Variation of Cross-Section Enhancement in Decay Spectra of CO under Resonant Raman Conditions

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We have measured participator and spectator decay at several photon energies within the range of the lifetime-broadened first vibrational component of the C $1s \rightarrow \pi^*$ resonance in CO. From the branching ratios it is evident that the resonant enhancement is different for single-hole and two-hole–one-electron states: The maximum in the resonant intensity peaks at different photon energies. It now becomes necessary to calculate energy-dependent transition matrix elements within the lifetime-broadening range. [S0031-9007(96)01669-9]

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The Auger equivalent of the resonant Raman effect has recently received much attention in the atomic and molecular photoionization literature. The basic feature, made possible by the availability of very narrow bandwidth photon sources, is the measurement of the decay spectrum of a particular resonant core state below the ionization threshold with a resolution better than the natural linewidth of the resonance. In this way, it is possible to "overcome" the lifetime of the core hole created in the primary excitation, and to measure decay spectra in a hitherto inaccessible linewidth regime. The possibility of getting into a new sub-lifetime-broadening range is very important in itself, since it allows the observation of phenomena which are, in principle, present but usually masked due to the poor instrumental resolution, which is the case for the majority of decay spectra published to date. The main results reported for decay spectra measured under resonant Raman conditions are the observation of energy dispersion and line narrowing for peaks resulting from both participator and spectator lines [1–4]. (Participator lines correspond to singly ionized valence final states and spectator lines to two-hole–one-electron final states.) The resonant Raman condition has, for example, been used in a study of condensed Ar on Pt(111), where it was nicely demonstrated that participator and spectator lines (often referred to as resonant Auger lines) show energy dispersion, while normal Auger lines do not [5]. Although these observations are important, however, they are essentially a consequence of energy conservation, and do not constitute in themselves a new class of phenomena.

In this Letter we report the first observation of an effect of a different nature which appears not to have been observed so far in resonant photoemission of atoms and molecules. We show that for CO the branching ratios of participator and spectator lines in the decay of the C $1s^{-1}\pi^*$ resonance exhibit significant changes as a function of photon energy in a range within the natural linewidth of the absorption curve. Decay spectra were measured at several different photon energies within the first vibrational sublevel ($\nu' = 0$) of the absorption curve (the study of vibrationally resolved decay spectra measured for different vibrational components will be the subject of a forthcoming paper [6]). This is only possible for CO; in all other diatomic molecules, either the absorption profile incorporates several vibrational states (as in the case of O_2) or, when the vibrational structure is partially resolved, vibrational interference is the strongest effect in the decay spectra (as in the case of N_2) [7]. There is no trivial explanation for this observation in CO, and we conclude that an energy-dependent transition matrix element picture of the resonant process has to be invoked. A consequence of this experimental finding is that the usual approximation of considering the matrix elements describing the resonant process as energy independent within the linewidth of the primary excitation [8] does not necessarily hold.

The measurements were performed on the X1B beam line at the NSLS, Brookhaven National Laboratory. The spherical grating monochromator and the angle-resolved cylindrical mirror electron energy analyzer (CMA) have been described elsewhere [9]. A recent improvement has been the installation of a new 800 lines/mm laminar grating which gives higher resolution and flux, particularly at the O K edge.

The absorption curve for the C $1s \rightarrow \pi^*$ resonance in CO, shown in Fig. 1, has three almost completely resolved vibrational components at 287.40, 287.66, and 287.91 eV [10]. The total width of the peaks, including the lifetime and the instrumental broadening, is 96(2) meV. From a fit of the absorption curve with a convolution of a Lorentzian to account for the natural linewidth and a Gaussian to include the monochromator function, we obtain values of 83 meV for the lifetime broadening [comparable with the value 85(3) meV reported in the literature [10]] and 30 meV for the photon bandwidth. We therefore took decay spectra in the photon energy range 287.28–287.56 eV in steps of 40 meV, which is wider than our monochromator function.

