background subtraction, it would be premature to regard this as evidence for a $T=\frac{3}{2}$ resonance in the $A=3$ system.

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# Ultraviolet Photoionization Cross Sections for $N_2$ and CO

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I have calculated ultraviolet photoionization cross sections for $N_2$ and CO in the gas phase and the differential cross sections for oriented molecules. The gas-phase results agree well with recent data and display shape resonances, predicted by Dehmer and Dill, about 1 Ry above threshold for certain levels. For oriented molecules I find distinctive angular distributions which could be used to identify levels or determine the bond geometry of molecules adsorbed at surfaces.

There is currently great interest in measurements of the angular distribution of electrons photoemitted from adsorbate-covered surfaces.[1] In general the analysis of these experiments is complicated by the strong adsorbate-substrate interaction which is the hallmark of chemisorption. However, in the case that the adsorbed molecule does not dissociate, the major features of the photoelectron spectrum should be determined by the molecule itself and be independent of the particular substrate. To study these cases I have calculated the partial photoionization cross sections of valence levels of oriented CO and $N_2$ molecules in the ultraviolet. I have also computed the angular-averaged cross sections and compared them with recent data for the gas phase.[2,3] These calculations agree with the data better than any others published to date and for the first time place theory and experiment in reasonable agreement. The calculations were performed with the scattered-wave (SW) $X\alpha$ method[4] which yields quite good ionization potentials and charge densities yet is sufficiently economical to be applied to relatively large molecules. Dill and Dehmer[5] have discussed its application to photoemission and calculated the cross sections for the core levels of $N_2$ in the gas phase.

The SW $X\alpha$ method uses an approximate exchange-correlation potential which is local and proportional to the one-third power of the charge density. This potential is sphere and volume averaged to the "muffin tin" form. The one-electron Schrödinger equation can then be solved using standard techniques and a new charge density and potential constructed. The entire process is repeated until self-consistency is achieved. I have used this potential to calculate the continuum states except that I have applied the Latter tail correction[6] to assure that it behaves asymptotically like $-2/r$ (I use rydberg units throughout). For photoemission the final states must have the asymptotic form of an incident Coulomb wave plus *incoming* spherical waves. I follow Ref. 5 and first calculate the real symmetric $K$ matrix since the solutions required for the $K$ matrix can be easily combined to satisfy the boundary conditions at infinity.

The differential photoionization cross section per electron is given by

$$\frac{d\sigma}{d\Omega}=\frac{\alpha}{\pi}\frac{k}{\omega}|\langle f|\hat{A}\cdot\vec{p}|i\rangle|^2 a_0^2,$$

where $\alpha = e^2/\hbar c$ is the fine-structure constant, $k^2$ is the kinetic energy of the outgoing electron and $\omega$ the photon energy both in rydbergs, $\hat{A}$ is the polarization of the incident radiation, $\vec{p}$ is the momentum operator (atomic units), and $a_0$ is the Bohr radius. The initial state is normalized to unity and the final state is normalized in a box. Since the orbitals are derived from a muffin-tin potential, the calculation of the transition dipole moment is simplified by use of the acceleration form

$$|\langle f|\hat{A}\cdot\vec{p}|i\rangle| = |\langle f|\hat{A}\cdot\nabla V|i\rangle|/(k^2-\epsilon_i),$$

where $\epsilon_i$ is the initial-state energy and $V$ is the potential, since then there is no contribution from the constant-potential regions. The acceleration form is valid here because all electrons move in the same local potential. It is not valid in the Hartree-Fock approximation where the acceleration form should be used with great caution.[7] Note that $\epsilon_i$ is not in general equal to the negative of the ionization potential in the $X\alpha$ method so that $k^2-\epsilon_i \neq \omega$. I have computed the initial state without the Latter tail correction; I believe that this has only a slight effect on the results. The cross section is then computed in the molecule's frame of reference and, for the gas phase, averaged over all molecular orientations to give

