Manifestation of Many-Electron Correlations in Photoionization of the K Shell of N_2

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It is demonstrated theoretically in the random phase approximation (RPA) that due to the intershell many-electron correlations the σ^* shape resonance in the photoionization of K shells of the N_2 molecule appears not only in the $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel as it was believed earlier on the basis of single particle calculations, but in both $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels. As a confirmation of this phenomenon we show that the experimental angular distributions of photoelectrons ejected from fixed-in-space N_2 molecules can be reproduced theoretically only after taking into account many-electron correlations.

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One of the most interesting features of K-shell photoabsorption spectra in diatomic molecules is a broad resonance above the ionization threshold called a σ^* shape resonance which does not exist in the corresponding atomic K-shell spectra. As was shown by Dehmer and Dill [1], the p-wave photoelectrons ejected from the essentially atomiclike $1\sigma_g$ shell interact with an anisotropic molecular field and are scattered into the states with another angular momentum, mostly with $l = 3$. As follows from their calculations for N_2 molecules, the σ_u continuum wave function with $l = 3$, which for low energies is concentrated outside the centrifugal barrier, is penetrating into the molecular core region at a kinetic energy of about 0.8 Ry. The penetration is rapid and leads to the appearance of a broad maximum in the cross section corresponding to the $1\sigma_g \rightarrow \varepsilon\sigma_u$ transition. Simultaneously, the corresponding phase shift is increasing by $\sim\pi$ radians which is a characteristic feature of every resonance. In other words, this means that the molecular field can support a quasibound f state oriented along the molecular axis. At the same time, there is no shape resonance in the $1\sigma_u \rightarrow \varepsilon\sigma_g$ transition. Also in π channels with the wave functions oriented perpendicular to the molecular axis the resonance does not appear. So, according to [1], only the $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel reveals the resonance behavior.

The fact that the σ^* shape resonance reveals itself only in the σ channels has recently been proved experimentally [2] by measuring the partial σ and π channel cross sections separately using the angle-resolved photoion spectroscopy. But there was no possibility to separate the contributions of $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels in that experiment because the difference between the ionization thresholds of the $1\sigma_g$ and $1\sigma_u$ shells is too small to be resolved (about 0.1 eV according to our calculations). The situation has changed only very recently when the angular distributions of photoelectrons ejected from fixed-in-space N_2 molecules have been measured for the first time [3]. They contain much more detailed information as compared to the angle integrated cross sections, and we show below that they can be used for disentangling the relative contributions of $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels. It is worthwhile to mention that the only published theoretical angular distributions [4] calculated using the multiple-scattering method do not agree with the experimental results of [3] and of this work in the σ^* shape resonance (see Fig. 3).

The calculations in Refs. [1,4] have been relatively simple and gave only a qualitative description of the experimental cross section in the σ^* shape resonance. More recent and more sophisticated calculations [5,6] have been still performed within the single-particle Hartree-Fock (HF) approximation and failed to reproduce correctly the experimental cross section in the σ^* shape resonance. An essential step forward has been made recently [7,8] when rather sophisticated calculations have been performed for the valence shells of N_2 with many-electron correlations taken into account in the random phase approximation (RPA). We extended the calculations of [8] to the K shells of N_2. It is well known from the atomic calculations [9] that the intershell many-electron correlations play a very important role when the ionization thresholds of interacting (sub)shells are close to each other, and when the photoionization cross section of one of them is much larger than that of the other one. As an example, one can mention a strong influence of the outer np^6 subshell of rare gas atoms on photoionization of the ns^2 subshell [9]. On the other hand, it was also well known that the role of many-electron correlations in photoionization of atomic core levels is rather negligible. In photoionization of K shells of homonuclear diatomic molecules the situation is strongly different from the atomic case because there are two closely spaced K shells. In addition, the photoionization cross section of one shell (the $1\sigma_g \rightarrow \varepsilon\sigma_u$ transition where the σ^* shape resonance occurs) in the HF approximation is 1 order of magnitude larger than in the transition $1\sigma_u \rightarrow \varepsilon\sigma_g$ from the other shell. So, both conditions for many-electron correlations being important are fulfilled. Therefore one can expect strong intershell correlations between the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels. Figure 1 shows the corresponding Feynman

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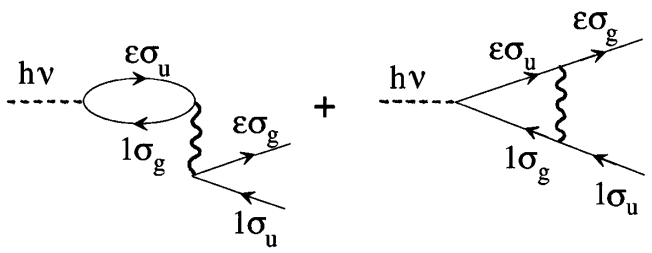