The decay spectra were measured at the magic angle, so that angular distribution effects do not affect the relative intensities. Three single lines are well resolved in the higher

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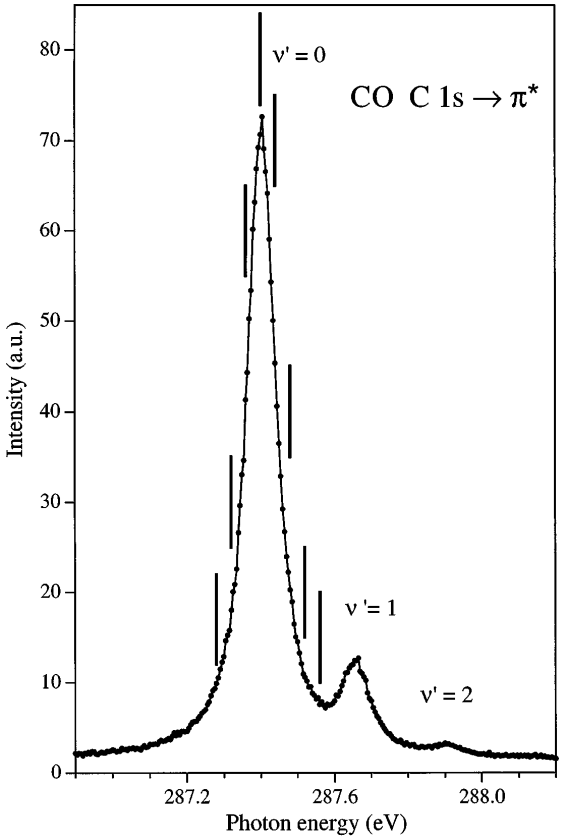

FIG. 1. Absorption spectrum of the C $1s \rightarrow \pi^*$ transition in CO. The curve was obtained in the total electron yield mode. The vertical lines mark the photon energy values (at intervals of 40 meV) where decay spectra were recorded.

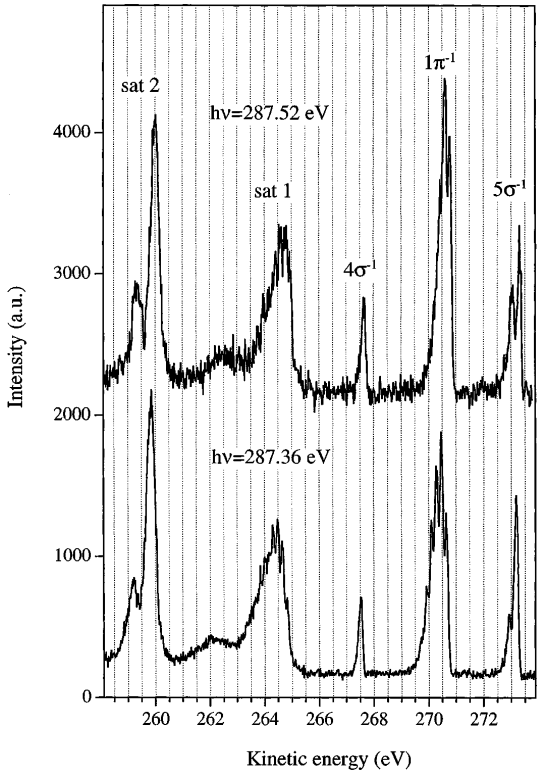

FIG. 2. Decay spectra taken at photon energies of 287.36 eV, close to the top of the absorption peak (bottom spectrum), and 287.52 eV, on the high-photon-energy side of the absorption peak (top spectrum). The participator lines are the valence single-hole states $5\sigma^{-1}$, $1\pi^{-1}$, and $4\sigma^{-1}$, while the spectator lines are the valence satellites, divided in two subgroups, sat1 and sat2. The purpose of the vertical grid lines is to highlight the shift of 160 meV to higher kinetic energy on going from the bottom to the top spectrum.

kinetic energy region at binding energies of 14.01, 17.00, and 19.70 eV, corresponding to the $5\sigma^{-1}$, $1\pi^{-1}$, and $4\sigma^{-1}$ single-hole valence states, respectively. The vibrational fine structure is well resolved on all three lines, although we chose not to set the CMA at the best attainable resolution, but rather to achieve a reasonable compromise between linewidth and measuring time. In the lower kinetic energy part of the spectrum, several overlapping lines are present, corresponding to several two-hole–one-particle states, or valence satellites. A detailed assignment has been reported in the literature, at least for the main components of this unresolved structure [11]. The satellite structure is divided here into two main kinetic energy regions, 265.5–260.5 eV and 260.5–258 eV, labeled sat1 and sat2, respectively. Figure 2 shows two spectra, taken at photon energies of 287.36 eV, slightly lower than the resonance maximum (bottom spectrum) and 287.52 eV, on the high-photon-energy side of the resonance (top spectrum).

