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Molecular-Photoelectron Angular Distributions as a Probe of Dynamic Symmetry Breaking

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(Received 20 July 1978)

Molecular-photoelectron angular distributions are shown to depend qualitatively on symmetry-breaking hole localization during inner-shell photoionization. This is illustrated by comparing localized and delocalized calculations of the asymmetry parameter $\beta(\epsilon)$ for K-shell photoionization of N_2 in the vicinity of the f-type shape resonance at approximately 10 eV above threshold. Comparison with the isoelectronic CO shows that the K-shell $\beta(\epsilon)$ for N_2, in the localized treatment, resembles that for the K shell of oxygen rather than carbon in CO.

Ionization of molecular core states which are distributed on two or more equivalent atomic sites can lead to states of the residual ion in which the vacancy is effectively localized on a single equivalent site, prior to becoming filled by Auger or radiative decay. In this Letter we show that the lowering of molecular symmetry accompanying hole localization during the photoionization process (dynamic symmetry breaking) has a dramatic effect on the spectral variation of molecular-photoelectron angular distributions. This effect can be traced to additional couplings in the final state, induced by the lowered symmetry of the molecular core. Hence, photoelectron angular distributions probe the effects of hole localization on the ejected-electron wave function, and thus complement the evidence based on the total energy of the ionic hole state first described by Bagus and Schaefer.[1]

To illustrate the effects of dynamic symmetry breaking on inner-shell photoionization, we calculated the integrated cross section and photoelectron asymmetry parameter for K-shell photoionization of N_2 in the vicinity of the f-type ($l = 3$) shape resonance at ~10 eV kinetic energy.[2-7] The calculations were performed using the continuum–multiple-scattering model,[8,9] and will be described fully elsewhere.[10] Briefly, the delocalized-case calculations were performed as before[4,5] with both the initial and final state calculated in the same self-consistent-field ground-state potential based on Slater exchange with $\alpha = 1$. This is known[4,5] to reproduce the position of the σ_u shape resonance rather well. The localized-case calculation employed the same initial state but a final state generated from a potential in which the energy-dependent Hara-exchange[11,12] approximation was used. This model permits one to explicitly specify the configuration of the residual ion, which in this case is N_2^+ with an electron removed from the $1s\sigma$ orbital of one atom. Thereby the spectators explicitly determine this potential (rather than the average of the ground-state charge distribution as in Slater exchange). The question which arises, however, is to what extent are the spectators relaxed (resembling N_2^+) or unrelaxed (resembling N_2). We are currently examining this problem, but as of yet we cannot give a definite answer. In the present preliminary calculation, we simply compromised and allowed the spectators to partially relax in a transition-state–like calculation with $\alpha = 1$, in which one-half of a hole resided in the $1s\sigma$ of the active atom. We vigorously stress that the magnitude of the effect we discuss below *does* depend on the energy position of the resonance and thus upon this choice (which places the resonance at approximately the energy of the delocalized calculation) and therefore results must be regarded as qualitative and schematic. In particular, the effect is enhanced the nearer the resonance to threshold. However, we must also stress that the qualitative aspects of the coupling mechanism discussed below do not depend on these details. Experimental results will be crucial to the further refinement of our ideas concerning hole-localization effects on β beyond this rather primitive stage.

The main results are given in Fig. 1, which clearly indicates the consequences of localized-versus delocalized-hole treatments on K-shell photoionization of N_2. In the absence of localization, β exhibits a flat behavior with only little variation in the vicinity of the shape resonance. Concentrating the hole on one nitrogen atom, however, induces a large ~0.9 oscillation in β through the resonance. By contrast, the integrated cross section is relatively insensitive to hole treatment. Based on this prototype calculation, we anticipate that inner-shell–photoelectron angular distribution measurements in the vicinity of molecular shape resonances will be a useful probe of the dynamics of hole localization during the photoionization process.

