PHYSICAL REVIEW A, **66**, 034701 (2002)

Molecular shape and the Bragg rule

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(Received 2 April 2002; published 5 September 2002)

To elucidate the effects of overall molecular shape upon the electronic response properties of molecules and nanoclusters we recently have considered various jellium cluster models for the mean excitation energy. Here we apply similar models to investigate the influence of gross molecular shape on Bragg's rule. We find a direct way of expressing deviations entirely in terms of geometrical features of the molecule and its constituent atoms.

DOI: 10.1103/PhysRevA.66.034701 PACS number(s): 34.50.Bw, 33.90.+h

I. INTRODUCTION

In a recent series of papers [1–6], we have related differences in molecular shape to changes in molecular response properties by considering molecules to be represented by sharp boundaried ellipsoids filled with uniform density jellium. These ellipsoids are constructed from a volume determined by atomic van der Waals radii filled with the appropriate number of electrons. Such a simplified model has proved remarkably useful in the prediction of trends in properties that depend upon the excitation properties of the molecule under consideration.

One property that has proved to provide fruitful ground for this model is the stopping power of molecular targets. The stopping power, or linear energy loss, measures the amount of energy deposited in a target by a projectile of velocity v, and is related to a stopping cross section, S, by the density of scattering centers (N) as

$$-\frac{dE(v)}{dx}=NS(v). \tag{1}$$

As the number of possible molecules is vastly greater than the number of atoms, it has been hoped since the earliest days of stopping power measurements that the stopping power of a molecular target could be obtained from that of its constituents, either atoms or molecular fragments [7]. An early expression of this is the Bragg or Bragg-Kleeman rule [8]

$$S_{molecule}=\sum_i f_i S_i(v), \tag{2}$$

where the sum runs over all types of constituent atoms or fragments. Here, S_i is the stopping cross section of the f_i fragments (atoms) of type i in the molecule.

A rule of this type will clearly only be satisfied approximately, and various studies [7,9–17] have shown that deviations from Bragg's rule of up to several tens of percent are not uncommon, depending on the target molecule and experimental circumstances, especially the projectile velocity. Clearly the largest deviations from the Bragg rule can be expected in cases where the molecular electronic excitation spectrum deviates most from that of the constituent atoms and at projectile velocities that produce these excitations.

The purpose of this contribution is to consider the Bragg rule and to predict deviations from it, based on the jellium-filled-ellipsoid model.

II. SHAPE AND DENSITY EFFECTS IN BRAGG'S RULE

In the spirit of Bragg's rule [8] we write the total stopping cross section $S(v)$ for a molecule composed of T different constituent types as

$$S_B(v)=\sum_{i=1}^{T} f_i S_i(v), \tag{3}$$

where f_i is the number of atoms or fragments of kind *i* and $S_i(v)$ the stopping cross section for atom or fragment *i*. For $S_i(v)$ we will use the explicit Bethe form

$$S_i(v)=S_o N_i \ln\frac{2mv^2}{I_i}, \tag{4}$$

where

$$S_o=\frac{4\pi}{mv^2}\left(\frac{Z_1 e^2}{4\pi\epsilon_o}\right)^2 \tag{5}$$

and N_i is the number of electrons associated with the fragment or atom of type *i* with characteristic excitation energy

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1050-2947/2002/66(3)/034701(4)/$20.00

scale I_i, to be specified below. Since we are interested in deviations from Bragg's rule, we introduce

$$D \equiv 2[S(v)-S_B(v)]/N_M S_o, \tag{6}$$

$$=2\left[S(v)-\sum_{i=1}^{T} f_i S_i(v)\right] \bigg/ N_M S_o, \tag{7}$$

where

$$N_M=\sum_{i=1}^{T} f_i N_i \tag{8}$$

is the total number of electrons on the molecule and S_o, defined above, sets the scale of the stopping cross section (8×10^{-15} eV cm^2 for $Z_1=1$ and v being the projectile velocity).

