Collapse of Vibrational Structure in the Auger Resonant Raman Spectrum of CO by Frequency Detuning

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Observations made in the $C1s \rightarrow \pi^*$ Auger resonant Raman spectra of carbon monoxide demonstrate that the vibrational structure in such spectra is strongly frequency dependent. In the limit of narrow bandpass photon excitation, the vibrational excitations of the 5σ participator transition collapse to one single line within a sub-eV detuning range. The effect is explained in terms of a generalized duration time for the resonance process, in which the lifetime of the core excited state and the inverse of the detuning frequency play equal roles.   [S0031-9007(97)03626-0]

Resonant autoionization of molecules has recently attracted considerable interest from both the experimental and the theoretical points of views. One important ground for this interest is that new synchrotron radiation facilities, notably undulator based sources, have become operative also for gas-phase measurements, and that electron spectrometers, capable of very high resolution even at high kinetic energies, have been developed for use together with synchrotron radiation. Although radiationless resonant inelastic scattering was observed as early as 1980 [1], it was not until 1993 that one could observe the first autoionization spectrum in the vacuum ultraviolet energy range, where the electron lines showed both dispersion with the photon energy and a subnatural line sharpening [2]. This is commonly referred to as the Auger resonant Raman (ARR) effect. Having subnatural resolution in the experiment, both in the excitation and deexcitation, opens up the possibility to study fine effects of detuning the excitation energy from the nominal resonance energy. The pioneering experiment in this context was performed on krypton [3], showing that measured Auger electron line profiles vary strongly with the detuning. This effect, which depends on the distribution of the exciting radiation, i.e., it is specific for the type of monochromator used and of its settings, may in some cases even lead to a doubling of the observed Auger lines. For atoms one has reached a rather detailed understanding of the influence of the photon spectral function on the dispersion law and shape of the x-ray Raman scattering profile, with several theoretical predictions [4–7] verified by experiment [3,8].

It has now become apparent that the dispersion law and the appearance of resonant Raman effect is also strongly influenced by nuclear dynamics, and that spectra of molecules show nontrivial behavior on detuning the frequency [9,10]. Most spectacular is the observation of Skytt *et al.* [9] that symmetry breaking in the x-ray resonant Raman spectrum of CO_2 is quenched when the excitation energy is detuned from the nominal resonance energy. In the present work, we show that frequency detuning not only is consequential for symmetry selection, but that the vibrational structure in general is distorted or even collapsed upon frequency detuning. This effect is principally different from the type of detuning observed for atoms [3,8].

We have measured the ARR spectrum of the CO molecule at several energies near to the $C1s^{-1}\pi^*(\nu' = 0)$ resonance, and we have observed the collapse of the vibrational fine structure of the band associated to the singly ionized X final state. We also observe an interesting "reverse" development of the band shape of the B state. The collapse effect, which also is a measure of the time it takes for the vibrational wave packet to develop, demonstrates the dynamic, frequency dependent, behavior of resonant ionization of molecules in general. The main result of the present work is that the vibrational structure in ARR spectra depends strongly on the excitation energy for narrow-band excitation. Thus when detuning the excitation energy below the x-ray absorption resonance, the effective vibrational structure is significantly distorted from its on-resonance pattern. For final states referring to ionization in nonbonding orbitals, as the 5σ orbital in CO, detuning leads to a complete collapse of the vibrational structure to one single line.

The buildup of the vibrational fine structure "takes time" (τ) and the degree of involvement of the core excited state potential energy surface critically depends on the duration (τ_c) of the ARR process (Fig. 1) [9,11,12]. If the duration time is much smaller than the time of the deformation of the nuclear wave packet at the intermediate state energy potential surface, the molecular frame does not adapt to this potential, but will be determined directly by the final state potential (Fig. 1). Far from resonance the resonant process is prompt while on-resonance the lifetime of the resonant state determines the interaction time. Detuning from resonance shortens the duration of the ARR process [9,11], and one probes preferentially transitions associated with shorter duration times, for which the influence from the core excited state
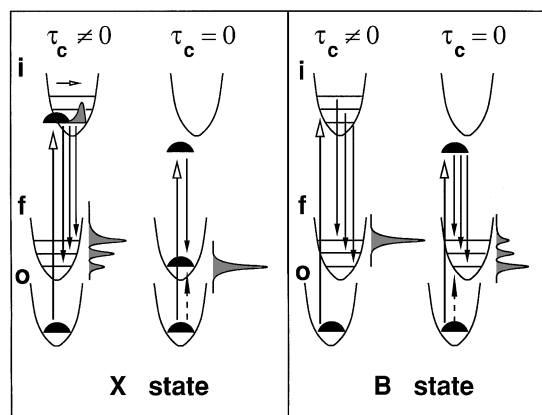
FIG. 1.   Pictorial representation of the ARR participator processes referring to the X and B states of CO^+ for on-resonance and for detuned excitation.

has diminished. The corresponding transition amplitude is then proportional to the Franck-Condon factor between ground state and final state vibrational wave functions. So if these two potential surfaces are close to each other, then the ARR spectral profile collapses to a single line (Figs. 1, 2, and 3).

