charges for thiourea are presented in Tables III(a) and III(b). It is interesting to compare the PD charges for similar atoms in thiourea and urea. The Mullikan charges for nitrogen and hydrogen atoms in urea vary only slightly from their values in thiourea, but the fitted values are significantly different in the two molecules. The difference in the chalcogen and carbon charges in urea and thiourea is striking and demonstrates the result of lengthening the carbon-chalcogen bond in thiourea and the reduced electron affinity of sulfur as compared to oxygen.

The scaling factors for thiourea for the STO-3G and 4-31G basis sets are given in Table IV. The scaling factors are not consistent for the individual atoms in the molecule for either the PD or Mullikan charges; this lack of consistency is particularly true for the carbon and sulfur atoms. Since the basic difference between thiourea and

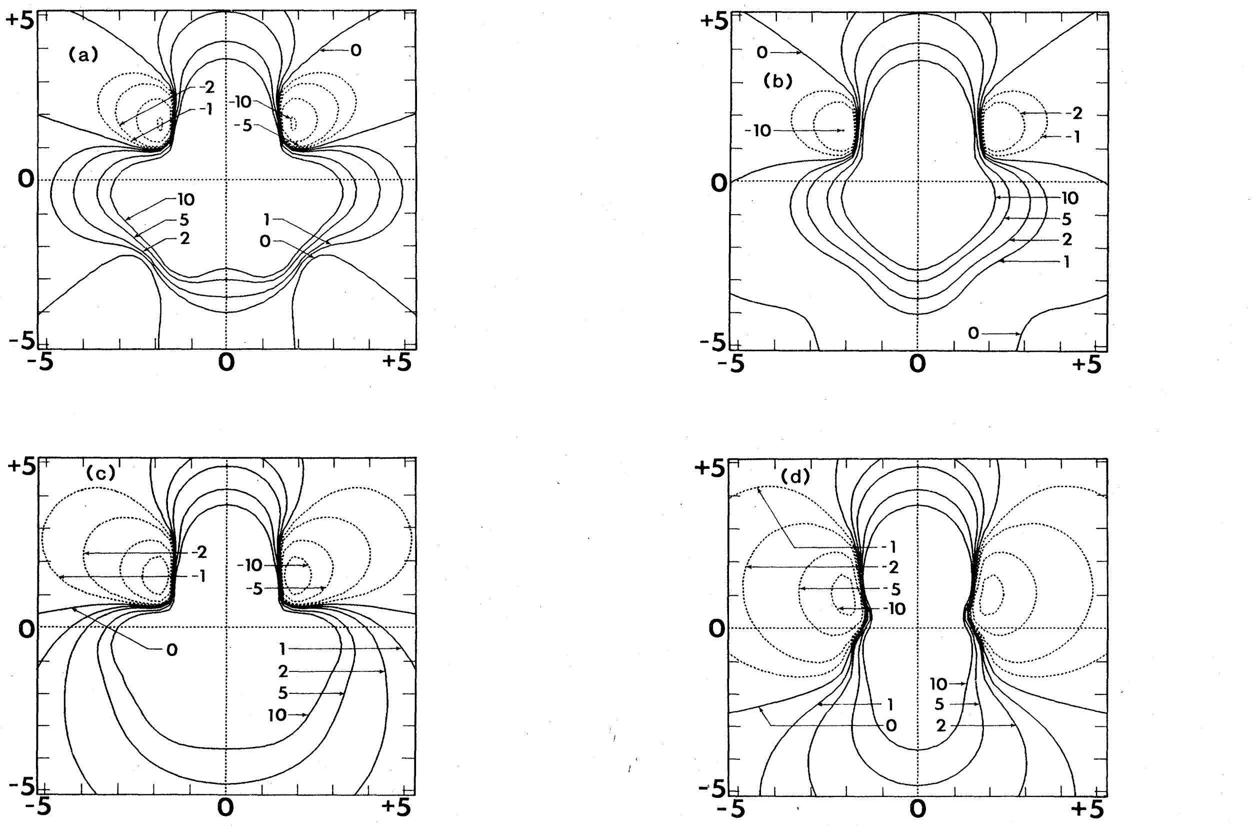

FIG. 5. Thiourea 4-31G** QMEP minus electrostatic potential 4-31G** charges: (a) PD charges, *yz* plane; (b) PD charges, *xz* plane; (c) Mullikan charges, *yz* plane; (d) Mullikan charges, *xz* plane. Potential values are in kcal/mol and distances are in angstroms.

