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AS MEASURED BY  $(e, 2e)$  EXPERIMENTS.

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## ELECTRON MOMENTUM DISTRIBUTION OF VALENCE STATES OF NH<sub>3</sub> AND THE 2σ<sub>g</sub> STATE OF N<sub>2</sub> AS MEASURED BY (e, 2e) EXPERIMENTS

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The (e,2e) coincidence method has been used to measure the momentum distributions of the outer electrons 3a<sub>1</sub>, 1e and 2a<sub>1</sub> of NH<sub>3</sub> and 2σ<sub>g</sub> of N<sub>2</sub> molecules in the gas phase. Results are reported and discussed after a short summary of the principles of the experiment.

The experimental determination of the electronic properties of molecules in the momentum space representation is a useful tool to study molecular properties and to judge the reliability of the computational methods employed for their calculation. Among these properties in this work we focus our attention on the electron momentum distribution (EMD) in simple molecules.

It has been first shown by our group [1], and confirmed in a series of papers [2] that the (e, 2e) technique offers a powerful method to directly measure the EMD. By (e, 2e) an impulsive ionization reaction is to be understood, induced by a fast electron, in which two fast electrons are ejected at large angles. The kinematics of the process is fully determined by detecting in coincidence these outgoing electrons after energy and direction analysis, and by knowing the direction and energy of the incoming electron. As already discussed elsewhere [1], the advantages of this technique over the more commonly used methods, such as Compton scattering [3] and position annihilation [4], consist in the possibility of measuring a non-integral EMD for separate one-electron orbitals provided that the energy resolution and the angular acceptances of the apparatus are good enough to distinguish different electronic

states and to determine a suitable momentum resolution.

This paper presents the results obtained for the three outermost orbitals of gaseous ammonia and for the 2σ<sub>g</sub> orbital of the N<sub>2</sub> molecule.

Before discussing the experimental results we briefly outline the connection between the (e, 2e) cross section and the EMD, which was more extensively treated in previous papers [1,2,5,6]. The (e, 2e) cross section, in the framework of the impulse approximation, and taking distortion effects into account, can be factorized as follows:

$$\frac{d^5\sigma}{d\Omega_1 d\Omega_2 dE_1} \propto \left(\frac{d^2\sigma}{d\Omega_1}\right)_{e,e} \rho_{\nu\lambda}(\bar{q}) k_{\nu\lambda}^I, \quad (1)$$

where  $(d^2\sigma/d\Omega_1)_{e,e}$  is the distorted electron-electron elastic cross section,  $\rho_{\nu\lambda}(\bar{q})$  is the squared Fourier transform of the spacial wavefunction of the bound electron in the  $(\nu\lambda)$  initial state (i.e. the EMD), and  $k_{\nu\lambda}^I$  is the probability of populating the  $I$ th ionic state by suddenly removing the  $(\nu\lambda)$  electron.

Experimental outcomings are: (i) energy spectra obtained by fixing angles and energies of the outgoing electron and varying the incident electron energy. In this way a set of peaks corresponding to the various se-

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paration energies of the observable ionic states is measured [2,5]; (ii) angular distributions obtained at constant values of the initial and final electron energies. In this way a particular ionic state can be selected and from the shape of the angular distribution the factor  $\rho_{\nu\lambda}(\bar{q})$  can be deduced according to expression (1).

The scattering apparatus used in this experiment has been described extensively elsewhere [7]. A monochromatic, well collimated electron beam is arranged to cross at right angles a gaseous beam in an  $\approx 2 \text{ mm}^2$  scattering volume. Two identical electron spectrometers, independently rotatable, are used to analyse the momentum of the outgoing electrons. They are formed by plane decelerating lenses, hemispherical electrostatic analyzers and channel electron detectors. The energy resolution can be varied by means of the lenses up to a minimum value of 3 eV (fwhm) for the coincidence peaks.

All the measurements were done in coplanar conditions, at equal kinetic energies and symmetrical scattering angles of the two final electrons. In this case only values of the momentum  $q$  of the bound electron parallel to the direction of the incoming electron are selected [8]. The incident electron energy was varied over a large range (400–1600 eV). The most significant data, at the intermediate energy of 800 eV will be here reported and discussed. In fact that by increasing the incoming electron energy, distortion effects become negligible, but the angular distribution shrinks making worse the momentum resolution [2,9]. At 800 eV the distortion effect can be still considered as a minor perturbation, hence the approximation used in deriving expression (1) is still valid; the momentum resolution is still good enough to permit a significant analysis of the data.

