AN AB-INITIO CALCULATION OF THE COULOMB EXPLOSION OF N_2 AFTER HEAVY-ION BOMBARDMENT ☆

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Self-consistent-field calculations for the total potential energy of highly ionized N_2 molecules are presented. We compare these calculations to the experimentally observed energy released in the Coulomb explosion of ionized N_2 molecules created after collision with fast heavy ions. The most important electronic states of the fragment ions are determined.

After collision of fast Ar^{13+} ions with N_2 molecules, the Auger electrons of the separating nitrogen ions have recently been measured by Mann et al. [1]. For the transition $(1s2s2p)^4P$ (metastable) $\rightarrow 1s^2 + e^-$ of the nitrogen fragments they found a nearly rectangular line shape with a broadening, $\Delta E = (4.37 \pm 0.2)$ eV. They interpret this line form as a kinematic effect due to the Coulomb explosion of the molecule after ionization by the heavy-ion beam. The observed line width is directly connected with the total energy released by the molecular dissociation. Within a simple point charge model for the potential of the separating atoms of ionization of the second nitrogen atom was found [1] to be +3.7, assuming a charge of 4+ for the other atom. Using relativistic SCF molecular calculations [2] for the total potential energy curve of this system we are able to show that both atoms have the same ionicity, namely 4+. In addition, the specific states of the two ions after the ionization can be determined.

The molecule is calculated within an adiabatic relativistic LCAO-MO model with Slater's exchange approximation using numerical atomic Dirac–Fock–Slater wave functions as a basis. The potential energy curves have been estimated by calculating the statistical total system energy [3] for each configuration at each internuclear distance R. The "theoretical" (including numerical) errors are assumed to be in the order of 5 eV in the system considered here.

In fig. 1 three potential energy curves normalized to zero at infinity are shown. The dashed curves give the potential of point charges for the system N^{3+} – N^{4+} and N^{4+}–N^{4+}. As an example the full curve shows the potential energy of the SCF calculations for a symmetric N^{4+}–N^{4+} system with a molecular electronic configuration which is connected with the configurations $N^{4+}(1s2s^2)$–$N^{4+}(1s2s^2)$ in the separated ion limit. For large distances the full curve coincides with the N^{4+}–N^{4+} curve of the point charge model as expected. As the energy released by the system is directly connected with the line width due to the Doppler shifts of the emitted electrons we include this line broadening as the second ordinate in the figure.

For the bond distance of the neutral molecule, $R_0 = 2.07$ au, we have calculated the total energies of all realistic configurations of the system N^{4+}–N^{4+} as well as N^{4+}–N^{3+} and N^{4+}–N^{5+} combinations (table 1). We classify the molecular orbitals by the adiabatically corresponding quantum numbers of the asymptotic atomic orbitals. Astonishingly, the energies for the same ionization vary by nearly 60 eV which is equivalent to

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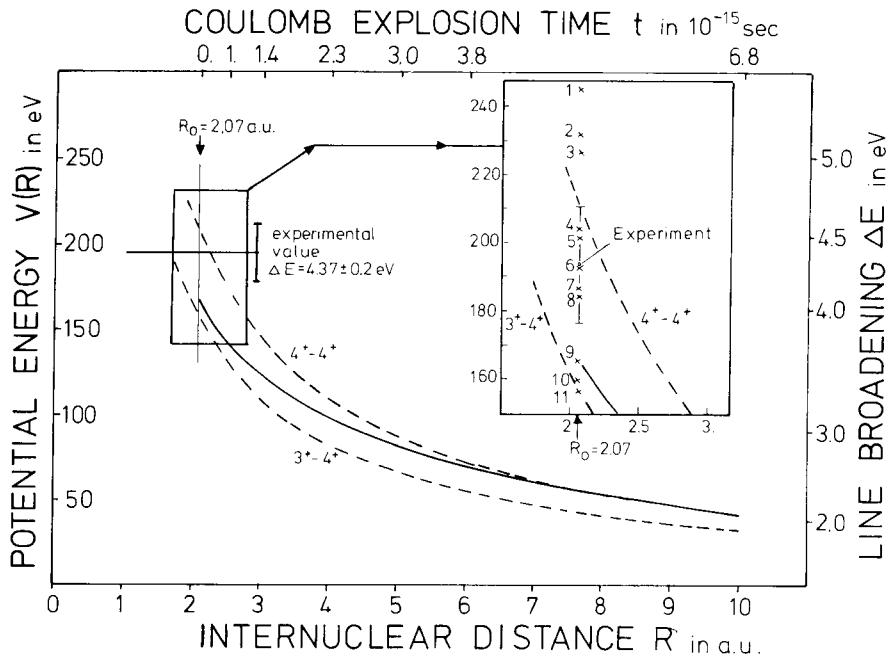

