Rapid Communications

Molecular orientation following K-shell photoionization

D. L. Lynch
Department of Chemistry, Brown University, Providence, Rhode Island 02912
(Received 26 December 1990)

Molecular-orientation parameters for K-shell photoionization of the $N(1s)$ and $C(1s)$ orbitals of N_2 and CO, calculated using Hartree-Fock continuum states, are reported. These studies were motivated by recent measurements of the $N(1s)$ orientation parameter, where substantial shape-resonance enhancement is observed, and by earlier indirect studies of molecular orientation for both $N(1s)$ and $C(1s)$ photoionization via the angular distributions of Auger-electron emission. Through the shape-resonance region nearly isotropic Auger-electron angular factors were obtained by fitting the calculated (continuum multiple-scattering method) molecular-orientation parameters to these latter measurements. However, based on the present results one can extract larger Auger angular factors than previously reported. This supports the earlier prediction of uniquely molecular effects in K-shell Auger processes, i.e., anisotropic emission. In addition, the present results show that to obtain accurate shape-resonance-enhanced molecular-orientation parameters, the Hartree-Fock approximation including relaxation effects must be invoked.

INTRODUCTION

Near-edge K-shell spectroscopy provides a wealth of information about the dynamics of photoabsorption and photoionization processes. Such studies include detailed analysis for the production of highly excited neutral molecules, above-threshold resonance structure, and core-hole relaxation pathways.[1] For example, intense features are observed below threshold in the photoabsorption spectrum.[2] This structure results from excitation into unoccupied valencelike levels, often characterized by $1s \rightarrow \pi^*$ transitions, and into Rydberg states. As the photon energy increases and crosses the ionization potential broad structure is observed in the photoionization cross sections and is attributed to single-particle shape resonances. These resonances can be viewed[3] as the $1s \rightarrow \sigma^*$ analog of the discrete, below-threshold, $1s \rightarrow \pi^*$ transitions. In either case one expects the photoabsorption to be enhanced in specific directions, i.e., either parallel or perpendicular to the electric-field vector, due to the definite symmetry of the resonance state, even for randomly oriented gas-phase molecules. The realization that resonances induce enhancement of photoabsorption in definite directions and creates orientation of the neutral or ionic molecular axis was originally predicted 10 years ago by Dill, Swanson, Wallace, and Dehmer.[4]

The photoexcitation of either discrete or quasibound resonant states, which have characteristic energies or energy regions, implies that molecular orientation has dramatic photon energy dependence. However, as a result of shorter lifetimes relative to discrete excited states, shape-resonance-enhanced molecular-orientation occurs over much broader energy ranges. In contrast to the photoexcitation of discrete states photoionization processes contain contributions from nonzero nonresonant final states, which typically absorb perpendicular to the resonant direction and, thereby, affect the degree of molecular orientation. In fact, using the continuum multiple-scattering method (CMSM), substantial enhancement of the molecular-orientation parameter in shape-resonance regions was predicted.[4]

Probing molecular orientation for both discrete and continuum resonances has been the goal of several recent experiments.[5-8] The earlier set of experiments[5-7] are attempts to investigate molecular orientation *indirectly* by measuring the angular distribution of Auger electrons. These electrons are emitted during the relaxation of the highly excited neutral or ionic state produced by K-shell photoabsorption or photoionization. Dill *et al.*[4] first proposed that these Auger angular distributions probe the anisotropy of photoabsorption.[4] The asymmetry of the Auger electrons carries information on both the initial molecular orientation and on the nature of the subsequent Auger emission. Therefore the K-shell hole must undergo nonisotropic Auger decay for the angular distributions of these electrons to be an effective probe of molecular orientation. Unlike rigorously isotropic atomic K-shell Auger decay,[9] Dill *et al.*[4] suggest that molecular K-shell holes

should undergo nonisotropic Auger decay due to the nonspherical potential.

Measurements by Lindle *et al.*[5] for N(1s) Auger decay of N_2^+ and by Truesdale *et al.*[6] and Becker *et al.*[7] for C(1s) Auger decay of CO^+ demonstrate that the asymmetry parameters for Auger electrons through shape-resonance regions are nearly zero, indicating isotropic emission. However, the discrete C(1s) $\rightarrow \pi^*$ transition in CO does produce significantly nonzero asymmetry parameters[7] in agreement with theoretical predictions.[4] Becker *et al.* have attributed the above threshold spherically symmetric angular distributions to isotropic Auger decay of the 1s molecular hole, analogous to atomic K-shell Auger processes and in contrast to the suggestion by Dill *et al.*[4] discussed above.