Energy spectra of  $\text{NH}_3$  (not reported here) have been taken at various angles [10]. Three main peaks interpreted as being due to the ejection of electrons from the  $3a_1$ ,  $1e$ ,  $2a_1$  orbitals are observed. They are centered respectively at  $11 \pm 1 \text{ eV}$ ,  $16 \pm 1 \text{ eV}$ ,  $28 \pm 1 \text{ eV}$  by experimentally referring to the Ne 2p level (IP = 21.6 eV). The last peak is quite large (about  $5 \pm 1 \text{ eV}$  fwhm) not in agreement with the previously quoted value of 2.6 eV [11]. Furthermore on the high energy side a broad tail is present up to about 20 eV from the center, as already found for other closed shell molecules [9,12].

The angular correlation spectra for the three main

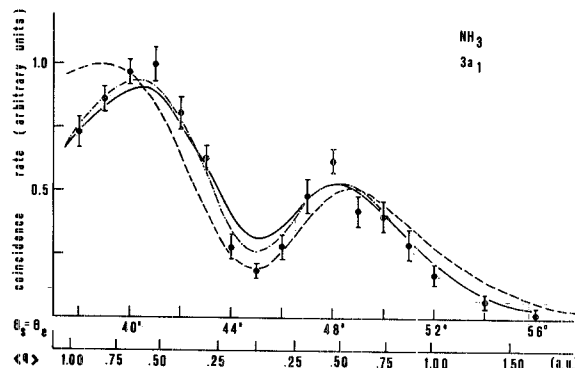


Fig. 1. Angular correlation for the  $3a_1$  orbital of ammonia. Measured coincidence rate is compared with theoretical shapes:  $3a_1$  ammonia orbital (full line) evaluated by Joshi's wavefunction [14] and DWIA ( $\bar{V} = 10 \text{ eV}$ ); 2p carbon atomic orbital (dashed line) and 2p nitrogen atomic orbital (dotted line) evaluated by Clementi's wavefunction [15] and DWIA ( $\bar{V} = 10 \text{ eV}$ ). In the scale underlying the abscissa the  $q$ -values corresponding to the scattering angles are reported.

peaks are reported in figs. 1, 2, and 3. In fig. 3 we also report the measured distribution for the  $2\sigma_g$  orbital of the  $\text{N}_2$  molecule (measured IP  $37 \pm 1 \text{ eV}$ ). The experimental distributions are compared with those computed starting from different orbital wavefunctions and convoluting them with the angular and energy resolution of the experimental set-up. The distortion effects are treated according to the distorted wave impulse ap-

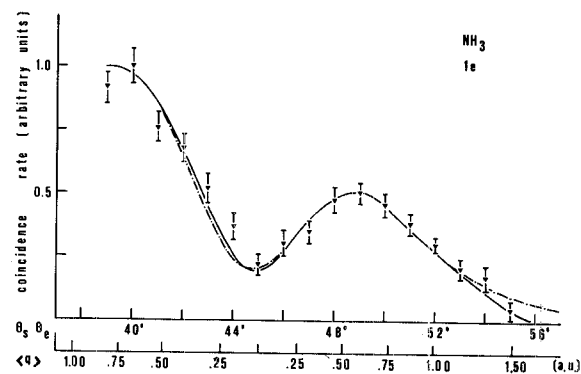


Fig. 2. Angular correlation for the  $1e$  orbital of ammonia. Measured coincidence rate is compared with theoretical shapes:  $2a_1$  ammonia orbital (full line) evaluated by Joshi's wavefunction [14] and DWIA ( $\bar{V} = 10 \text{ eV}$ ); 2p nitrogen atomic orbital (dashed line) evaluated by Clementi's wavefunction [15] and DWIA ( $\bar{V} = 10 \text{ eV}$ ). The correspondence between scattering angle and initial momentum of the bound electron is also given.

