Ionization Surfaces for Small Molecules

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An *ab initio* molecular orbital method is used to calculate total ionization cross sections for small molecules as a function of the projectile electron−molecule orientation. Calculations over many angles are used to construct three-dimensional ionization surfaces for molecules, such that, if an electron penetrates the surface, ionization follows. Total ionization cross sections deduced by averaging over the positive and negative Cartesian coordinates and from the volume enclosed by the ionization surface are compared to experimental values and those calculated from the binary-encounter-Bethe method and the additivity method of Deutsch and Märk. Good agreement between the orientation-averaged cross section, experiment, and other theories, and between the calculated and experimental steric factor for the total ionization of CH_3Cl supports the concept of orientation dependence for the electron impact ionization probability.

Introduction

In a recent paper we described an *ab initio* quantum mechanical method for the calculation of maximum ionization cross sections for atoms and small molecules.[1] An extensive comparison of the cross sections calculated using this approach was made with the more sophisticated binary-encounter-Bethe (BEB) method[2,3] and the additivity method of Deutsch and Märk (DM).[4,5] Although the quantum method does not predict the variation of cross section with electron impact energy available with the BEB and DM methods, the cross section can be readily calculated as a function of the projectile electron−target molecule orientation. A recent cross-particle beam experiment has shown that the cross section for electron impact ionization of several symmetric top molecules is dependent on the electron−molecule orientation.[6,7] For example, the ratio of molecular ion formation, CH_3Cl^+, for collisions of electrons on the CH_3-end of the CH_3Cl molecule was 2.6 times higher than that for collisions on the Cl-end of the molecule, while for total ionization this ratio is close to 1.6. This suggests that molecules exhibit a shape with respect to electron impact ionization. In this communication we have used the quantum method to calculate these shapes for the total ionization of several small molecules, including CH_3Cl. The three-dimensional shapes which emerge from the computations represent a molecular ionization volume, ionization occurring when the projectile electron penetrates the surface.

Method and Results

The quantum method is based on a simple Coulomb model which assumes that ionization occurs when the increasing Coulomb potential experienced by a molecule due to the electric field of an approaching electron matches the ionization potential of the molecule.[7,8] Standard quantum mechanical packages such as *Gaussian 94*[9] allow the calculation of the energy of a molecule in the presence of a point-charge electric field. The position of the point-charge can be varied with respect to the molecular orientation in the geometry input. In order to treat the ionization process, the relative orientation of the projectile electron with respect to the target molecule is specified, leading to the maximum cross section as a function of the direction of approach. Repeating the calculation over a wide range of orientations allows an ionization surface to be constructed, effectively showing the “shape” of the electron impact ionization cross section.

Calculations were carried out using *Gaussian 94*[9] at the HF/6-31G* level, unless otherwise specified. Earlier work on CO, H_2O, and the inert gases showed that the method is relatively insensitive to the level of theory or the basis set used in the molecular orbital calculations.[1] The molecular geometry is optimized and the vertical ionization potential calculated. This is taken as the difference in energy of the positive ion at the geometry of the neutral and the zero-point energy of the neutral molecule. A “critical energy”, the energy of the electron−molecule system at which ionization occurs, is then determined from the neutral energy plus the Coulomb potential due to the electron at the critical impact parameter or, since the Coulomb potential at ionization is equal to the ionization potential of the molecule,

$$E_c = E_0 - \mathrm{IP} \qquad (1)$$

where E_c is the critical energy, E_0 is the neutral energy, and IP is the ionization potential. A series of single-point energy calculations are carried out on the neutral molecule in the presence of a charge distribution consisting of a single electron. Initially, the electron−molecule separation at which ionization occurs is estimated. The radial distance r of the electron from the center of mass of the molecule is then varied to obtain an energy equal to the critical energy defined above. When the critical separation r has been determined by this procedure, the electron impact ionization cross section for the orientation under consideration is given by

$$\sigma = \pi r^2 \qquad (2)$$

In general, measurements of electron impact ionization cross sections are carried out on randomly oriented molecules in the gas phase, so that the total ionization cross section is given by the average over all possible relative orientations of the molecule with respect to the electron. The input for the *Gaussian 94* calculations requires that the charge distribution be entered in Cartesian coordinates. A convenient approximate total cross section can therefore be found using the present method by averaging the cross sections for approach along each of the positive and negative Cartesian axes.