More recently Yagishita *et al.*[8] have *directly* measured the molecular-orientation parameter for K-shell photoabsorption of N(1s) in N_2 for both the discrete and continuous portion of the spectrum using angle-resolved photon spectroscopy. These experiments measure the angular distributions of the photofragments produced in the K-shell photoexcitation process and explicitly demonstrate significant molecular orientation through both the discrete (≈ 401 eV) and quasibound shape-resonance (≈ 419 eV) regions confirming the prediction[4] of anisotropy in K-shell photoabsorption. Indeed the CMSM calculations of Dill *et al.*[4,10] are in qualitative agreement with measured molecular-orientation parameters and cross sections.

In efforts to obtain a more complete picture of the shape-resonance enhanced photoionization dynamics, static exchange calculations for the molecular-orientation parameters have been performed for N(1s) and C(1s) photoionization of N_2 and CO using the iterative Schwinger variational method.[11-13] The purpose of these studies is to provide a quantitative estimate of the molecular-orientation parameter and to investigate the relation between these calculated values and the observed isotropic Auger-electron emission. While the CMSM often provides a reasonable qualitative description of photoionization, it is known to overestimate the effects of shape-resonance features.[11,12] In fact, the present studies show that the shape-resonance enhanced molecular-orientation parameter is smaller than the values obtained using the CMSM, leading to the conclusion that molecular Auger-electron emission may be more anisotropic than previously reported, and illustrate the value of performing calculations at the Hartree-Fock level of approximation.

Previous studies in atomic[14,15] and molecular[12,13] photoionization have shown that the frozen-core approximation, where the restructuring of the molecular ion upon creation of a K-shell hole is neglected, is inadequate for K-shell shape-resonance regions. In the calculations reported here, well recognized relaxation effects have been approximately included by using the fully relaxed ion core wave function, which provides a reasonable description of K-shell photoionization.[12-15] The results of these calculations for the molecular-orientation parameter are compared to available experimental data and help in under-

standing the observed isotropy of the Auger-electron emission measurements.[5-7] The methodology and calculational details are presented in the next section, results and discussion follow, and the final section contains conclusions.

METHOD AND CALCULATIONS

In the static exchange approximation the Hartree-Fock continuum orbitals are solutions of the following one-electron Schrödinger equation

$$\left[-\tfrac{1}{2}\nabla^2 + V(\mathbf{r},R) - \frac{1}{r} - \frac{k^2}{2} \right] \phi_{\mathbf{k}}(\mathbf{r},R) = 0 , \qquad (1)$$

where $k^2/2$ is the kinetic energy, V is the static exchange potential for the core-hole molecular ion with the Coulomb component removed, and $\phi_{\mathbf{k}}$ satisfies the appropriate boundary conditions.[11] The scattering potential V is determined by either the core orbitals of the neutral molecule [frozen core Hartree-Fock approximation (FCHF)] or by the orbitals of the relaxed ion [relaxed core Hartree-Fock approximation (RCHF)]. The solution of Eq. (1) for the single-particle continuum functions was obtained using the iterative Schwinger variational method.[11-13]

The Hartree-Fock solutions of Eq. (1) are used to calculate the dipole transition moments required for the photoionization cross sections and photoelectron angular distributions. In the FCHF approximation, where orthogonality is maintained between the initial- and final-state wave function, the photoionization cross section reduces to

$$\sigma = \frac{4\pi^2\omega}{3c} |\langle \varphi_{1s}|\mu|\varphi_{\mathbf{k}}\rangle|^2 , \qquad (2)$$

where $\varphi_{1s}(\varphi_{\mathbf{k}})$ is the single-particle function representing the 1s core hole (photoelectron), μ denotes the dipole moment operator, ω is the photon frequency, and c is the speed of light. However, in the RCHF approximation the initial- and final-state wave functions are nonorthogonal since the final state is constructed with the orbitals of the molecular ion while the initial state is represented by the orbitals appropriate for the neutral molecule. The treatment of this nonorthogonality as well as the details of the calculations for the bound and continuum functions have been described and discussed previously.[12,13]