$$\frac{d\sigma}{d\Omega}=\frac{\alpha}{4\pi}[1+\beta P_2(\cos\theta)],$$

in accordance with Yang's theorem.[8] Here $\sigma$ is the integrated cross section, $\beta$ is the asymmetry parameter, and $\hat{A}\cdot\hat{k}=\cos\theta$. For CO and $N_2$ the sphere radii were $r_C = 1.15$, $r_O = 0.98$, and $r_N = 1.04$, in atomic units. Touching spheres were used which means that the bond lengths were $r_{CO} = 2.13$ and $r_{NN} = 2.08$. The values of the parameter $\alpha$ in the exchange-correlation potential were taken from Schwarz's[9] tables and were $\alpha_C = 0.759\,28$, $\alpha_O = 0.744\,47$, and $\alpha_N = 0.751\,00$. These are essentially the same as in Connolly *et al.*[10] and the orbital and transition-state energies agreed with theirs. The Coulomb wave functions were generated by the method of Barnett *et al.*[11]

The angle-averaged cross sections for the valence levels of $N_2$ and CO are shown in Figs. 1 and 2, respectively, for photon energies $\omega = 16$–44 eV. The photon energy was related to $k^2$ by $\omega = k^2 + I$, where $I$ is the measured adiabatic ionization potential.[12] The data are those of Gustafsson *et al.*[2] In $N_2$ the $3\sigma_g$ level shows the same resonant behavior about 10 eV above threshold as found by Dehmer and Dill[5] for the $1\sigma_g$ core level. As they showed it is a final-state resonance in the $l = 3$ partial wave which has $\sigma_u$ symmetry. Therefore states which are odd under inversion cannot couple to it and it is not present for the $2\sigma_u$ or the $1\sigma_u$ level. The data clearly show this effect and I interpret the peak at $\omega \simeq 28$ eV as due to the resonance. The other peak is discussed below. For CO a similar resonance occurs but since the states are not restricted by inversion symmetry both the $4\sigma$ and the $5\sigma$ couple to it, leading to the peaks observed at $\omega \simeq 32$ and 23.5 eV, respectively. Note that the peaks in the $4\sigma$ and $5\sigma$ cross sections do not occur at the same *final*-state energies ($k^2$), which shows that the initial-state wave function is important as well. The experimental difference in $k^2$ between the peak positions is about 2.8 eV and the calculated difference is 2.7 eV (I have used $I_{5\sigma} = 14.0$ eV and $I_{4\sigma} = 19.7$ eV). In Ref. 5 the resonance was calculated to be at a slightly lower $k^2$ because $\alpha = 1$ was used in the exchange-correlation potential rather than the Schwarz value. This makes the potential more attractive and shifts the resonance to lower energy which is actually in better agreement with experiment. However I believe that $\alpha = 0.751$ is correct for the ground state and that the shift to lower energy should be accounted for