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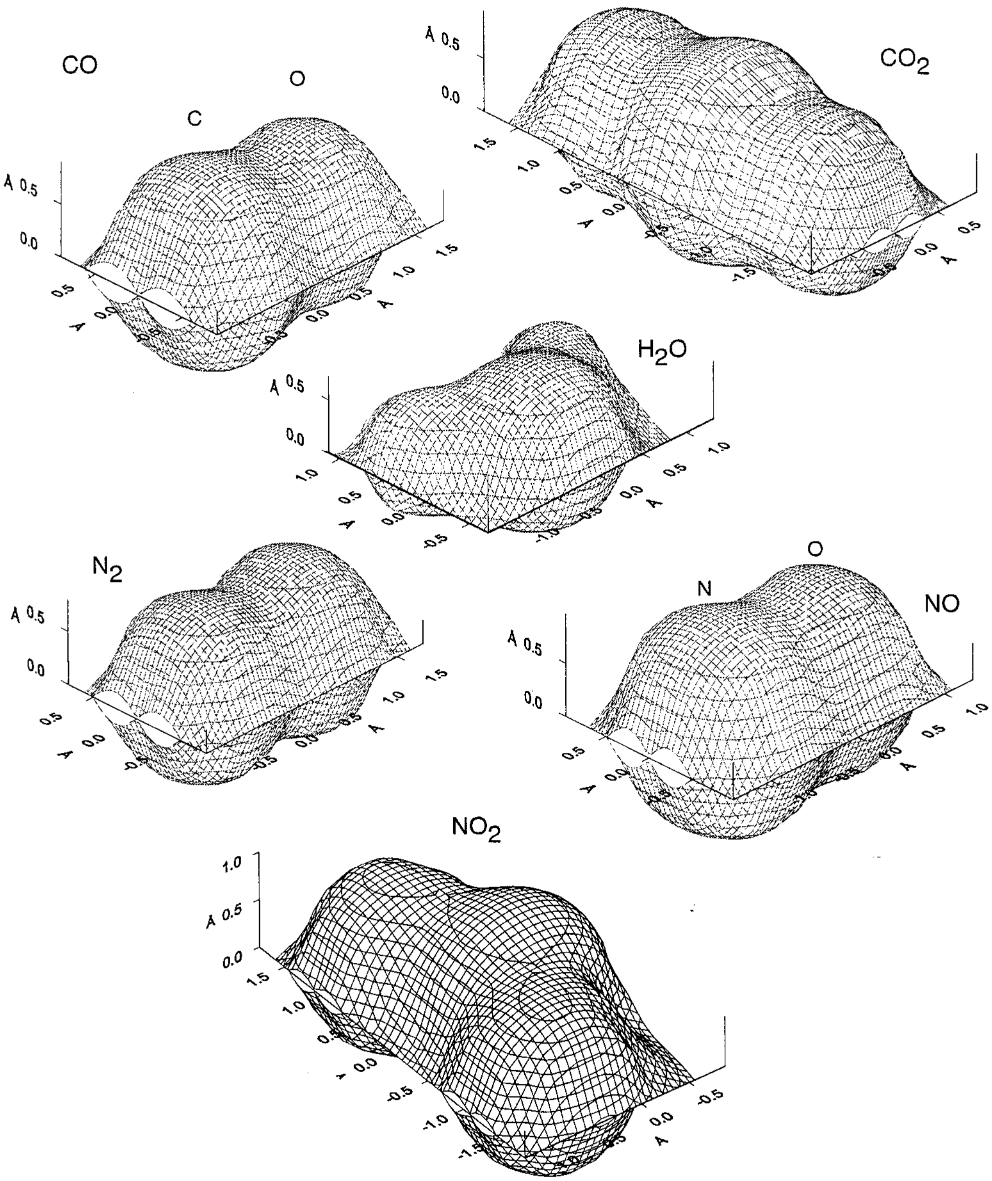

Figure 1. Ionization surfaces for CO, CO_2, H_2O, N_2, NO, and NO_2. Scales are critical distances in angstrom units calculated from the center-of-mass.

$$\sigma = 1/6[\sigma_{+x} + \sigma_{-x} + \sigma_{+y} + \sigma_{-y} + \sigma_{+z} + \sigma_{-z}] \qquad (3)$$

The cross section can be calculated assuming the energy of the projectile electron is equal to the Hartree–Fock ionization potential. Although the calculated ionization potentials are usually within 10% of the "best" experimental values, experimental ionization potentials may be used in place of the calculated values in order to determine the critical energy. An experimental ionization potential that is higher than the calculated value leads to a decrease in the calculated cross section and, vice versa, for the case where the experimental ionization potential is smaller. This is intuitively correct, since according to the model the molecule requires a closer approach of the electron (larger Coulomb potential) in order to overcome the larger barrier to ionization. The Cartesian-averaged cross section is in good accord with experimental measurements for molecules such as diatomics, nonlinear triatomics, NH_3, CH_4, and substituted methanes, which can all be regarded as roughly spherical. For rod-shaped molecules, such as CO_2 and N_2O, the cross section averaged in this way is overestimated as too much weight is afforded the larger cross section components for end-on approach.