Assuming the two-step mechanism for Auger decay, i.e., the photoionization and Auger emission are independent, the form of the angular distribution of Auger electrons was derived by Dill *et al.*[4] As pointed out in Ref. 4, Auger lifetimes are typically much shorter than rotational state spacing so that it is reasonable to assume that the Auger decay occurs before the molecule rotates. The asymmetry parameter for Auger-electron emission is

$$\beta = \beta_m c_a , \qquad (3)$$

where β_m is the photon-energy-dependent molecular-orientation parameter and measures the degree of molecular orientation along or perpendicular to the electric-field

vector. This orientation parameter is determined by the difference of the σ and π components of the photoabsorption strengths;

$$\beta_m = \frac{2D_\sigma^2 - 2D_\pi^2}{D_\sigma^2 + 2D_\pi^2} . \qquad (4)$$

The photon-energy-independent constant c_a characterizes the angular distribution of Auger-electron emission and is given in Ref. 4. Dill et al.[4] remark that by calculating (or measuring) β_m, the Auger angular factor (c_a) can be extracted from the measured β values. This is how c_a is obtained in Refs. 5-7. For the discussion below it is important to note that each two-hole final-state produced via Auger decay will be characterized by different Auger coefficients, c_a. However, the experiments to date have not resolved individual Auger two-hole final states, therefore the extracted constants (c_a) are averaged values.

RESULTS AND DISCUSSION

A. $N_2 K$-shell photoionization

In Fig. 1 the calculated molecular-orientation parameters β_m for $N(1s)$ photoionization are reported in both the FCHF and RCHF approximations and are compared to the experimental results of Yagishita et al.[8] As discussed earlier[12] the use of the frozen-core approximation overestimates the intensity and underestimates the width of the shape resonance feature in both the cross section and photoelectron asymmetry parameters. Moreover, use of the FCHF approximation places the resonance too close to threshold relative to the experimental position. Use of the relaxed core approximation is a more appropriate choice for calculating resonant K-shell photoionization parameters. In this case the resonance is broadened, reduced in magnitude, and shifted to higher energy. Using the RCHF approximation the overall shape of the photoionization cross section is significantly improved, although the resonance appears ≈ 4 eV above the experimental position.[12] As displayed in Fig. 1 these same effects are observed in the molecular-orientation parameters and reinforce the use of the RCHF approximation for K-shell studies. For example, the position where β_m increases as a
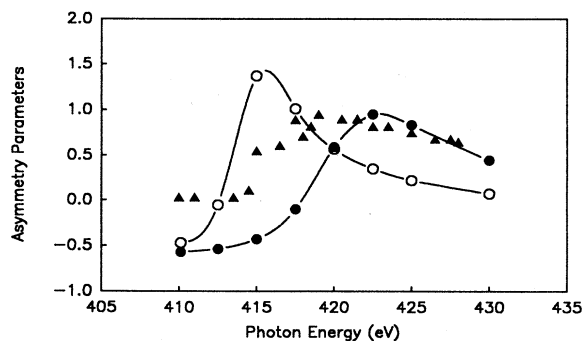
result of the shape resonance is ≈ 4 eV too high in these calculations but the overall shape is in good agreement with the experimental results of Yagishita et al.[8] This 4 eV shift coincides with the difference between the peak in the calculated versus experimental cross sections and most likely results from the use of the fully relaxed, delocalized hole representation of the molecular ion.

The $k\sigma$ shape-resonance enhances photoionization and produces the photon-energy dependent structure observed in the molecular-orientation parameter through the $\approx 415-425$ eV energy range. Comparisons to the CMSM results[4] (not shown) indicate that the use of this model potential overestimates the maximum of β_m (≈ 1.25 at maximum versus the present value of ≈ 1). However qualitative agreement is obtained between the present and the earlier CMSM calculations. It is important to note that the maximum in the molecular-orientation parameter is significantly reduced in magnitude when the more realistic RCHF approximation, relative to the CMSM or FCHF approaches, is used. This reduction in magnitude has important consequences for the understanding of the apparent isotropic Auger-electron emission of the K-shell hole.

