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Relaxation effects in molecular K-shell photoionization

D. L. Lynch and V. McKoy
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125
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The effects of core relaxation on the shape-resonant K-shell photoionization cross sections in N_2 are shown to be very significant. Core relaxation produces substantial broadening and shifting of the shape resonance to higher energy. The results suggest that the frozen-core approximation may not be an appropriate model for K-shell photoionization involving a low-energy shape resonance.

I. INTRODUCTION

The important role of shape resonances in molecular photoionization has now been well established.[1,2] These resonances, or quasibound states, are essentially one electron in nature and are formed by the trapping of the photoelectron by the centrifugal barrier of the molecular force field. The importance of these resonances arises primarily from their strong influence on the photoionization cross-section vibrational branching ratios, and photoelectron angular distributions. Hence, it is not surprising that shape resonances have attracted considerable experimental interest and that, moreover, they have stimulated the development of several new theoretical approaches to molecular photoionization.[3,4] These aproaches include the Stieltjes-Tchebycheff moment-theory (STMT) method,[5] the continuum multiple-scattering model (CMSM),[6,7] and several methods for the direct solution of the Hartree-Fock equations for the photoelectron continuum orbitals.[8–12]

To date most applications of the STMT method[13] and the direct methods[9–12] to molecular photoionization have been carried out in the frozen-core Hartree-Fock (FCHF) approximation. In this approximation the final state is described by a single electronic configuration in which the ionic core orbitals are constrained to be identical to those of the neutral molecule, and the photoelectron continuum orbital is determined in the field of this unrelaxed core. This sudden approximation completely neglects any restructuring of the molecular core upon ionization and should be much more appropriate for photoionization of valence levels than of the deeper or K-shell levels. The shape-resonant nature of many K-shell cross sections can make this approximation even poorer than expected. Nevertheless, the frozen-core approximation has been used extensively in studies of K-shell molecular photoionization.[13–16]

The purpose of this Rapid Communication is to present results for the K-shell photoionization of N_2 which include the effects of core relaxation. Relaxation effects are included using continuum orbitals determined in the field of the completely relaxed ion core. Although the assumption that the photoelectron moves in the field of such a relaxed ion is not rigorous, applications to atomic inner-shell photoionization have shown that it is a very reasonable model.[17,18] Our results show that the effects of core relaxation on this K-shell σ_u shape-resonant cross section are dramatic. Whereas with an unrelaxed core the cross sections are strongly peaked near threshold and differ substantially in shape from the measured values, relaxation of the core produces significant broadening and shifting of the resonance to higher energy. The resonant feature now occurs at too high an energy suggesting an overscreening of the K-shell hole in our model but the general shape of the cross section is quite close to what is seen experimentally. The corresponding photoelectron asymmetry parameters behave in a very similar way. To our knowledge this significant role of core relaxation in resonant K-shell molecular photoionization has been hitherto unrecognized.[14]

A summary of the paper is as follows. In Sec. II we give a very brief outline of our method for obtaining the molecular photoinization cross sections and in Sec. III we discuss our results for the K-shell of N_2. Section IV summarizes our conclusions.

II. METHOD

The rotationally unresolved, fixed-nuclei, photoionization cross section is given by

$$\sigma(R)=\frac{4\pi^2\omega}{3c}|\langle\Psi_i(\vec{r},R)|\vec{\mu}|\Psi_f(\vec{r},R)\rangle|^2 \ , \tag{1}$$

where $\vec{\mu}$ is the dipole moment operator and ω the photon frequency. In Eq. (1) Ψ_i represents the initial state of the molecule with N bound electrons and Ψ_f the final state with a photoelectron in the electronic continuum. In most studies of molecules to date, the FCHF approximation has been used for Ψ_f. This approximation, which completely neglects any restructuring of the charge density in the course of ionization and hence allows for no hole charge screening, should work best for valence orbitals. However, it could be a very poor approximation for photoionization of deep core levels involving a shape resonant continuum. In this case the trapping of the photoelectron by the centrifugal barrier will increase its time of emission. During this time significant relaxation of the ionic core can occur. This core relaxation could be accounted for by inclusion of the appropriate terms in the expansion of the wave function or, equivalently, through the use of an optical potential. However, these relaxation effects could be approximately included by assuming that the photoelectron moves in the field of the completely restructured core.[17,18] This relaxed-core Hartree-Fock model should be particularly meaningful around shape resonances.