TABLE III. (a) PD and (b) Mullikan partial charges for thiourea.

Atom	STO-3G	4-31G	4-31G**
	(a) PD		
S	−0.427	−0.452	−0.400
C	0.509	0.349	0.166
N(1),N(2)	−0.619	−0.672	−0.547
H(1),H(3)	0.295	0.377	0.349
H(2),H(4)	0.283	0.347	0.316
	(b) Mullikan		
S	−0.204	−0.114	−0.519
C	0.186	0.342	0.642
N(1),N(2)	−0.426	−0.884	−0.680
H(1),H(3)	0.202	0.366	0.289
H(2),H(4)	0.233	0.404	0.330

TABLE IV. Charge scaling factors for thiourea.

Atom	M STO-3G	M 4-31G	PD STO-3G	PD 4-31G
S	2.544	4.553	0.937	0.885
C	3.452	1.877	0.326	0.476
N(1),N(2)	1.596	0.769	0.884	0.814
H(1),H(3)	1.431	0.790	1.183	0.926
H(2),H(4)	1.416	0.817	1.117	0.911
Average scale factor	1.860	1.395	0.954	0.833
rms fit	0.699	1.322	0.265	0.142
Maximum deviation from average scale factor	1.592	3.158	0.628	0.357
Maximum percentage deviation from average	86%	226%	66%	43%

TABLE V. Dipole moments for urea and thiourea.

	Urea	Thiourea
Observed[a]	4.56	4.89
PD STO-3G	3.49	4.79
M STO-3G	2.66	2.63
QMEP STO-3G	3.45	4.76
PD 4-31G	5.18	6.13
M 4-31G	4.51	1.86
QMEP 4-31G	5.14	6.07
PD 4-31G**	4.95	6.03
M 4-31G**	4.47	5.14
QMEP 4-31G**	4.90	5.98

[a] Reference 10.

urea is the presence of the second-row sulfur atom, it would appear that the concept of basis-set scaling factors is inappropriate for partial charge calculations involving molecules which contain second-row atoms.

Plots of the quantum-mechanical potential for thiourea derived from the 4-31G** basis set minus the Coulomb potential due to partial charges located on atom sites are shown in Figs. 5(a)—5(d). The plots are in the xz and yz planes as previously defined. For both molecules, the PD charges give a much better fit to the quantum-mechanical potential on the "hydrogen end" of the molecules than do the Mullikan charges.

In order to evaluate the partial charge fitting procedure, the dipole moments for urea and thiourea were calculated using the Mullikan and PD charges obtained from the STO-3G, 4-31G, and 4-31G** basis sets. The calculated and observed[10] dipole moments and dipole moments computed directly from the Hartree-Fock wave functions are given in Table V. Dipole moments obtained from the STO-3G basis set are smaller than the observed values, while the 4-31G and 4-31G** basis sets yield values greater than the measured moments. However, the PD charges yield dipole moments which agree very closely with the values calculated directly from the quantum-mechanical wave functions, and they serve as a valuable consistency check on the fitting procedure.

IV. DYNAMIC PARTIAL CHARGE CALCULATIONS FOR UREA AND THIOUREA

A. Method

Since relative IETS intensities were discovered to be very sensitive to atomic charge values, the assumption that these charges remained constant during a molecular vibration was tested. To do this, Cartesian displacements normalized to zero-point motion were used to calculate the average position of an atom during a vibrational mode as follows:

$$R_n^{kl}=R_n^{0l}+\delta_n^{kl} \ ,$$

where R_n^{kl} is the average position of atom n in the lth Cartesian direction during the kth vibrational mode, R_n^{0l} is the equilibrium position of atom n in the lth Cartesian direction, and δ_n^{kl} is the normalized displacement for the nth atom during the kth vibrational mode in the lth Cartesian direction.

After the new atom positions were determined, the quantum-mechanical electrostatic potentials were recalculated for urea and thiourea; new dynamic atomic partial charges were then calculated to fit the vibrational mode QMEP's.