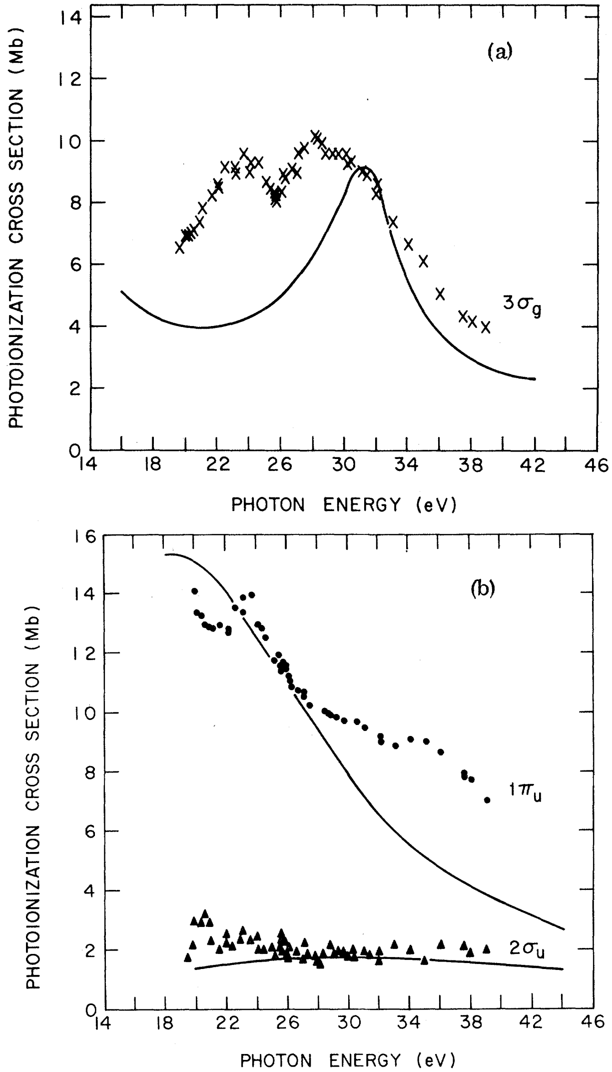

FIG. 1. Photoionization cross sections for $N_2$. (a) $3\sigma_g$ level and (b) $1\pi_u$ and $2\sigma_u$ levels. The solid curves are SW $X\alpha$ results and the data points are from Ref. 2. 1 Mb $=10^{-18}$ cm$^2$.

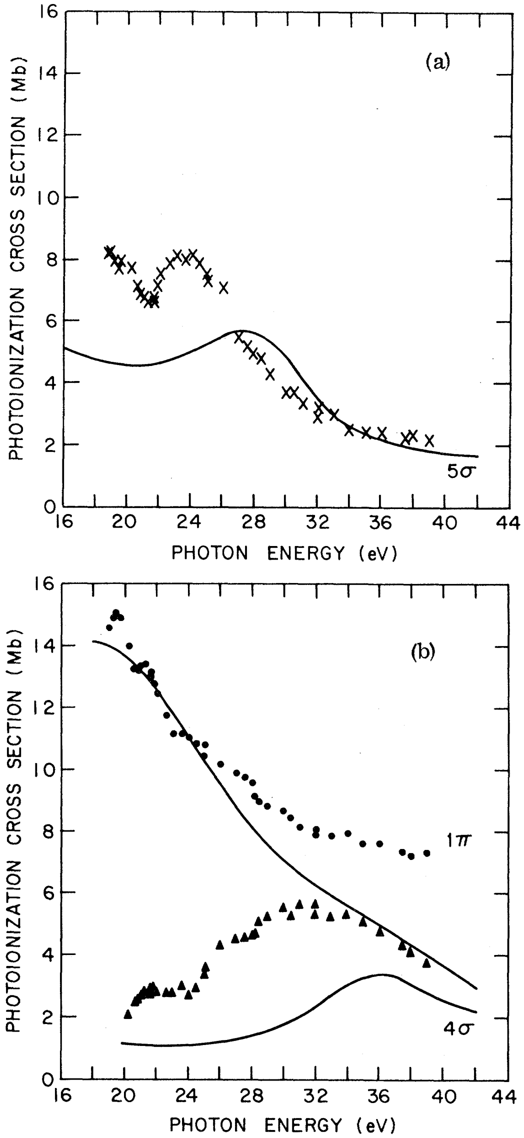

FIG. 2. Photoionization cross sections for CO. (a) $5\sigma$ level and (b) $1\pi$ and $4\sigma$ levels. Theory and experiment are as in Fig. 1.

by some form of "relaxation," e.g., by use of the transition-state potential.[4] Recently Ellis and Goscinski[13] have calculated oscillator strengths for various transitions in Li, Na, and K and found better agreement with experiment in this way; I plan similar calculations.