We now introduce a specific form for the mean excitation energy, I_i, to illustrate the density and shape influence for deviations from Bragg's rule, i.e., D as defined in Eq. (7). In a previous publication [1] we have shown that a good predictor for I_i is

$$I_i=\sqrt{n_i}\hbar\omega_p^i, \tag{9}$$

where $\omega_p^i=\sqrt{4\pi\rho_i}$ is the plasma frequency of the system (in units of $e^2\rho_i/m\epsilon_0$) which in general scales as the root of the density ρ_i and n_i is a general shape factor (depolarization factor, $0\leqslant n_i\leqslant 1$) for a jellium blob representation of constituant i. For oblate and prolate spheroids those factors are [18,19]

$$n^{(z)}=\frac{1+e^2}{e^3}[e-\arctan(e)], \tag{10}$$

$$n^{(z)}=\frac{1-e^2}{e^3}\left(\ln\sqrt{\frac{1+e}{1-e}}-e\right), \tag{11}$$

where the eccentricity e is defined as

$$e=\frac{1}{c}\sqrt{|a^2-c^2|} \tag{12}$$

for a spheroid with major and minor axes c, a. In this way we can represent anything from particles to solids. Notice that the index on the depolarization factor above does not index a particular constituent or atom but instead denotes a specific axis corresponding to the one of an applied electric field, and that in general $n^{(x)}+n^{(y)}+n^{(z)}=1$. Since we consider only systems with rotational symmetry about the c axis, i.e., those that have $a=b$, $n^{(x)}=n^{(y)}$ are determined by $n^{(z)}=n$. Below, indices on n will refer to fragments.

Equation (7) can now be rewritten in the following form separating density and shape dependent contributions to the deviation from Bragg's rule:

$$D=2\ln\prod_{i=1}^{T}\left(\frac{I_i}{I_M}\right)^{q_i}\equiv D_d+D_s, \tag{13}$$

where inserting the explicit form of $I_i\propto\sqrt{\rho_i n_i}$,

$$D_d=\ln\prod_{i=1}^{T}\left(\frac{\rho_i}{\rho_M}\right)^{q_i}=\sum_{i=1}^{T} q_i\ln(\rho_i/\rho_M) \tag{14}$$

and

$$D_s=\ln\prod_{i=1}^{T}\left(\frac{n_i}{n_M}\right)^{q_i}=\sum_{i=1}^{T} q_i\ln(n_i/n_M). \tag{15}$$

Here, M denotes quantities characteristic of the molecule as a whole, and we have defined a new variable $q_i=f_iN_i/N_M$ (where $\Sigma_{i=1}^{T}q_i=1$) measuring the contributing fraction of electrons from each type of atom, i.e., $q_1=1$ if we only have atoms of one kind. To arrive at the equations above we have also written $S(v)$ for the whole molecule on the Bethe form reflected in Eq. (4) above:

$$S(v)=S_oN_M\ln\frac{2mv^2}{I_M} \tag{16}$$

with $I_M\propto\sqrt{\rho_M n_M}$.

To analyze our results we will make some general observations first before considering the specific example of a homonuclear diatomic molecule. If the new molecule has the same electron density as that of the constituents, $D_d=0$, as it should. On the other hand, if the shape of the resulting molecule is the same as that of its constituents, that is, the eccentricity does not change (although the size may), then $D_s=0$. Since in general $n_z=1/3$ (atoms are spherical), the shape deviation relates to how far n_M is from 1/3. Notice furthermore that adding identical atoms (A) $D_d=\ln(\rho_A/\rho_M)$ and $D_s=\ln(n_A/n_M)$.

Let us now assume we add two (spherical) atoms (A and B) to form our molecule (M). Then

$$D_d=\ln\frac{\rho_A^{q_A}\rho_B^{q_B}}{\rho_M} \tag{17}$$

and

$$D_s=\ln\frac{n_A^{q_A}n_B^{q_B}}{n_M}=-\ln 3n_M \tag{18}$$

since $q_A+q_B=1$. If we assume the atoms are identical and have radius R and the resulting molecular spheroid has minor and major axes a and c, respectively, we can express Eqs. (17) and (18) entirely in terms of geometry alone,

$$D_d=\ln\frac{V_M}{2V_A}=\ln\frac{ca^2}{2R^3} \tag{19}$$

and

$$D_s=-\ln 3n_M\approx\alpha_{o,p}e^2. \tag{20}$$

Note that this formulation eliminates the dependence of the deviation from the Bragg rule on the projectile velocity.