B. Urea

We were fortunate to receive a set of Cartesian displacements for the planar modes of urea from Duncan.[11,12] These were normalized to zero-point motion and then used to determine the vibrational-mode dependence of the partial charges. The dynamic partial charges for urea calculated using the 4-31G** basis set changed significantly from equilibrium values during many of the vibrational modes. These changes were typically 10% to 15%, but in a few cases exceeded 25%.

C. Thiourea

1. In-plane calculations

Cartesian displacements for thiourea could not be found. Consequently, the literature was searched for force constants which could be used to generate Cartesian displacements using standard techniques of vibrational spectroscopy. We referenced several infrared and Raman peak assignments and found that the peak assignments of Aitken, Duncan, and McQuillan[13] for the in-plane (IP) modes of thiourea gave the best agreement with our tunneling results. Several sets of force constants for the planar modes[13–16] of thiourea were found which gave fre-

TABLE VI. In-plane vibrational frequencies for thiourea calculated using the force constants of Bleckmann *et al.* (Ref. 16). All frequencies in cm^{-1}.

Observed frequency[a]	Calculated frequency before iteration of force constants	Calculated frequency after iteration of force constants
3390	3357	3409
3385	3305	3359
3290	3233	3284
3280	3183	3234
1628	1617	1625
1620	1617	1621
1470	1489	1476
1415	1358	1419
1088	1054	1083
1054	1007	1034
732	733	711
468	447	462
415	401	398

[a] G. B. Aitken, J. L. Duncan, and G. P. McQuillan, J. Chem. Soc. A 2695 (1971).

TABLE VII. Out-of-plane vibrational frequencies for thiourea calculated using the force constants of Bleckmann *et al.* (Ref. 16). All frequencies are in cm^{-1}.

Observed frequency (cm^{-1})	Calculated frequency before iteration of force constants	Calculated frequency after iteration of force constants
769[a]	702	784
635[a]	534	632
577[a]	487	537
505[a]	480	495
463[b]	456	491

[a] J. E. Stewart, J. Chem. Phys. **26**, 248 (1956).

[b] Stewart's mode assignment, frequency corrected by G. B. Aitken, J. L. Duncan, and G. P. McQuillan, J. Chem. Soc. A 2695 (1971).

quencies in reasonable agreement with experiment, but the force constants of Bleckmann, Schrader, and Meier[16] gave the best fit to our observed IP frequencies. The force constants were iterated slightly to reduce the differences between calculated and observed frequencies. The observed and calculated frequencies are shown in Table VI. The program QCPE No. 342 (Ref. 17) was used to calculate the Cartesian displacements from the iterated force constants. (The mode patterns were normalized by zero point motion using the calculated frequency values.)

2. *Out-of-plane calculations*

One plausible set of force constants was found for the out-of-plane (OP) modes of thiourea; namely, those of Bleckmann *et al.*[16] Unfortunately, these OP force constants did not yield frequencies in good agreement with our experimental values. Consequently, the iterative feature of QCPE No. 342 was used to refine the fit.[17] The fitted force constants changed significantly during the iteration process, and these changes caused difficulties in the resultant Cartesian displacements. The observed and calculated frequencies are shown in Table VII. It is very important to emphasize the effect of iteration on the vibrational displacements. For example, the second highest frequency mode originally had a calculated frequency of 534 cm^{-1}. After interaction the mode was shifted upward to 632 cm^{-1}, but the mode pattern was essentially unchanged. Interestingly, the theoretical intensities for modes containing OP vibrations were the furthest from experimental values, as is shown in Sec. V of paper II.[3] These differences may be entirely due to the initial discrepancies between the observed OP frequencies and calculated values.

For both thiourea and urea, there is a measurable change in the charges during displacement from equilibrium for many of the vibrational modes. While these differences may be insignificant for many applications, they are important in electron tunneling calculations, as is shown in the following paper.[3] The IETS intensity theory developed by Kirtley, Scalapino, and Hansma[18] requires that partial charges remain constant during a vibrational mode. Consequently, for an atomic charge model to be useful for tunneling calculations, it must have *constant* charges associated with each atom; and it must be capable of fitting the electrostatic potential for both the equilibrium and vibrating states of a molecule. An approach to obtain realistic atomic partial charges which would satisfy these criteria is briefly described in the next section.