For both molecules there is additional structure below the resonant peak which is not seen in the calculation. These I identify with two-electron excitations which are not included in the present model. For example for the $3\sigma_g$ and $1\pi_u$ levels in $N_2$ there are peaks at $\omega \simeq 23.6$ eV which are due to the excitation of the $C^2\Sigma_u^+$ state of $N_2^+$ ($\lambda = 525$ Å). This is clearly shown in the absorption data of Lee *et al.*[14] (which were used to obtain the partial cross sections). For CO it is known[3] that autoionization plays an important role for photon energies less than 19 eV and is presumably responsible for the structure observed near threshold.

Several other calculations of these cross sections have been performed. Rabalais *et al.*[15] used plane-wave final states which means that no final-state resonances could be obtained. Schneider and Berry[16] have applied a pseudopotential formalism and Tuckwell[16] a two-center expansion to

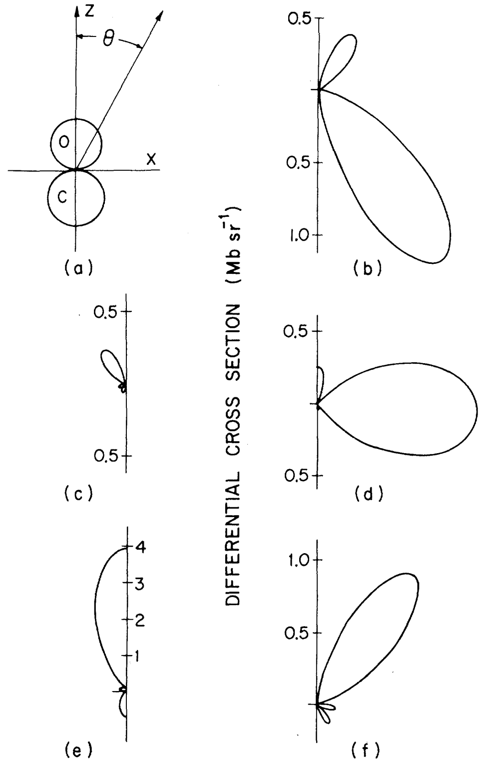

FIG. 3. Angular distribution of photoemitted electrons from an oriented CO molecule at $\omega = 41$ eV. (a) Molecular orientation. (b)–(f) Polar plots of differential cross section in Mb sr$^{-1}$ for the (b) $5\sigma$ level with $\hat{A}$ along $X$ axis, (c) $1\pi$ level with $\hat{A}$ along $Z$, (d) $1\pi$ level with $\hat{A}$ along $X$, (e) $4\sigma$ level with $\hat{A}$ along $Z$, and (f) $4\sigma$ level with $\hat{A}$ along $X$. For clarity only half of each distribution is shown but they are all symmetrical about the $Z$ axis. Note the different scales.

$N_2$. The SW $X\alpha$ method gives much better qualitative and quantitative results for all the levels.

Figure 3(a) shows an oriented CO molecule and Figs. 3(b)–3(f) the angular distribution of the differential cross section in the $X$-$Z$ plane for polar angle $\theta$ between 0 and 180°. The photon energy $\omega$ is approximately 41 eV (He II) and the vector potential is oriented either parallel or perpendicular to the molecular axis. The $5\sigma$ level with $\hat{A}$ parallel to the axis is one order of magnitude smaller than the others and so not shown. Note for example that for $\hat{A}$ perpendicular to the axis the $\pi$ level has a relatively large cross section for emission at $\theta = 0°$. Only the $4\sigma$ level with $\hat{A}$ parallel to the axis is larger in that direction. For a plane-wave final state there would be no emission in that case because the matrix element is proportional to $\vec{k}\cdot\hat{A}$.

Recently Gustafsson *et al.*[17] have determined the assignments for the levels observed for CO adsorbed on Ni and Pd by measuring the photon-energy dependence of the branching ratio and comparing with that for the gas phase. However direct comparison with the gas-phase branching ratios can be misleading in some cases because in the gas phase one measures an average over all molecular orientations whereas for the adsorbed gas one measures only over the half-space which lies outside the metal and (possibly) only for a fixed polarization relative to the molecular axis.

