Polarizabilities of Organic Ions

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Dear Sir

Polarizabilities of Organic Ions

Organic ion polarizabilities are necessary as input information to model the long- and intermediate-range interactions[1,2] of gas phase singly-charged ions. Ionic polarizabilities are particularly important in describing potential energies of interaction between singly charged $[AB]^+ + [CD]^+$ products formed in reactions of $[AB]^{2+}$ with CD. Transfer of an electron from CD to $[AB]^{2+}$ occurs in these doubly-charged ion reactions when reactant and product system potential energy curves cross. Ionic polarizabilities are used in the calculations of product potential energies given by:[3] $(e^2/R) - e^2[\alpha([AB]^+) + \alpha([CD]^+)]/2R^4 - \Delta E$, where R is the ion–ion separation distance, ΔE is the energy defect of reaction, and α refers to the polarizabilities of $[AB]^+$ and $[CD]^+$ ions, respectively. However, very little information is available on the polarizabilities of gaseous organic ions. We wish to point out the applicability of a self-consistent molecular orbital method, MNDO, developed by Dewar and co-workers[4-8] and made available through QCPE,[9] for the computation of organic ion polarizabilities.

In the MNDO formalism, valence shell electrons are assumed to move in the field of a fixed core of nuclei and inner shell electrons. Molecular as well as ionic geometries are found by minimizing the energy with respect to all geometric variables. The leading terms in the expansion for the change in energy δE of a molecule in an electric field F are $\{(\delta E/\delta F)F + (\delta^2 E/\delta F^2)F^2 + \ldots\}$ where $(\delta E/\delta F)$ is given by μ, and the polarizability α is denoted by the change in dipole moment μ induced by the field $(\delta\mu/\delta F)$ and given by $(\delta^2 E/\delta F^2)$.[8] Polarizabilities for geometry-optimized structures are determined from energies of polarization calculated by placing the structure in a uniform external electric field.[8] Diagonal terms in the polarizability matrix are determined from differences between the zero field energy and energies computed when the molecular axis is aligned with the field. Off-diagonal terms in the polarizability matrix are determined from energy differences computed for various orientations in the field. Diagonalization of the polarizability matrix gives α_{xx}, α_{yy} and α_{zz}. The MNDO minimum basis set treatment underestimates contributions of non-valence shell electrons to the polarization. This deficiency has been corrected by the automatic addition of isotropic atomic polarizability contributions to the molecular polarizability components, from which average molecular polarizabilities α are obtained.

The utility of the MNDO method can be assessed by comparing experimental molecular polarizabilities with values predicted from MNDO computations. Calculated MNDO polarizabilities, given in the first column of Table 1, compare favorably (2% average deviation) with the experimental polarizabilities listed for a range of common organic compounds. Predicted values are generally slightly less or equal to the experimental results, with a 0.20-$Å^3$ deviation for ethanal being the widest discrepancy for the nine organic molecules listed in Table 1. These results lend support to the MNDO computational method for polarizabilities. The third column of Table 1 lists polarizabilities for the nine molecular ions, which are observed to be slightly larger than polarizabilities computed for the respective neutral molecules. Average polarizabilities have been

Table 1. Polarizabilities of organic molecules and molecular ions

System	Molecular polarizability (10^{-24} cm³)		Molecular ion polarizability (10^{-24} cm³)
	Calculated	Experimental[a]	Calculated
C_2H_6	4.37	4.47	5.17
C_3H_8	6.24	6.23	7.38
CH_3OH	3.14	3.31	3.88
C_2H_5OH	5.01	5.06	5.97
CH_3CHO	4.39	4.59	4.53
CH_3CN	4.24	4.40	6.06
C_4H_5N (pyrrole)	7.94	7.94	8.16
C_4H_4O (furan)	7.11	7.23	7.51
C_6H_6 (benzene)	10.19	10.33	10.50

[a] Experimental values are given by: N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc.* (*London*) *Ser.* **A295**, 334 (1966); E. R. Lippincott, G. Nagarajan and J. M. Stutman, *J. Phys. Chem.* **70**, 78 (1966); C. G. LeFevre, R. J. W. LeFevre, B. P. Ras and M. R. Smith, *J. Chem. Soc.* 1188 (1959); *and Ref. 8.*

Table 2. Comparison of bond distances for neutral and singly-charged ethanol
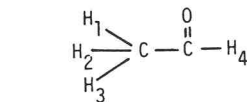
Bond	Bond distances (Å)	
	Neutral	Molecular ion
H_1—C	1.107	1.107
H_2—C	1.109	1.111
H_3—C	1.109	1.111
C—C	1.516	1.537
C—O	1.221	1.233
H_4—C	1.112	1.125

related to the approximate magnitudes of molecular volumes,[2,10] and as shown in Table 1 the ion polarizabilities are slightly larger than those for the respective molecules. Comparisons of neutral and ionic bond distances in a typical molecule, ethanal, in Table 2 illustrate a slight expansion of the molecular entity upon removal of one electron. This expansion of the molecule upon ionization is a general feature of the systems illustrated in Table 1, where polarization volumes tend to increase slightly in going from neutral to ion.

Yours

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