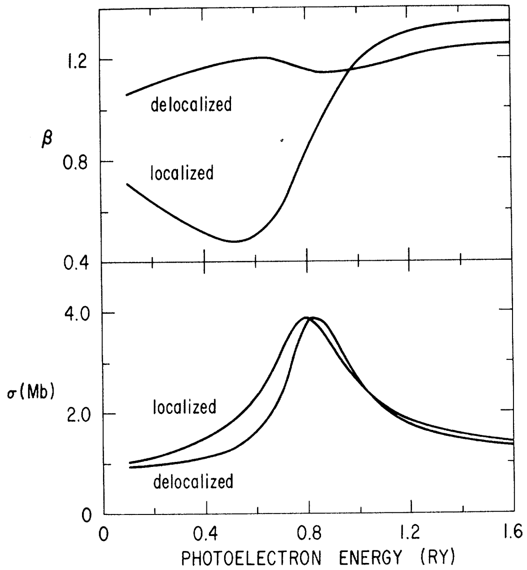

FIG. 1. Photoelectron asymmetry parameter, β, and integrated cross section, σ, for localized and delocalized treatments of K-shell photoionization of N_2.

The large difference between the $\beta(\epsilon)$ curves in Fig. 1 is a direct consequence of the symmetry-breaking aspect of hole localization. In the absence of localization, the molecular field is identical on the two atomic sites, and the residual molecular ion and the photoelectron each exhibit inversion symmetry separately. Hence, even and odd partial-wave components of the photoelectron wave function are uncoupled. Our earlier calculation[4,5] based on this picture exhibited a prominent shape resonance in the integrated cross section, which was traced to the $l = 3$ component of the σ_u channel. Note that the (delocalized-case) asymmetry parameter reported in Refs. 4 and 5 is wrong,[13] because of a phase error in Eq. (12) of Ref. 5, and that the comment there comparing the (incorrectly) calculated structure with the well-known[14,15] oscillations of atomic β's across shape resonances is inappropriate anyhow. In the atomic cases most often cited—the outer p-shell photoionization in Ar, Kr, and Xe—the oscillation in β is due to the Cooper minimum[16] which falls on the high-energy side of the d-type shape resonance. At the resonance position the $p \to \epsilon d$ channel completely dominates over the $p \to \epsilon s$ channel, resulting in very little interference between them and a smooth behavior in β. Near the Cooper minimum in the $p \to \epsilon d$ channel, however, the $p \to \epsilon d$ photocurrent is reduced by the cancellation in its dipole matrix element and the $p \to \epsilon s$ and ϵd channels are thereby of comparable magnitude, resulting in substantial interference and a large oscillation in β. However, for atoms and molecules alike, this effect does not occur in ionization from compact localized states, such as the N_2 core levels, because the nodal structure of the final-state wave function depends only weakly on energy within the inner shell because of the depth of the well near the nucleus. Significant energy variation in this case requires[17] the substantial interference of two or more partial waves populated by coupling through the anisotropic molecular field. The failure of the delocalized $\beta(\epsilon)$ curve to have such variation can clearly be attributed to the dominance of a single asymptotic partial wave (essentially pure f). When the symmetry is broken,[18] however, by hole localization, coupling to the s and d partial-wave components is allowed and, although the resonance is still predominantly f in character, the interferences with induced resonances in the $l=0$ and $l=2$ components in the σ ionization channel cause the large oscillation in $\beta(\epsilon)$ in the localized treatment. By contrast, these induced resonances do not substantially alter the integrated cross section since they have the same spectral variation as the uncoupled f resonance and their interference vanishes.

To create some perspective for these results, localized-hole calculations of $\beta(\epsilon)$ were performed on the K shells of CO. In CO, of course, even and odd asymptotic partial waves are coupled regardless of vacancy treatment. The CO and N_2 K-shell $\beta(\epsilon)$ results are shown in Fig. 2. This comparison makes one immediate, qualitative statement: The localized-hole N_2 $\beta(\epsilon)$ resembles $\beta(\epsilon)$ for the oxygen end of CO, and not the carbon end. We tentatively attribute this to the effective increase in nuclear charge on the ionized nitrogen atom which would cause it to resemble more closely the higher-atomic-number atom in CO (cf. Table III of Ref. 1). It is this qualitative feature, independent of actual numerical values, which could be most easily tested by experiment.