The Hartree-Fock continuum orbitals used in these studies hence satisfy the one-electron Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+V_{N-1}(\vec{r},R)-\tfrac{1}{2}k^2]\phi_{\vec{k}}=0 \ , \tag{2}$$

where the potential V_{N-1} is determined either by the core orbitals of the neutral molecule or by the orbitals of the relaxed ion. The nonspherical character of these molecular potentials introduces several complications into the solution of this equation for $\phi_{\vec{k}}$ which do not arise in atomic systems.[3] Various approaches have been developed for obtaining these molecular electronic continuum states $\phi_{\vec{k}}$.[8-12] Our approach, which has been discussed in detail elsewhere,[2,9] begins with the integral form of Eq. (2), i.e.,

$$\phi_{\vec{k}} = \phi^{C}_{\vec{k}} + G_c^{(-)} V \phi_{\vec{k}} \ , \tag{3}$$

where $\phi^{C}_{\vec{k}}$ is the Coulomb scattering wave function and

$$V = V_{N-1} + \frac{1}{r} \ , \tag{4a}$$

and

$$G_c^{(-)} = \frac{1}{2}\left(\nabla^2 + \frac{2}{r} + k^2 - i\epsilon\right)^{-1} \ . \tag{4b}$$

The continuum orbital $\phi_{\vec{k}}(\vec{r})$ can be expanded in terms of $\Omega_{\hat{k}}$, the direction of $\vec{k}$, as

$$\phi_{\vec{k}}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{lm} \frac{i^l}{k} \Phi_{klm}(\vec{r}) Y^*_{lm}(\Omega_{\hat{k}}) \ , \tag{5}$$

where $\phi_{klm}(\vec{r})$ are the partial wave scattering functions. Each ϕ_{klm} satisfies its own Lippmann-Schwinger equation

$$\phi_{klm} = \phi^{C}_{klm} + G_c^{(-)} V \phi_{klm} \ . \tag{6}$$

We solve Eq. (6) for the ϕ_{klm} by the iterative Schwinger variational method which has been previously applied to several molecules, e.g., N_2,[9] CO,[19] CO_2,[15] C_2H_2,[16] and C_2N_2.[20] The method is essentially a procedure for the numerical solution of Eq. (6) which avoids the integration of coupled integrodifferential equations but relies on single-center expansion techniques in the evaluation of all matrix elements. Although the method utilizes discrete basis functions in solving Eq. (6), the approximate solutions satisfy scattering boundary conditions and can be systematically improved through an iterative procedure.[21]

For Ψ_i in Eq. (1) we again use the Hartree-Fock wave function. In the FCHF approximation, orbital orthogonality makes the evaluation of the transition dipole matrix element in Eq. (1) very straightforward. This feature makes this approximation particularly convenient in molecular applications. With the relaxed Hartree-Fock ionic core in Ψ_f the lack of orbital orthogonality complicates the evaluation of this transition matrix element. In these studies we have used a biorthogonalization procedure in the computation of these matrix elements.[22,23] Details of these calculations will be presented elsewhere.[24]

III. RESULTS

The SCF wave functions for the initial state and relaxed N_2^+ cores were all obtained in a $[4s3p1d]$ contracted Gaussian basis set[25] and for an internuclear distance of 2.068 a.u. With the minor difference that the present calculations use the complete set of $1d$ functions, this basis is essentially equivalent to that of Ref. 14. In this basis the ground-state SCF energy of N_2 is -108.9648 a.u. and the $1\sigma_g$ and $1\sigma_u$ orbital energies are 426.73 and 426.63 eV, respectively. The $1\sigma_g$ and $1\sigma_u$ ionization potentials using the SCF energies of the relaxed N_2^+ ions are 419.75 and 419.61 eV, respectively. The difference of about 10 eV between these ionization potentials and the experimental value of 409.9 eV is essentially due to hole localization.[23]