V. FLOATING-VALENCE MODEL

Since the single atomic charge model did not adequately reproduce the QMEP for vibrating molecules, we attempted to develop a feasible alternative. The simplest improvement was to use two charges for each atom in-

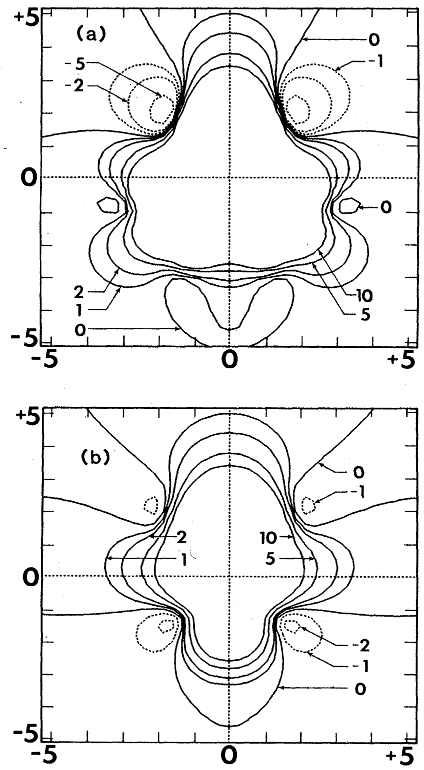

FIG. 6. Thiourea 4-31G** QMEP minus electrostatic potential floating valence 4-31G** PD charges: (a) *yz* plane, (b) *xz* plane. Potential values in kcal/mol and distances are in angstroms.

stead of one. A core charge was associated with each atom; its value was the proton charge minus the charge of core electrons. Next, a valence charge was defined; its value was the static partial charge for the atom minus the core charge. For example, an oxygen atom which had a static PD charge of -0.8 would have a core charge of $+6.0$ (eight protons minus two $1s$ core electrons) and a valence charge of -6.8. This valence charge was allowed to "float," which means that its position was allowed to vary relative to the core charge to give the best possible fit to the quantum-mechanical molecular potential. As in previous calculations, SAS NLIN (Ref. 7) was used to accomplish the fitting procedure; it was found that residuals were reduced by approximately a factor of 4 as compared to the PD atom charges. The displacements of the valence charges from their associated cores for urea and thiourea as well as plots illustrating the difference between 4-31G** the quantum-mechanical potential and the floating-valence model for both molecules were made. Two representative plots showing these differences for thiourea are shown in Figs. 6(a) and 6(b). A comparison of these plots with the previous PD difference plots clearly demonstrates a significant improvement in fitting the quantum-mechanical potential by using the floating-valence model.

One major advantage of the floating-valence model is its ability to fit the electronic potential of a vibrating molecule. The core charges were constrained to move as indicated by the vibrational-mode pattern, while the displacement magnitude and direction of the floating-valence charges were free to vary to best minimize the difference between the quantum-mechanical potential and the Coulomb potential resulting from the point charges. With this method, it was demonstrated that dynamic potentials could be fit to the same degree of accuracy as were the static potentials.

The difference between the floating-valence-charge model and the single atomic partial charge model was evident in graphical depictions of the core and valence charge displacements during a vibrational mode. These displacements for a symmetric planar mode of thiourea are shown in Fig. 7. Since this is a symmetric mode, the displacements for $N(2)$, H(3), and H(4) are omitted. The core and valence-charge displacements for each atom are drawn originating from the same point to emphasize the differences in directions, except that when both displacements are nearly colinear, they have been shifted for clarity. The results clearly demonstrated that the core and valence charges do not have the same displacements during a molecular vibration. The differences are small for the chalcogen, carbon, and nitrogen atoms, but they are quite marked in the hydrogen atoms. These results support conclusions which we have inferred from the work of Rath and Wolfram[19] and explain the problems with hydrogenic modes in IETS intensity analyses. One conclusion is that a single point charge located at the nucleus is a reasonable approximation for heavier atoms; however, it does not accurately model the electrostatic potential of a vibrating hydrogen atom.