FIG. 1. The lowest order Feynman diagrams corresponding to the RPA intershell correlations between the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels. Dashed lines describe the photon, wavy lines the Coulomb interaction, and full lines with arrows the particle or hole states.

diagrams of the lowest order in the Coulomb interaction which give the main contribution in the RPA approximation. It is important to mention that the $1\sigma \rightarrow \varepsilon\sigma$ channels do not interact with the $1\sigma \rightarrow \varepsilon\pi$ channels because they correspond to different projections of the total angular momentum of the system in the final state, and the internal forces in a closed system (the Coulomb interaction in our case) could not change the projection of the total angular momentum. Therefore we need to take into account many-electron correlations only between the channels $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$. The interaction with the valence shells can be neglected due to a large difference between the ionization potentials.

The calculations have been performed by us using the RPA method developed earlier for atoms [9] and successfully applied recently to H_2 [10] and N_2 [8] molecules. According to Ref. [10] at first the HF ground state wave functions are found in prolate spheroidal coordinates in the fixed-nuclei approximation using the method developed in [11]. With their help the zero order basis set of single particle HF excited state wave functions of discrete and continuous spectrum is calculated in the field of a frozen core of a singly charged ion. With this bases the dipole and Coulomb matrix elements are calculated which enter the RPA equation [8]. In the integral RPA equation for the dipole matrix elements the infinite integration over the continuous spectrum is substituted approximately by a finite summation, and in that way the integral equation is transformed into a set of algebraic equations which is solved numerically by matrix inversion [9].

As was shown earlier [5], a relaxation of the ionic core plays an important role in the photoionization of K shells of N_2 changing the position and magnitude of the σ^* shape resonance. In particular, in the case of a frozen core (unrelaxed) HF calculation the maximum appears 5 eV above threshold and has the magnitude 2 times larger than the experimental one [5]. In the relaxed core HF (RCHF) calculation the maximum is 13 eV above threshold and its magnitude is slightly lower than the experimental one, while the experimental position of maximum is 9 eV above threshold. Since the core relaxation effects are not taken into account in the RPA method itself, one can take them into account by performing the RPA calculations with the basis set of the RCHF photoelectron wave functions. The latter is found in the following way. At first the self-consistent HF molecular ion wave functions are calculated with the hole in an appropriate shell, either $1\sigma_g$ or $1\sigma_u$, then a set of photoelectron wave functions in the frozen field of the corresponding molecular ion state is found. With these wave functions the dipole and Coulomb matrix elements are calculated entering the RPA equation. The justification for such a procedure was given in [12] for the case of atomic calculations, and it is equally applied to the molecular case. We performed our RPA calculations with both HF and RCHF basis sets. The results are qualitatively similar, but differ by the position and magnitude of the σ^* shape resonance as was mentioned above. Since with the RCHF basis set we take into account a larger part of correlations, in the subsequent discussion we will present only our RPA results obtained with the RCHF basis set.

The photoionization cross sections for the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels both in RCHF and RPA approximations are shown in Fig. 2. All the results presented in this paper have been obtained with the length form of the dipole operator, and the experimental thresholds have been used in the RPA calculations. Under these conditions the RPA cross sections in the length and velocity forms practically coincide while in the RCHF the cross section in the length form is about 5% higher than in the velocity form. Our RPA cross section for the sum of the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels is in reasonable agreement with the experimental cross section [2] also shown in Fig. 2, only the position of maximum is shifted to higher energies by about 2 eV. In accordance with the calculations of Dehmer and Dill [1] the cross section for the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel in the RCHF approximation is nearly constant in a

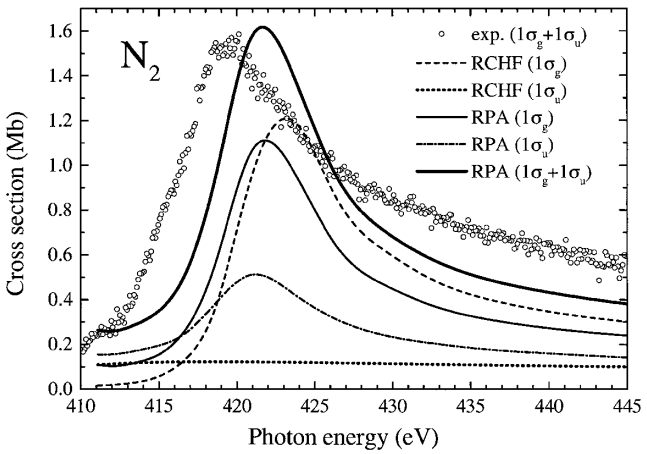

FIG. 2. Photoionization cross sections for the K shells of N_2 molecule corresponding to the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ transitions calculated in the RCHF and RPA approximations in the length form. The experimental data of Ref. [2] corresponding to the sum of $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ transitions have been normalized to the absolute cross section published in [13].