The σ_g, σ_u, π_u, and π_g continuum orbitals of both the frozen and relaxed N_2^+ ions were obtained by the iterative Schwinger procedure outlined above. The numerical details of these calculations such as partial-wave expansions and starting basis sets have been discussed previously.[2,9] Considerable effort has been taken to ensure the convergence of these calculations. For example, our expansion parameters[24] give a normalization of about 0.9995 for the $1\sigma_g$ and $1\sigma_u$ orbitals, and the final photoionization cross sections were calculated with continuum orbitals obtained after two steps in the iterative procedure.[9]

In Fig. 1 we show our calculated frozen-core photoionization cross sections along with the frozen-core results obtained previously by the STMT method[14] and the experimental data obtained by $(e,2e)$ measurements.[26] The present frozen-core results differ significantly from the experimental data. The σ_u resonance feature is quite strongly peaked and concentrates much of the cross section too close to threshold. On the other hand, the frozen-core cross sections of the STMT method show a much broader resonance feature than the present results and, moreover, are apparently in better agreement with the measured cross sections. In principle our procedure should give the same frozen-core cross sections as the STMT method. We are not completely certain of the reasons for these differences. We have tested the convergence of these calculations and we believe that the partial-wave expansions are sufficient to yield the correct results. A possible explanation is that the pseudospectrum of the STMT calculations[14] did not have a

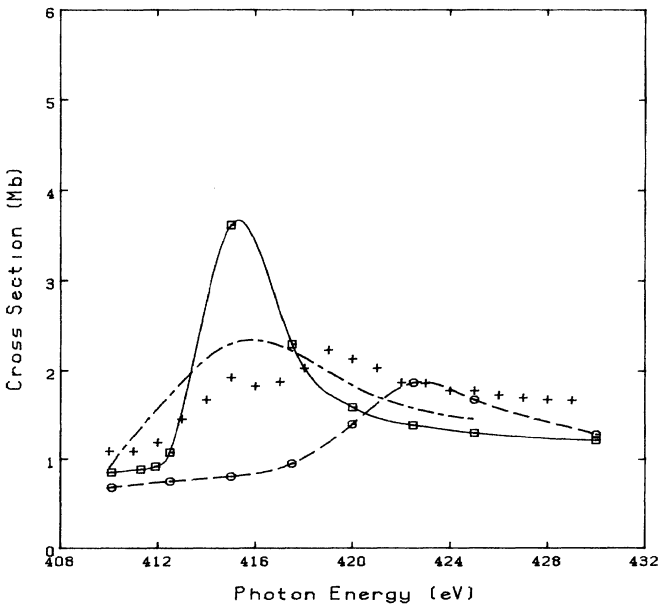

FIG. 1. K-shell photoionization cross sections for N_2: ——, present FCHF results; — — —, present results with a relaxed ion core; —·—·—, FCHF results of the STMT method (Ref. 14); +, experimental data of Ref. 26.

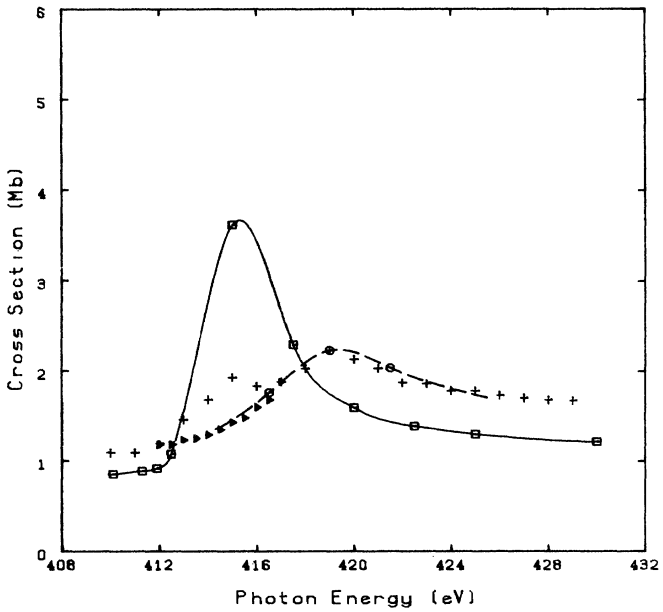

FIG. 2. K-shell photoionization cross sections for N_2: ——, present FCHF results; — — —, present results with a relaxed ion core shifted so as to agree with the experimental data at 419.5 eV; +, experimental data of Ref. 26; ▲, estimated one-electron portion of the experimental cross sections (Ref. 26).