Provided that substrate effects are small one could also use the angular distribution at fixed photon energy to identify the levels. This of course requires a calculation. Alternatively, if the level assignment were known from the photon-energy dependence the angular distributions could be used to find the orientation of the molecule relative to the surface, again provided that substrate interactions are small. This information has not been obtained so far by any other technique.

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# Multiphoton Ionization of Rare Gases at Very High Laser Intensity ($10^{15}$ W/cm$^2$) by a 30-psec Laser Pulse at 1.06 $\mu$m

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A bandwidth-limited 30-psec laser pulse at 1.06 $\mu$m is used to investigate multiphoton ionization of noble gases at very high laser intensity ($10^{15}$ W/cm$^2$). For helium atoms interacting with a laser intensity of $1.1\times10^{15}$ W/cm$^2$, no departure from a pure 22-photon ionization process is observed, in contradiction with the few theoretical calculations which predict that a tunneling effect should appear in this laser-intensity range.

Multiphoton ionization processes have been investigated especially on $10^{-8}$-sec time scales, by using $Q$-switched lasers.[1-4] It is of interest to investigate multiphoton ionization of atoms with much shorter pulses for various reasons. First, it is only with picosecond pulses that very high laser intensity ($10^{16}$ W/cm$^2$) can be obtained at the present time. Thus the effect of very high intensity on multiphoton ionization can be investigated with such short pulses. Second, the shortening of the interaction time could greatly influence resonant multiphoton ionization processes which have been observed with $10^{-8}$-sec pulses. Finally, a bandwidth-limited picosecond pulse is defined as a pulse completely devoid of intensity or frequency modulation. It has a regular and well-defined temporal behavior, similar to a single-mode laser pulse. Such a pulse has no fluctuation and its $K$th-order peak-intensity autocorrelation function, or $K$th-order peak-intensity moment, $f_K$ equals 1.[5] Thus it makes for easier comparison between theoretical and experimental multiphoton-ionization probabilities.

The purpose of this Letter is to present some preliminary results of the first investigation of multiphoton ionization of rare gases by a 30-psec laser pulse. The laser used in the present experiment has been described elsewhere.[6] It is a mode-locked Nd-doped yttrium-aluminum-garnet oscillator using Kodak 9740 saturable dye. The $\mathrm{TEM}_{00}$ mode is selected with a 1.4-mm pinhole. The mode-locked output consists of a 10-mJ train of ten pulses. A single pulse is isolated from the train, outside the cavity, by the well-known method of a Pockels switch. The single pulse is selected in the rising edge of the train where pulses are usually bandwidth-limited. This single pulse goes through a beam-expanding telescope before entering a three-stage Nd:glass amplifier. The single pulse can thus be amplified to an energy up to 1 J. This laser radiation is linearly polarized and is centered at 10 643.5 Å with a linewidth of 0.8 Å. A linear measurement of the laser pulse shape was carried out by using a picosecond streak camera incorporating a storage-memory video system to visualize instantly and record the shape of the laser pulse. The laser pulse width was measured to be 28± 2.5 psec.[6] The corresponding time-bandwidth product had a value $\Delta\nu\,\Delta t = 0.7$.

Multiphoton ionization of five rare gases was performed by using an experimental arrangement identical to that employed in previous works.[5] Briefly, the laser pulse is focused into a vacuum chamber by an $f/3$ aspheric lens corrected for spherical aberrations. The gas under investigation is released into the vacuum chamber at a static pressure of $10^{-4}$ Torr for which no avalanche effects occur. The ions resulting from the laser interaction with atoms at the focal volume are extracted with a transverse electric field of 400 V cm$^{-1}$ and then detected with an electron multiplier; 10 to $10^4$ ions are generally collected. It should be stated that all the multiphoton ions formed at the focal volume can be extracted and detected when the transverse electric field is larger than about 200 V cm$^{-1}$. Ion data are the same when a transverse electric field of 400 or 500 V cm$^{-1}$ is used to extract ions.

The experiment consists of measurements of the number of ions formed as a function of the laser intensity. In usual multiphoton-ionization