There are some obvious differences between the two spectra in Fig. 2, the main one being the relative intensity of the 1π main line which is clearly larger in the top spectrum. The change in the satellite structure in the kinetic energy range 265.50–260.50 eV is not quite so obvious, but is evident from the branching ratios (see Fig. 3 and discussion below). We can also detect the fingerprint of vibrational interference, which slightly affects the general appearance of the single-hole participator features in spectra taken at the photon energies of 287.52 and 287.56 eV, i.e., close to the $\nu' = 1$ absorption peak. This effect has already been demonstrated [7,12], although only one spectrum at the maximum of the $\nu' = 0$ peak was recorded due to wider photon bandwidth. The main effect of interference, however, is to change the line shape, and not the total intensity, so that it is not important in the following discussion.

We also observe that all participator and spectator lines show energy dispersion, shifting in kinetic energy according to the photon energy change. This energy dispersion is one of the main effects claimed in the literature as a fingerprint of the resonant Raman effect. Since, in the present case, however, the initial and final states are uniquely defined by the primary excitation, this shift is simply a consequence of energy conservation, and we feel it should not be categorized as a new effect.

In Fig. 3 (top panel) we show the branching ratios (B.R.) determined in the photon energy range 287.28–287.56 eV.

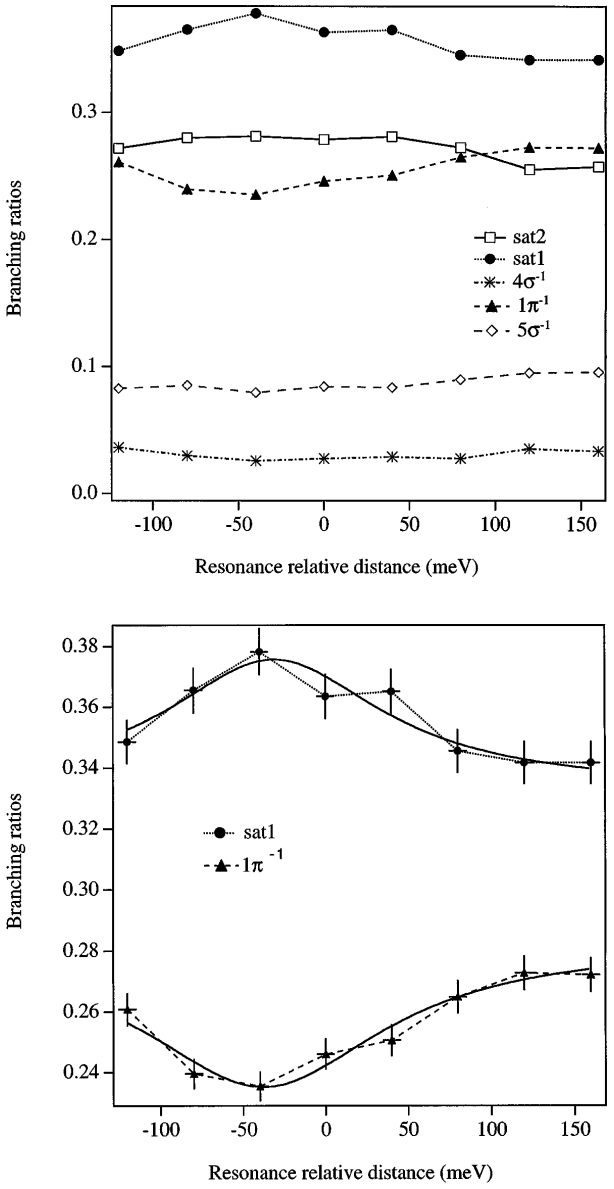

FIG. 3. Top panel: branching ratios for the participator and spectator lines shown in Fig. 2. Bottom panel: expanded view of the branching ratios for the states $1\pi^{-1}$ and sat1, which show the strongest effects. The smooth fit serves to underline the observed trend. A shift of the extrema in the B.R. with respect to the absorption maximum (about 40 meV) is evident.

The B.R. for the sat1 and $1\pi^{-1}$ lines are shown in the bottom panel on an expanded scale, together with a smooth fit intended to underline the observed trend. The B.R. were obtained by deriving the integrated intensity separately for the three single-hole states and for the two satellite regions sat1 and sat2. No attempt was made to deconvolute these complex satellite structures. The integrated intensities were obtained using the same fitting procedure for all peaks to avoid systematic errors. The error bars shown are related only to the fitting procedure, since other possible fluctuations cancel when the B.R. are derived. We also include errors deriving from a slight drift in photon energy due to the heating of optical elements in the undulator beam line, which is corrected by measuring the absorption curve every few decay spectra. The general trend in Fig. 3 is well outside the error bars; as noted above, the effect can already be qualitatively observed by simply looking at the spectra.