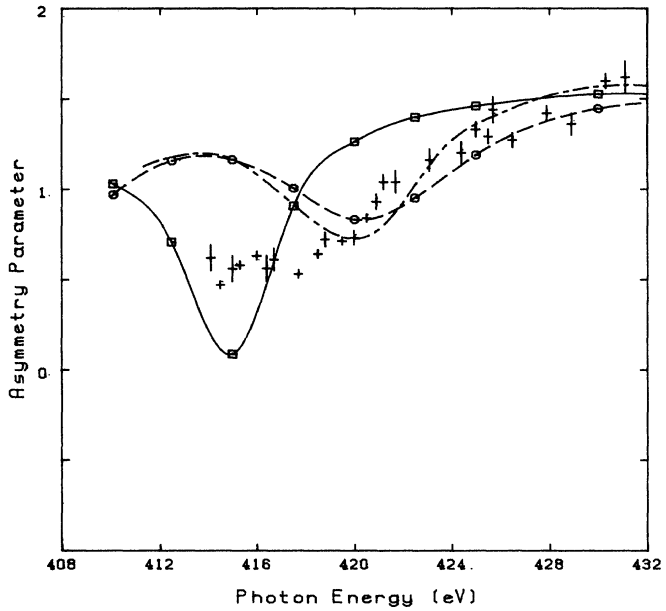

FIG. 3. K-shell photoelectron asymmetry parameters in N_2: ——, present FCHF results; — — —, presents results with a relaxed core; —·—·—, CMSM results of Ref. 6; +, synchrotron radiation data of Ref. 28.

dense enough distribution of poles in the resonance region and, in turn, this led to a broadening of the resonance structure. These differences are analogous to those seen in the calculated cross sections for the $C\,^2\Sigma_g{}^+$ state of $CO_2{}^+$ where a prominent resonant feature both in our results[15] and those of Collins and Schneider[10] is essentially smoothed away by the STMT method.[27]

Figure 1 also shows the K-shell cross sections obtained using a relaxed HF ionic core and the corresponding continuum orbitals. A comparison with the frozen-core results shows that core relaxation has decreased the cross section near threshold dramatically, broadened the resonance, and shifted it to higher energy. The resonance position is now at too high an energy suggesting that the model of a completely relaxed ionic core has led to excessive screening of the hole.[17] The use of a localized hole potential should reduce this screening and pull the resonance down to lower energy. However, the general shape of the relaxed-core cross sections is quite similar to that of the experimental data and, to illustrate this, Fig. 2 shows these cross sections for a limited range of photon energy shifted so that their peak position coincides with that of the measured cross sections. In this figure we also show the one-electron portion of the photoionization cross section as estimated by Kay, van der Leeuw, and van der Wiel.[26] As expected, relaxation effects are seen to be much less important in resonant photoionization of the $3\sigma_g$ level of N_2.[24]

Figure 3 shows our calculated photoelectron asymmetry parameters using both the frozen- and relaxed-ionic core models, the CMSM results,[6] and the experimental data of Lindle.[28] From these results we see that core relaxation has broadened and shifted the pronounced minimum seen in these asymmetry parameters in the frozen-core model. Although the asymmetry parameters of the relaxed-core model again show a minimum at higher energy than do the measured values, the overall shapes of these curves are quite similar around their minima. A shift of these calculated asymmetry parameters to lower energy by the same amount as the cross sections were shifted in Fig. 2 shows this more clearly.[24]

IV. CONCLUSIONS

We have studied the effects of core relaxation on resonant K-shell photoionization in N_2. Our results, obtained using the model of a completely relaxed ion core for the final state, show that these effects are very important for this system. The role of core relaxation will have to be carefully evaluated in studies of related K-shell processes in other systems, e.g., CO and CO_2.

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