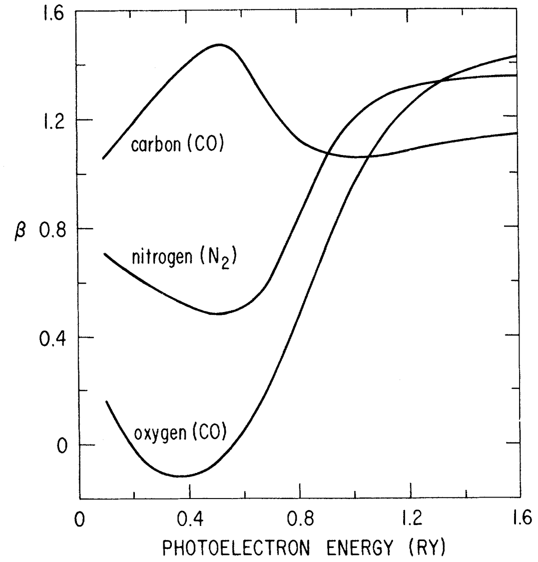

FIG. 2. Photoelectron asymmetry parameters for K-shell photoionization of CO and N_2.

The importance of analogous effects in photoelectron angular distributions of other molecules depends on three circumstances which are satisfied in several molecular systems. First, the molecule must contain equivalent atoms, whose alteration leads to a reduction of molecular symmetry. Second, the lifetime of the inner-shell hole (both with respect to filling and redistribution on equivalent atoms) must exceed the escape time of the photoelectron. K-hole lifetimes in light atoms are limited by Auger decay, whose lifetime[19] is $\hbar/\tau < 0.3$ eV for Ne and $\hbar/\tau < 0.6$ eV for Ar. Therefore for molecules containing atoms from the first two rows, and having shape resonances with half-widths exceeding these decay rates, the hole will live long enough to influence the resonant photoelectron. (Here we assume that the atomic Auger widths are not appreciably changed by the molecular environment.) This situation definitely obtains in N_2, SF_6, and BF_3, to name a few examples. Third, the equivalent-atom, inner-shell spectrum must exhibit shape resonances which indicate a band of quasibound, localized states in the continuum. Dynamic-symmetry-breaking effects on β may be important in nonresonant cases as well, but we tentatively suggest that resonances help amplify the effect and make it clearly observable.

This work was performed under the auspices of the U. S. Department of Energy and supported by National Science Foundation Grant No. CHE78-08707 and American Chemical Society Petroleum Research Fund Grant No. 10785-AC6.

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Collisional Redistribution of Weak Resonance Radiation

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(Received 24 May 1978)

We derive simple expressions for the collisional redistribution function which are not restricted by impact theory and hence encompass the cases of excitation and detection far from resonance. For an isolated resonance line, the redistribution function depends only on quantities already involved in the absorption profile. This implies simple relations between results obtained from light-scattering experiments and those obtained in emission or absorption spectroscopy.

In recent years increasing theoretical[1-3] and experimental[4-7] activity has centered on the study of the redistribution of resonance radiation by collisions. While this problem has for long been prominent in astrophysics,[8] it has received renewed interest in laboratory physics with the advent of tunable dye lasers. Frequency-selective laser scattering has indeed been revealed as a powerful tool for gas and plasma diagnostics as well as for the determination of atomic and molecular properties, interatomic potentials, etc.

The theoretical framework in which the redistribution problem has generally been treated is the impact theory.[1,2] As was stressed repeatedly,[6,7] this theory imposes serious restrictions on the frequency domain of both the incident and scattered light. Indeed, the validity is limited to frequency separations from the line center smaller than typical inverse collision durations. Hence this theory does not account for excitation nor detection far from resonance.

The breakdown of the impact theory on the line wings has recently been demonstrated experimentally[6,7] by displaying a strong asymmetry of the fluorescence signal with respect to the sign of the laser detuning around the resonance frequency. According to the predictions of the impact theory, the signal would not depend on the sign of the detuning.

A recent approach aimed at a more general theory[8] seems to be of limited validity in the frequency region beyond the impact domain because it leads to a fluoresence line profile which in some cases of far-wing excitation may become partly negative. This is to be traced to a factorization, in Ref. 3, of the time-evolution operator corresponding to separate time intervals in which collisions are treated independently.

Our purpose is to establish an expression for the redistribution function in the framework of quantum electrodynamics and quantum statistics. We define this function formally as the probability per unit time, $p(a,b)$, for an atom (undergoing collisions) to scatter one present photon from mode a into mode b. This notion makes sense for weak radiation intensities because the scattering probability in the presence of any number n_a of photons in mode a is then just proportional to n_a.

Let us consider one atom (A) embedded in a gas of N perturbers (P) and a radiation field (R). Using obvious notation, we write the Hamiltonian of the whole system APR as

$$H = H_A + H_P + H_R + V_{AP} + V_{AR} + V_{PR}. \quad (1)$$

To write transition probabilities we will em-