Measurement of the angular distributions of the Auger electrons produced in $N(1s)$ decay has been performed by Lindle et al.[5] These measurements reveal that the Auger asymmetry parameter β, Eq. (3), is essentially zero through the shape-resonance region. Using the calculated β_m^4, which indicate substantial molecular orientation ($\beta_m^{max} \approx 1.25$), and their experimental β values, Lindle et al.[5] extract a $c_a \approx 0.06$. Various explanations for this near zero value were discussed[5] and include the following: (i) Since the measurements did not resolve individual two-hole final states the c_a is an averaged value and the averaging produces a nearly zero result. (ii) All the two-hole final states individually decay isotropically. (iii) The two step mechanism for Auger decay is invalid. However as Fig. 1 reveals the β_m maximum is closer to 1 than 1.25. This reduction, when using the calculated β_m to fit c_a from the experimental β values, allows an increase in c_a of roughly 25%. In contrast to the $C(1s)$ of CO, more thoroughly discussed below, this still leaves c_a very small, i.e., unresolved Auger emission in N_2 is essentially isotropic in shape-resonance regions.

B. $C(1s)$ K-shell photoionization

The molecular-orientation parameters for $C(1s)$ photoionization of CO have not been measured directly. However similar to N_2, calculations by Dill et al.[4] indicate that molecular orientation is enhanced through the shape-resonance region. The angular distributions of the Auger electrons for the decay of the $C(1s)$ hole state of CO^+ have been measured by Truesdale et al.[6] and Becker et al.[7] As in $N(1s)$ photoionization the measured β is essentially zero above the ionization threshold. Becker et al.[7] fit the measured β values with the calculated β_m of Ref. 4 to extract a $c_a \approx 0.15$ and attribute the isotropy of the emitted Auger electrons to the nearly spherically symmetric $1s$ decay of molecular K-shell levels. Again it is very important to note that the measurements in both Refs. 6 and

FIG. 1. The molecular-orientation parameter β_m for $N(1s)$ photoionization of N_2; -O-, present results using the FCHF approximation; -●-, present results using the RCHF approximation; ▲, measured values from Yagishita et al. (Ref. 8).

7 are averaged over several two-hole final states. For example, in the experiments by Becker et al.[7] the Auger electrons from several of the most intense two-hole final states were collected.

Static-exchange calculations for the $C(1s)\,\beta_m$ of CO have been performed to determine the degree of molecular orientation in the shape-resonance region. The results of the RCHF calculations are displayed in Fig. 2 and compared to the CMSM results.[4] The FCHF and RCHF approximations have been invoked and again a dramatic reduction in the maximum of β_m occurs when the RCHF is used. For clarity only the RCHF results are plotted in Fig. 2.

As seen in Fig. 2 the present results produce a $\beta_m^{max} \approx 0.75$, which is substantially smaller than the original CMSM estimate. While no explicit fitting procedure has been performed for c_a one can estimate that a substantially larger value can be extracted from the measured β values using the smaller RCHF β_m results reported in Fig. 2. A larger c_a coefficient indicates *intrinsic anisotropy* of molecular K-shell Auger-electron emission. This is in contrast to purely isotropic atomic K-shell decay and in agreement with the original prediction of nonspherical Auger decay by Dill et al.[4] It is important to reemphasize that the Auger data is averaged over several two-hole final states. Such averaging could reduce the observed anisotropy in the Auger emission. In fact, preliminary calculations[16] for these Auger factors as a function of different two-hole final states suggest that averaging the most intense peaks significantly reduces c_a. Such averaging effects may also play a role in producing the observed isotropic distributions of Auger electrons in the $N(1s)$ decay discussed above. In light of these results additional experiments, with resolution of individual two-hole final states, would be extremely helpful in unraveling the underlying physics of the angular distributions of Auger-electron emission.