broad energy range while after taking many electron correlations into account it acquires a maximum in the σ^* shape resonance which is only 2 times lower in magnitude than the maximum in the main $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel. It means that the σ^* shape resonance exists in both $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels, contrary to the earlier conclusion [1] based on a single-particle calculation. Though it is not possible to measure these cross sections directly, there is a possibility to prove the existence of maximum in the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel by investigating the angular distributions of photoelectrons ejected from fixed-in-space molecules.

As follows from the dipole selection rules, when σ shells of a fixed-in-space linear molecule are ionized by linearly polarized light with the electric vector parallel to the molecular axis, only the $n\sigma \rightarrow \varepsilon\sigma$ transitions are contributing, that is the transitions under discussion. In the following, we shall consider solely this geometry of experiment. The final state in the $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel has odd parity and therefore contains only the contribution of partial waves with odd l. The corresponding partial waves are proportional to the Legendre polynomials $P_l(\theta)$ with odd l which have zero at $\theta = 90°$ (θ is the angle between the molecular axis and the direction of photoelectron ejection, and the angular distribution is axially symmetric about the molecular axis). Besides, according to Ref. [1] the main contribution in the shape resonance is given by just one partial wave with $l = 3$ which has an additional zero at $\theta = 39.23°$. Then the angular distributions of photoelectrons in this channel must have an exact zero at $\theta = 90°$ and a value close to zero at about $\theta = 40°$. Contrary to that, in the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel the final state is even, and the corresponding wave function contains the contribution of partial waves with even l. They are proportional to the Legendre polynomials with even l having a nonzero value at $\theta = 90°$, and they also do not have a zero near $\theta = 40°$, at least for low l values. The corresponding angular distributions will have nonzero values at both $\theta = 40°$ and 90°. Therefore there is a possibility to establish the relative contribution of the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel by investigating the behavior of the angular distributions of photoelectrons ejected from fixed-in-space molecules at the angles θ close to 40° and 90° (measured with respect to the N_2 molecular axis). If the cross section in the $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel is really 1 order of magnitude larger than in the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel, the observed angular distributions must have deep minima at both angles $\theta = 40°$ and 90°.

To check it experimentally, we have remeasured the angular distributions of $1s$ photoelectrons from fixed-in-space N_2 molecules at a newly constructed soft x-ray undulator beam line BL-2C [14] of the Photon Factory. The experimental apparatus described in detail in [15] consists of two electron-ion coincidence circuits. Compared to previous measurements [3] we have reduced an effective acceptance angle of the parallel-plate ion analyzed by detecting fragment ions with higher kinetic energies ($\approx$10 eV instead of $\geq$3 eV) and reduced the statistical errors of the coincidence rate by improving the efficiency of the analyzers. As a result of these improvements the intensities in two minima of the angular distribution at 419 eV have been reduced by approximately a factor of 2 as compared to [3].

In Fig. 3 we compare the measured and calculated angular distributions at two photon energies, 415 and 419 eV, in the region of the σ^* shape resonance. Since the position of maximum in theory is shifted to higher energies by about 2 eV as compared to the experiment, the theoretical angular distributions have been obtained at photon energies 417 and 421 eV, respectively. In both cases the RCHF results as well as the results of multiple-scattering calculations of Dill *et al.* [4] have a very deep minimum at about $\theta = 40°$ with the intensity approaching zero, which is in strong disagreement with the observed intensities. In contrast to that, in the RPA the intensities in this minimum are in close agreement with the experiment, and the RPA angular distributions reproduce the experimental ones fairly well at all angles. The minimum at $\theta = 90°$ at photon energy 415 eV is also reproduced well only in the RPA approximation, while at photon energy 419 eV the experimental intensity at $\theta = 90°$ is small and hardly can be used in qualitative discussion. Relative contributions of the $1\sigma_g$ and $1\sigma_u$ shells to the angular distribution both in RCHF and RPA approximations at the maximum of the shape resonance are displayed in Fig. 4, from which it follows