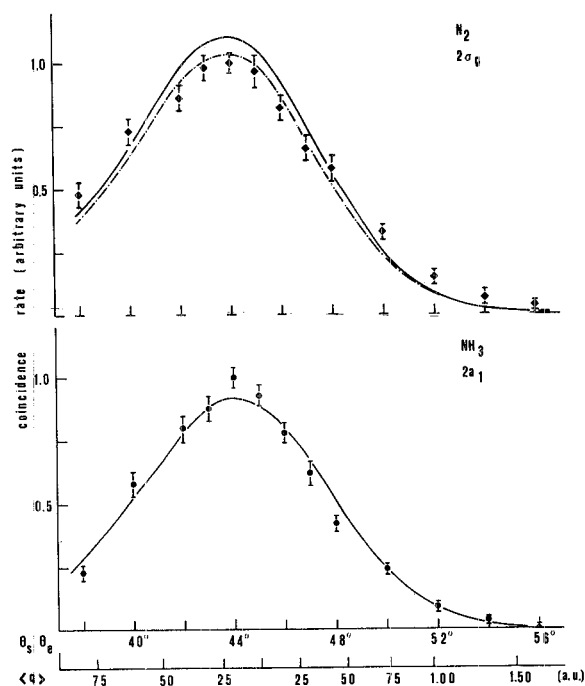


Fig. 3. (a) Angular correlation for the  $2\sigma_g$  nitrogen molecular wavefunction orbital. Measured coincidence rate is compared with theoretical shapes:  $N_2$   $2\sigma_g$  orbital evaluated by Ransil's wavefunction [17] (full curve) and by nitrogen  $2s$  [15] (dashed line), both in DWIA ( $\bar{V} = 30$  eV). (b) Angular correlation for the  $2a_1$  orbital of ammonia compared with the one predicted by the ammonia  $2a_1$  orbital wavefunction of ref. [14] and by the nitrogen  $2s$  atomic orbital wavefunction of ref. [15] (indistinguishable). The correspondence between scattering angle and initial momentum of the bound electron is also given.

proximation (DWIA) [13] where the wave numbers of the free electrons are modified by using a suitable parameter  $\bar{V}$ , representing the average complex potential in the interaction region.

The instrumental resolutions in momentum space used in the convolution procedure were deduced from the best fit of the Ne  $2p$  angular distribution [10], with values predicted by Clementi's wavefunction. For all the distributions the value  $\Delta q = 0.2$  au (fwhm) was found, varying slightly with the scattering angle. This value is consistent with the nominal angular spread of the electron gun  $\Delta\theta \approx 1^\circ$ , the computed analyzer solid angle  $\Delta\Omega \approx 3 \times 10^{-4}$  steradians and a target volume of  $\approx 2$  mm<sup>3</sup>.

Presently we are not able to measure absolute values of the cross section, so that minimum  $\chi^2$  fits to the

data are performed with a free normalization constant. On the basis of the confidence level of the  $\chi^2$  test the trial wavefunction considered is accepted or rejected.

The  $3a_1$  measured EMD does not fit well with the one calculated from the  $3a_1$  wavefunction given by Joshi [14] (confidence level less than 1%). The presence around the  $q = 0$  value of an experimental minimum deeper than the one predicted by that wavefunction (full line curve in fig. 1) as well as by any  $s-p$  hybridised orbital (not reported in the figure) lets us suppose that the  $3a_1$  orbital is a non-bonding, atomic like, orbital. The  $\chi^2$  test applied to some realistic atomic orbitals such as N  $2p$  or C  $2p$  [15], while leading to rejection of the N  $2p$ , gives a confidence level of 20% for the  $2p$  wavefunction of carbon, making consistent the hypothesis that in  $NH_3$  the non-bonding electrons of nitrogen are screened by electronic charges coming from the hydrogen atoms.

However, the one-center  $1e$  bonding molecular orbital of Joshi [14] appears to be good enough to predict the experimental EMD of the peak at 16 eV (confidence level more than 60%). It has to be pointed out that the EMD computed from the N  $2p$  of Clementi's wavefunction also fits the data well. That is not surprising as the Fourier transforms of the two above-mentioned functions are very similar, except at momenta higher than 1.2 au which correspond to scattering angles larger than  $52^\circ$  where our data are lacking. To discriminate between the above-mentioned wavefunctions it would then be necessary to carefully measure the high momentum tails of the distributions, or to be able to measure the absolute value of the cross sections.

The situation is different in the case of the  $2a_1$  orbital. Here in fact the experimental distribution is slightly sharper than the  $2a_1$  distribution predicted by Joshi [14], as is shown by the full curve of fig. 3b. This behavior cannot be interpreted on the basis of a non-bonding N  $2s$  atomic orbital. In fact it has already been shown, by previous theoretical studies [16] of  $NH_3$ , that the  $2a_1$  orbital contributes very much to the overlap population and therefore to the binding in ammonia. This property of the  $2s$  electrons of nitrogen, namely to be perturbed by molecule formation, is also observed in the  $2\sigma_g$  molecular orbital of  $N_2$ . In this case the experimental EMD is slightly broader than that expected from the Ransil [17]  $2\sigma_g$   $N_2$  and N  $2s$  wavefunctions [15], so that the

effect due to molecule formation seems to be different in these two cases of homonuclear and heteronuclear nitrogen-containing molecules.

From the arguments above and even at the present stage of the work, we can conclude that the wavefunctions commonly used in calculating molecular properties are not always very realistic, and that this experimental technique is able to at least partially discriminate among them. To this purpose, it is necessary to measure with better statistics the high momentum details of the angular correlations, and the absolute values of the cross sections.

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