If the critical separation is determined for a large number of relative geometries of the electron and molecule, it is possible to obtain a three-dimensional picture of the probability of ionization as a function of the orientation of the molecule. Effectively, the idea of an ionization cross section, the area the target molecule presents to the electron, is extended to a three-dimensional object defined by the critical distances, with ionization occurring when the electron penetrates the surface enclosing this volume. Ionization surfaces have been calculated for several of the molecules previously considered and are shown in Figure 1. The graphs were produced using the *Surfer* graphics package.[10] Because *Surfer* can only plot single-valued functions, the complete closed ionization surfaces had to be constructed from two separate plots. In the case of molecules such as CH_3F, CH_3Cl, and NH_3, the total surfaces are time consuming to generate in this way and this has been done only for CH_3F in Figure 2. The relative cross sections presented to an electron attacking from either end of the dipole are readily plotted and this is illustrated for CH_3Cl in Figure 2. The ionization surfaces shown in Figures 1 and 2 will be energy dependent. Experiments have shown that the ratio of the ionization cross section for the positive end to the negative end

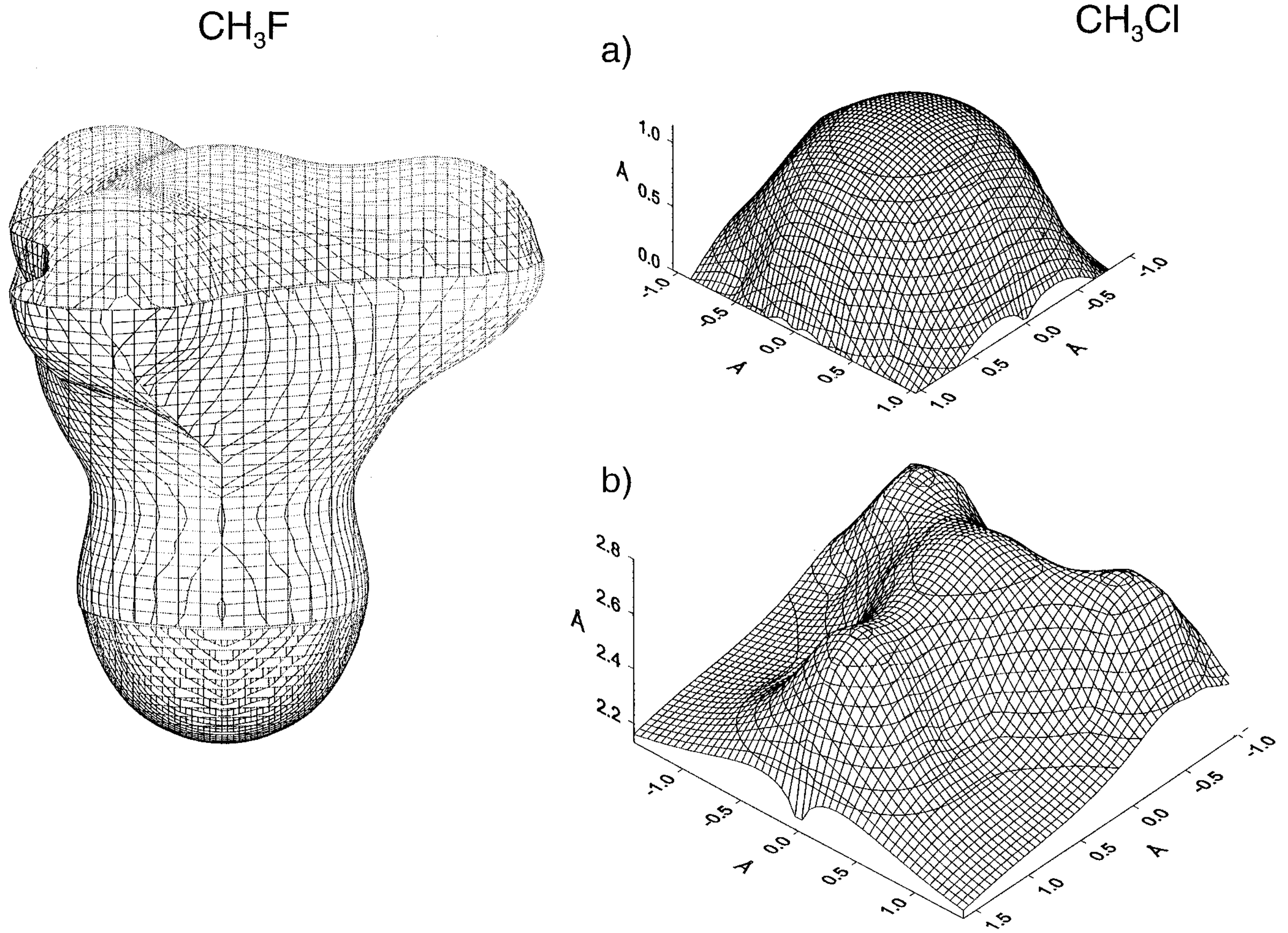

Figure 2. Ionization surface for CH_3F and for CH_3Cl: (a) from the Cl-end of the molecule and (b) from the CH_3-end of the molecule.