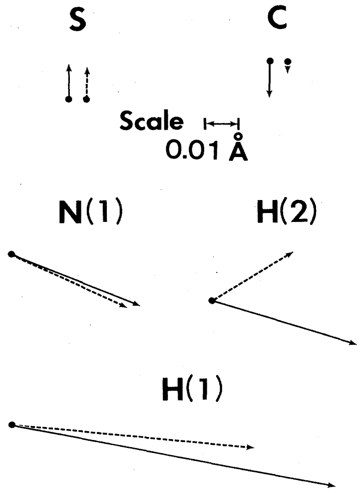

FIG. 7. Core (——) and valence (— — —) charge displacements for the symmetric in-plane mode of thiourea at 92.2 meV.

VI. CONCLUSIONS

The partial charges for urea and thiourea have been calculated using a variety of Gaussian basis sets. The concept of basis-set scaling factors were examined; they work reasonably well for urea, but the concept was not valid for thiourea. Evaluation of the effects of a vibrational mode on the calculated partial charges revealed that the PD charges varied by 10% to 15% during a vibrational excitation. It was concluded that the use of a single point charge was not sufficiently accurate to model each atom for IETS applications. Much better fits to the equilibrium and vibrational-mode potentials of the molecules were obtained when each atom was modeled with two point charges—one for the core and one for the valence electrons. Within this model the core and valence electron charges do not displace in the same direction, especially for hydrogen atoms. In the following paper[3] it is shown that tunneling intensities for thiourea calculated with core and valence electron displacements are in considerably better agreement with experimental values than are those calculated using a single point charge on each atom.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Lindsay Duncan for graciously providing us with a copy of his calculated vibrational displacements for urea and Rosalie G. Tompson for useful discussions. Work supported in part by the U.S. Army Research Office, the U.S. Office of Naval Research, and Martin Marietta Corporation under Contract No. N0014-80-C-0718. One of us (C.D.C.) was supported in part by National Science Foundation Nos. Grants SPI-80-19153, SPI-81-66360, and SPE-82-64085.

[1] Frank A. Momany, J. Phys. Chem. **82**, 592 (1978).

[2] S. R. Cox and D. E. Williams, J. Comput. Phys. **2**, 304 (1981).

[3] C. D. Crowder, H. W. White, and G. P. Alldredge, following paper, Phys. Rev. **31**, 6685 (1985).

[4] P. N. van Kampen, F. A. A. M. de Leeuw, G. F. Smits, and C. Altona, Quantum Chemistry Program Exchange (Chemistry Department, Indiana University, Bloomington, Indiana 47405) **13**, 437 (1982).

[5] F. Albert Cotton and Geoffrey Wilkinson, *Advanced Inorganic Chemistry,* 2nd ed. (Wiley, London, 1966), p. 120.

[6] J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969), p. 357.

[7] J. H. Goodnight and J. P. Sall, computer code SAS NLIN (SAS Institute Inc., Cary, NC, 1982). See also SAS User's Guide: Statistics, 1982 Edition, SAS Institute Inc., Cary, NC., p. 584.

[8] J. E. Worsham, H. A. Levy, and S. W. Peterson, Acta Crystallogr. **10**, 319 (1957).

[9] N. R. Kunchur and M. R. Truter, J. Chem. Soc. **1958**, 2551 (1958).

[10] W. D. Kumler and G. M. Fohlen, J. Am. Chem. Soc. **64**, 1944 (1942).

[11] J. L. Duncan, Spectrochim. Acta, Part A **27**, 1197 (1971).

[12] J. L. Duncan (private communication).

[13] G. B. Aitken, J. L. Duncan, and G. P. McQuillan, J. Chem. Soc. A 2695 (1971).

[14] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, Columbra Curran, and J. V. Quagliano, J. Am. Chem. Soc. **80**, 527 (1958).

[15] D. Hadzi, J. Kidric, Z. V. Knezevic, and B. Barlic, Spectrochim. Acta, Part A **32**, 693 (1976).

[16] P. Bleckmann, B. Schrader, and W. Meier, Ber. Bunsenges. Phys. Chem. **75**, 1279 (1971).

[17] D. F. McIntosh and M. R. Peterson, Quantum Chemistry Program Exchange (Chemistry Department, Indiana University, Bloomington, Indiana 47405) **11**, 342 (1977).

[18] John Kirtly, D. J. Scalapino, and P. K. Hansma, Phys. Rev. B **14**, 3177 (1976).

[19] J. Rath and T. Wolfram, in *Inelastic Electron Tunneling Spectroscopy,* edited by T. Wolfram (Springer, Berlin, 1978), pp. 92—102.