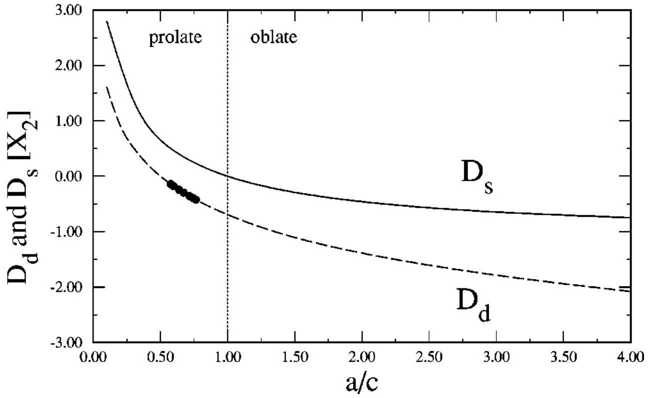

FIG. 1. Deviation from Bragg's rule due to shape (D_s) and density (D_d) changes as a function of geometry (a/c) when forming a homonuclear diatomic molecule. The dots represent Li_2, I_2, Se_2, F_2, O_2, N_2, and H_2 in increasing a/c order.

If we expand D_s to first order in e^2, the coefficients for oblate and prolate spheroids are, respectively, $\alpha_o = 3/16 = -2\alpha_p$. Thus if the volume increases D_d is positive. If the molecular volume $V_M = 2V_A(1+\delta)$, $D_d \simeq \delta$ is a direct measure of the relative volume change. For a prolate molecule D_s is positive and it is negative for an oblate resulting shape. For small devations from the spherical shape, the shape deviation is proportional to the squared eccentricity as indicated. Also since $0 \leqslant n_M \leqslant 1$, D_s is bounded from below by $-\ln 3$.

Figure 1 shows D_s and D_d as functions of the ratio a/c. It is clear from the figure that density chances have a larger influence on deviations from the Bragg rule than do shape variations, but the differences are factors rather than orders of magnitude.

We see that for reasonable changes in shape there can be quite substantial deviations from the Bragg rule. For comparison, we include D_s [Eq. (20)] and D_d [Eq. (19)] calculated for the homonuclear diatomics Li_2, I_2, Se_2, F_2, O_2, N_2, and H_2. In these cases, c is calculated from the bond length [20] plus twice the van der Waals radius [21] of the atom, and $a = b$ is the van der Waals radius, as done previously [1]. In all these cases, the resulting diatomic molecule is prolate, and $D_s, D_d < 1$.

It is difficult to get experimental data with which to compare, as the stopping for atomic targets is hard to measure. However, a careful theoretical study by Zeiss *et al.* [22] has reported atomic and molecular mean excitation energies calculated from the dipole oscillator strength distributions for H, N, and O, as well as for their diatomics. Since the atomic and molecular data are calculated using the same methods, they may be compared, and one need not worry about methodological differences skewing the conclusions.

Using the mean excitation energy form of the Bragg rule, to wit

$$\ln I_{molecule} = \frac{1}{N} \sum_i N_i \ln I_i \tag{21}$$

one finds that deviations from fulfillment of the Bragg rule increase in the order $O < N < H$, which agrees with our prediction.

III. SUMMARY

We have analyzed deviations from the Bragg rule in using the jellium blob model that has previously been applied to other response properties of molecules. As in previous cases, we have found that the model predicts the trends in these response properties as functions of molecular shape, as loosely defined by bond distances, angles, and van der Waals radii. In the present case, we find that both differences in shape and in density contribute to deviations from the Bragg rule, and that more the eccentricity deviates from that of a sphere, the larger the deviation from the Bragg rule is.

ACKNOWLEDGMENTS

This work was supported in part by grants from the Office of Naval Research (Grant No. N0014-86-1-0707 to JRS) and the National Science Foundation (Grant No. CHE-9974385 to J.R.S.). S.P.A. acknowledges support from the Swedish Natural Science Research Council.

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