for CH_3Cl decreases by ~14% over the electron energy range from 240 to 100 eV.[11] The shapes shown in the figures represent the maximum ionization cross section, corresponding to electron energies in the range 80−100 eV for most molecules. As the electron energy decreases toward the ionization threshold and the electron wavelength increases to molecular dimensions, the ionization surfaces would smoothly lose their shapes, transforming to spherical symmetry and shrinking toward the threshold. Conversely, as the electron energy increases above the maximum in the ionization efficiency curve, the shapes shown in the figures would sharpen up slightly, as the electron wavelength decreases below the dimensions of the atomic orbitals.

The volume enclosed by the electron impact ionization surface may be used to obtain an estimate for the cross section which assumes that the molecule is spherical.

$$\sigma = \pi r^2 = \pi\left(\frac{3V}{4\pi}\right)^{2/3} \tag{4}$$

Volumes were determined using the Trapezoidal Rule, Simpsons's rule, and Simpson's $^3/_8$.[12] The difference between the values determined by these methods was negligible. The cross sections determined in this way are compared with those deduced from averaging over Cartesian coordinates, BEB and DM calculations, and literature experimental measurements in Table 1. The volume-averaging method gives a marked improvement in the calculated cross section for CO_2, consistent with the idea that the poor performance of Cartesian averaging is due to the large departure from a spherical shape for this molecule. Improved agreement with experiment was also obtained for NH_3, and for H_2O if the lower experimental value is correct, which seems likely since the cross section of O_2 is less than 3 Å^2 and H_2O would be expected to have a smaller cross section than that of O_2. In most cases, the difference in the cross sections calculated by the two methods was small, indicating that averaging the values obtained for approach along each of the positive and negative Cartesian axes does give a reasonable estimate of the cross section.

TABLE 1: Experimental and Theoretical Maximum Total Ionization Cross Sections for Small Molecules

	maximum total ionization cross section/Å^2				
molecule	volume averaged	cartesian averaged	exptl[a]	BEB	DM
N_2	2.82	2.40	2.53[13]	2.52	2.90
CO	3.13	2.91	2.05[b]−2.66[13−16]	2.53	3.31
CO_2	4.00	5.61	2.05,[14c] 3.27,[15] 3.55[13]	3.57	4.51
NO	3.62	3.42	3.15[13]	2.54	2.64
NO_2	4.23	5.30		3.69	4.02
H_2O	2.09	2.42	2.05,[17] 4.40[16d]	2.25	2.38
NH_3	3.47	3.58	2.4[c]−3.01[18−21]	2.96	3.31
CH_3F	4.13	3.41	3.72[22]	3.64	4.99
CH_3Cl	5.57	5.76	6.91[22]	5.06	7.53

[a] Where a range of literature values is available, only the extreme values are shown in the table. [b] For CO, it is likely that the true cross section lies close to the maximum value in the range. The dipole moment of CO is small and the polarizability of the CO molecule is slightly higher than that for isoelectronic N_2. [c] Values of 2.05 Å^2 for CO_2 and the lower end of the range for NH_3 are not consistent with the values for other molecules of similar physical properties. [d] Value of 4.40 Å^2 for H_2O is unlikely, the cross section for O_2 is less than 3 Å^2 and H_2O would be expected to exhibit a lower cross section than that of O_2.

Conclusion

The experimental study of the effect of orientation on electron impact ionization showed that for dipolar molecules electron impact ionization is more probable at the positive end of the dipole. This follows from simple electrostatics, since this end of the dipole presents a small positive charge to the projectile electron. These calculations qualitatively reproduce this observation, with the plots clearly showing a larger volume of ionization at the positive ends of dipolar molecules such as CO, NO, CH_3F, and CH_3Cl. The ionization surfaces also show that cross sections are strongly dependent on molecular orientation, with distinct "spheres of ionization" centered on each atom. The additivity rules, which reproduce the energy dependence of the ionization cross section with a fair degree of success, represent the molecular cross section as the sum of the cross sections of the constituent atoms. According to the quantum calculations, represented graphically in Figures 1 and 2, this is very close to the true case, supporting one of the fundamental assumptions implicit in many current theories for the calculation of molecular electron impact ionization cross sections.

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