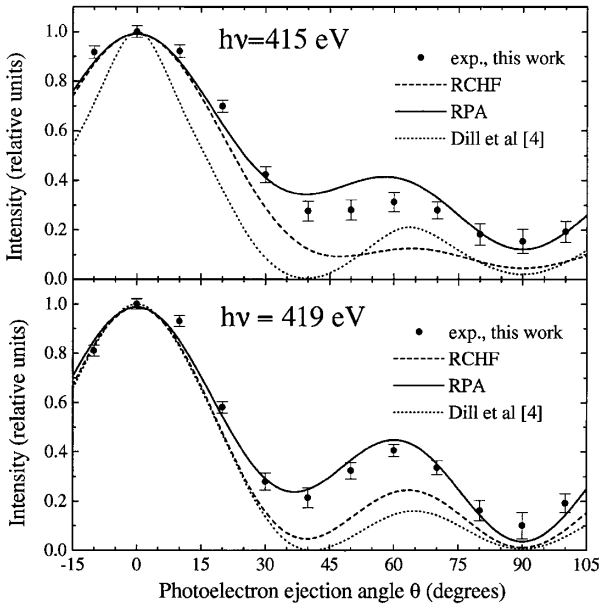

FIG. 3. Comparison of different calculated angular distributions of photoelectrons with experiment at two photon energies in the region of the σ^* shape resonance for fixed-in-space N_2 molecules ionized by linearly polarized light with electric vector parallel to the molecular axis. All the data are normalized to unity at $\theta = 0$. Theoretical results correspond to the sum of the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ transitions.

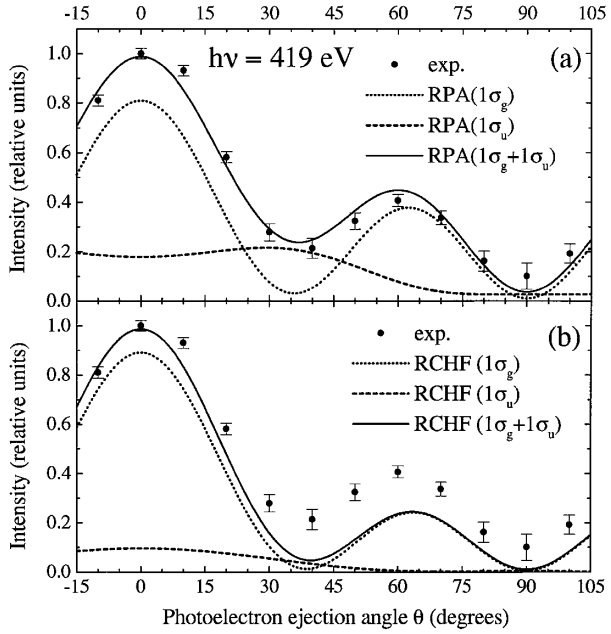

FIG. 4. The contributions of the $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels to the angular distributions of photoelectrons shown in Fig. 3 in the RPA (a) and in RCHF (b) approximations in the maximum of the σ^* shape resonance compared to the experiment.

that the nonzero intensity at $\theta = 40°$ comes mainly from the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel.

As further evidence of the important contribution of the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel, one can consider the x-ray emission spectra obtained in [16] by tuning the x-ray excitation energy to different parts of the σ^* shape resonance. Because of the parity selection rule the relative intensities of the $3\sigma_g$ and $1\pi_u$ emissions are proportional to the probabilities of creating the $1\sigma_u$ and $1\sigma_g$ holes, respectively. As it follows from Fig. 4 of Ref. [16], the probability of creating the $1\sigma_u$ hole in the σ^* shape resonance is of the same order of magnitude as for the $1\sigma_g$ hole in accordance with our RPA calculations.

In conclusion, we for the first time demonstrated theoretically that due to the contribution of many-electron correlations the σ^* shape resonance in the K-shell photoionization of the N_2 molecule reveals itself not solely in the $1\sigma_g \rightarrow \varepsilon\sigma_u$ channel as it follows from single-particle calculations [1], but in both $1\sigma_g \rightarrow \varepsilon\sigma_u$ and $1\sigma_u \rightarrow \varepsilon\sigma_g$ channels. This conclusion is supported by our measurements of the angular distributions of photoelectrons ejected from fixed-in-space N_2 molecules by light linearly polarized along the molecular axis which can be correctly described theoretically only provided that the contribution of the $1\sigma_u \rightarrow \varepsilon\sigma_g$ channel in the σ^* shape resonance is greatly enhanced in accord with the RPA calculations. This conclusion is expected to be valid also for other homonuclear diatomic molecules as well as for polyatomic molecules provided the two conditions mentioned above are fulfilled, namely, there are two closely spaced shells, and the photoionization cross section of one of them is much larger than of the other one. On the other hand, in HCCH, the molecule isoelectronic with N_2, gerade and ungerade ionization channels has the cross sections of the same order of magnitude [17], therefore the correlations are not expected to be important. In heteronuclear diatomic molecules like CO the two K shells have strongly different ionization thresholds, and due to that the role of many-electron correlations must be relatively small.

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