Fig. 1. Potential energy of a highly ionized N_2 molecule as function of the internuclear distance R during the Coulomb explosion. The dashed curves show a N^{4+}–N^{4+} and N^{3+}–N^{4+} system calculated within the point charge model. The full curve is the result of a SCF-calculation for a realistic $N^{4+}(1s2s^2)$–$N^{4+}(1s2s^2)$ system as an example. In the enlarged field we show the results for 11 configurations calculated for the normal molecular distance R_0 = 2.07 au. The descriptions of the configurations are given in table 1.

Table 1
Calculated values for the energy which will be released in the Coulomb explosion of highly ionized N_2 molecules. The molecular configurations are classified by the adiabatically corresponding quantum numbers of the asymptotic atomic orbitals which also will be the end product after Coulomb explosion. The numbers of the configurations are also given in fig. 1.

No.	Configuration		Energy (eV)
1	$N^{4+}(1s2s2p)$	– $N^{5+}(1s2s)$	245.7
2	$N^{4+}(1s2s2p)$	– $N^{5+}(1s^2)$	232.4
3	$N^{4+}(1s2p^2)$	– $N^{4+}(1s2p^2)$	227.7
4	$N^{4+}(1s2s2p)$	– $N^{4+}(1s2s2p)$	204.3
5	$N^{4+}(1s^22p)$	– $N^{4+}(1s2s2p)$	202.0
6	$N^{4+}(1s^22s)$	– $N^{4+}(1s^22s)$	193.8
7	$N^{4+}(1s^22s)$	– $N^{4+}(1s2s2p)$	187.3
8	$N^{4+}(1s2s^2)$	–$N^{4+}(1s2s2p)$	185.0
9	$N^{4+}(1s2s^2)$	– $N^{4+}(1s2s^2)$	165.7
10	$N^{4+}(1s^22p)$	– $N^{3+}(1s2s2p^2)$	160.4
11	$N^{4+}(1s2s2p)$	– $N^{3+}(1s2s2p^2)$	157.3

the difference of one charge within the point charge model. Only a small number of all possible configurations are within the experimental energy range. Of those considered in this work we find that only the configurations, which include the metastable 1s2s2p state in at least one of the ions reproduce the experimental line width (configurations 4, 5, 7 and 8 of table 1). Configuration 6 can be excluded since asymptotically no ^4P states can be created. Number 4 and 8 within the experimental error bars are very unlikely because they need to have 1s holes in both ions, simultaneously. This is very improbable because these configurations can only be created in the collision if the molecular axis is more or less parallel to the ion beam direction. The experimental measurements are done nearly perpendicular to the beam axis and as the events of such a Coulomb explosion have very little Doppler shift, they do not contribute to the observed line width. This discussion shows that configuration 5 and 7 will be the ones which are actually observed in the experiments.

The second abscissa on top of fig. 1 shows the time scale which is connected with the Coulomb explosion of the highly ionized system. One can see that the life time of the observed [1] metastable transition ($J \approx 10^{-9}$s) is many orders of magnitude larger than the dissociation time of the highly ionized molecule. On the other hand, if the molecule emits Auger electrons or X-rays with life times $J \lesssim 3 \times 10^{-15}$ they probably will be shifted and broadened [4] due to the molecular effects.

This work shows for the first time that an ab-initio calculation is able to extract detailed information of a highly ionized molecular system.

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