CONCLUSIONS

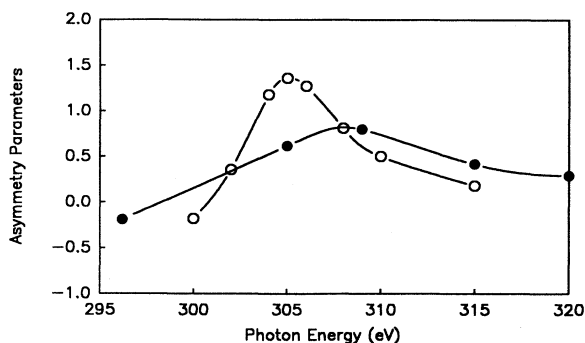The degree of molecular-orientation produced in $N(1s)$ and $C(1s)$ photoionization of N_2 and CO has been calcu-

FIG. 2. The molecular-orientation parameter β_m for $C(1s)$ photoionization of CO; -●-, present RCHF results; -O-, CMSM values from Ref. 4.

lated in the RCHF approximation. It has been seen that the use of a realistic scattering potential, i.e., the static-exchange level with core relaxation included, is crucial for a quantitative calculation of photionization parameters such as the molecular-orientation parameter. The use of these accurate scattering potentials reduces the peak magnitude of β_m in shape-resonance regions which in turn increases the expected anisotropy of Auger-electron emission. In the case of $C(1s)$ photoionization this increase is significant and supports the earlier predictions that, unlike atomic systems, molecular K-shell Auger-electron emission can be anisotropic. More elaborate calculations for the $N(1s)$ and $C(1s)$ Auger angular factors, including relaxation and correlation effects, for both K-shell molecular ions and the $1s \rightarrow \pi^*$ neutral excited states are in progress.

ACKNOWLEDGMENTS

[1]See, for example, *EXAFS and Near Edge Structure*, edited by A. Bianconi, L. Incoccia, and S. Stipcich, Series in Chemical Physics 27 (Springer-Verlag, New York, 1983).

[2]C. T. Chen, Y. Ma, and F. Sette, Phys. Rev. A **40**, 6737 (1989).

[3]See, for example, H. Lefebvre-Brion, in *Giant Resonances in Atoms, Molecules, and Solids*, edited by J. P. Connerade, J. M. Esteva, and R. C. Karnatak, NATO Advanced Studies Institutes Series B Vol. 151 (Plenum, New York, 1987), p. 301.

[4]D. Dill, J. R. Swanson, S. Wallace, and J. L. Dehmer, Phys. Rev. Lett. **45**, 1393 (1980).

[5]D. W. Lindle, C. M. Truesdale, P. H. Kobrin, T. A. Ferrett, P. A. Heimann, U. Becker, H. G. Kerkhoff, and D. A. Shirley, J. Chem. Phys. **81**, 5375 (1984).

[6]C. M. Truesdale, D. W. Lindle, P. H. Kobrin, U. E. Becker, H. G. Kerkhoff, P. A. Heimann, T. A. Ferrett, and D. A. Shirley, J. Chem. Phys. **80**, 2319 (1984).

[7]U. Becker, R. Holzel, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, Phys. Rev. Lett. **56**, 1455 (1986).

[8]Akira Yagishita, Hideki Maezawa, Masatoshi Ukai, and Eiji Shigemas, Phys. Rev. Lett. **62**, 36 (1989).

[9]W. Mehlhorn, Phys. Lett. **26A**, 166 (1968); B. Cleff and W. Mehlhorn, Phys. Lett. **37A**, 3 (1971); J. Phys. B **7**, 593 (1974).

[10]D. Dill, S. Wallace, J. Siegel, and J. L. Dehmer, Phys. Rev. Lett. **41**, 1230 (1978); **42**, 411(E) 1979.

[11]R. R. Lucchese, K. Takatsuka, and V. McKoy, Phys. Rep. **131**, 147 (1986).

[12]D. L. Lynch and V. McKoy, Phys. Rev. A **30**, 1561 (1984).

[13]J. Schirmer, M. Braunstein, and V. McKoy, Phys. Rev. A **41**, 283 (1990).

[14]See, for example, H. P. Kelly, S. L. Carter, and B. E. Norum, Phys. Rev. A **25**, 2052 (1982); M. Ya. Amusya, V. K. Ivanov, S. A. Scheinerman, S. I. Sheftel, and A. F. Ioffe, Zh. Eksp. Teor. Fiz. **78**, 910 (1980) [Sov. Phys. JETP **51**, 458 (1980)].

[15]R. S. Williams and D. A. Shirley, J. Chem. Phys. **66**, 2378 (1977).

[16]D. L. Lynch (unpublished).