The most evident experimental finding while scanning across the resonance is, of course, an overall increase in the count rate for all participator and spectator lines on going from the minimum toward the resonance maximum. This is due to photon "detuning," and it is a well-known and rather obvious effect. The most interesting new finding in the present case is that the cross sections do not increase to the same extent for all peaks in the decay spectrum. The most evident features in Fig. 3 are a maximum and minimum in the B.R. for the sat1 and $1\pi^{-1}$ lines, respectively, which are centered slightly below the absorption maximum.

The first relevant finding is that such an effect is observed at all. One could expect the B.R. to be constant because the initial and final states are the same, and therefore effects resulting from different degrees of transferred energy (as would be the case for different vibrational components of the absorption feature) cannot play a role. The results thus show that, under resonant Raman conditions, other effects may occur which are usually masked by the core-hole lifetime broadening. These can only be probed when the photon bandwidth is much narrower than the linewidth of the primary excitation. Although the effect may appear rather small, we note that the change in relative intensity of the $1\pi^{-1}$ line is actually about 15%, which is not at all negligible.

The next step is to try to explain the observed variation in cross-section enhancement on the basis of the states involved. We note that both the single-hole state and some of the satellites contributing to the peak labeled sat1 in Fig. 2 have π symmetry. According to the experimental [11] and theoretical [13] assignments, the main contribution to sat1 derives from $^2\Pi\, 5\sigma^{-2}2\pi^1$ and $^2\Pi\, 1\pi^{-2}2\pi^1$ states. Symmetry is likely to play a role in the observed variation in the B.R. because it is well known that states with π symmetry will couple more strongly to the primary excitation. For example, it has already been reported that the $1\pi^{-1}$ main line in the decay spectrum is more strongly enhanced than the main lines with σ symmetry; the satellites with π symmetry also show the same effect [11]. Although the effect in the B.R. is more evident in the states with π symmetry, we cannot entirely rule out similar, but weaker, effects in the σ channels. Such an effect cannot be seen clearly in the present data, although there are possibly hints for it in the B.R. of the $4\sigma^{-1}$ and $5\sigma^{-1}$ states.

We propose here a qualitative explanation for the effect, with the aim of also stimulating further theoretical work. The main point is that resonant phenomena cannot be described in terms of a primary excitation followed by

subsequent decay, but, rather, a unified picture is needed, since the key point is the "memory" of the intermediate state which is reflected in the final states. We attribute the observed effect to the fact that, for different photon energies within the lifetime-broadened resonance, the intermediate excited state is slightly different, and therefore its projection onto each of the final states can vary as a function of photon energy. The variation in the branching ratios is due to the fact that the maximum overlap occurs at slightly different photon energies for spectator and participator lines, namely, at lower photon energy for the satellite states, which explains the slight offset of the features in the B.R. with respect to the absorption maximum.

We are also able to rule out a more trivial explanation for the observed effect: the relative weight of direct photoemission. A constant contribution to the single-hole lines from direct photoemission could lead to a "flattening" of the resonant intensity compared with the satellite intensity, and thus to the observed effect in the branching ratios. We have therefore measured a valence photoemission spectrum at 290.30 eV, i.e., at a photon energy value close to the resonance but off the main absorption peak. The spectrum shows only detectable intensity in the single-hole states. The total contribution of direct photoemission for all three main lines, however, is found to be in the range 0.3%–3% across the resonance, and therefore is too weak to explain the observed trend in the branching ratios.

In conclusion, we have observed different cross-section enhancement for spectator and participator decay as a function of photon energy across the $\nu' = 0$ component of the C $1s^{-1}\pi^*$ resonance in CO using a photon bandwidth much narrower than the lifetime-broadened linewidth of the absorption peak. There are stringent instrumental requirements for this experiment, and even then it is only possible for CO, where well-defined vibrational states can be prepared. A relative increase and a relative decrease, respectively, in intensity are observed for satellite states (spectator decay) and single-hole states (participator decay) with π symmetry. We stress the usefulness of operating under the so-called resonant Raman conditions to derive information not readily available otherwise. The observation reported here appears to be the first example of a resonant Raman "effect" not simply related to energy conservation. It now appears necessary to reconsider resonant processes in terms of transition matrix elements which vary over the photon energy range of the lifetime-broadened primary excitation.

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