The experiments were performed at the high energy undulator beamline 51 at the MAX I storage ring in Lund, Sweden [13]. This beamline is provided with a high resolution SX-700 plane grating monochromator. Recently, an end station [14] including a high resolution electron spectrometer has been installed at the beamline. The spectrometer is rotatable around the direction of the photon beam. In the present study, for intensity reasons, the electron spectrometer was set in the plane of the polarization of the almost completely linearly polarized light. At the photon energy corresponding to the maximum of

the π^* resonance, the ratio between direct photoemission and the resonant participator contribution has been estimated to be on average 0.7% for the X, A, and B final states. This value was obtained by recording the one-hole (1h) part of the spectrum at resonance and at 4.5 eV below resonance where the resonant population of (1h) final states is negligible. We refer to the works of Domke $et\ al.$ [15] and Ma $et\ al.$ [16] for recent recordings of the C1s x-ray absorption spectrum of CO.

To study the resonant contribution corresponding to a finite detuning frequency, numerical simulations based upon Eqs. (1) and (3) (see below) have also been carried out. For these simulations we have used an intermediate state lifetime width of 85 meV [17,18] and a photon bandwidth of 100 meV. The Franck-Condon factors for ground to intermediate and intermediate to final states were calculated from Morse potential curves. Any possible lifetime vibrational interference effects are included in this simulation method. For comparison with experiment, the spectrometer broadening was taken into account by a convolution with a Gaussian of 100 meV. In Ref. [18] a detailed description of the numerical simulation method together with the spectroscopic constants used to generate the Morse potential curves for ground, core-excited, and final ionic states is given. The parameters used in the present simulations are recapitulated in Table I.

The collapse effect is very well illustrated by the participator Auger decay from the $C1s^{-1}\pi^*$ state of the CO molecule. This decay leads to three main final states of CO^+; the $X\,5\sigma^{-1}\,{}^2\Sigma^+$, $A\,1\pi^{-1}\,{}^2\Pi$, and $B\,4\sigma^{-1}\,{}^2\Sigma^+$ states. As seen in Figs. 2 and 3, the vibrational envelopes of these transitions are very sensitive to frequency detuning. Following the trends from small to large detuning frequencies, the vibrational profiles soon resume the
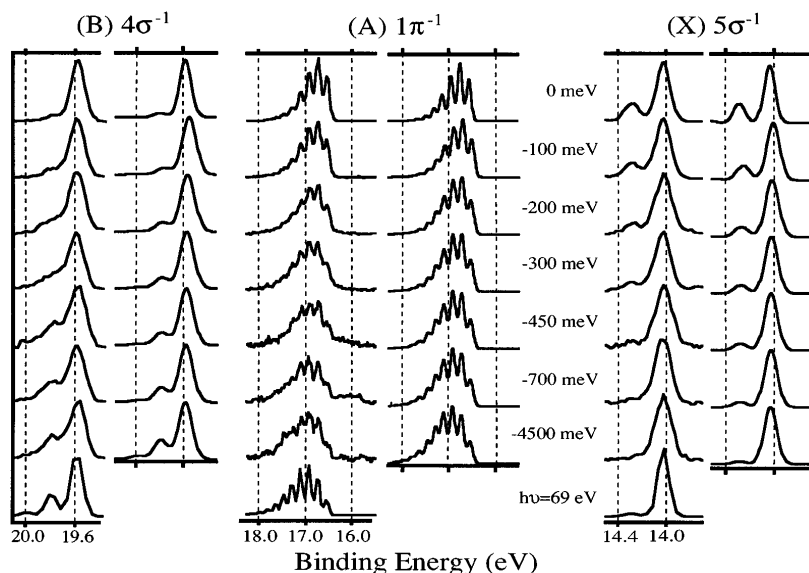

FIG. 2.   Frequency detuned $C1s^{-1}\pi^*$ ARR participator spectra of CO leading to three main final states of CO^+; the $X\,5\sigma^{-1}\,{}^2\Sigma^+$, $A\,1\pi^{-1}\,{}^2\Pi$, and $B\,4\sigma^{-1}\,{}^2\Sigma^+$ states. Left columns display the measured spectra; right columns display results of the simulations.
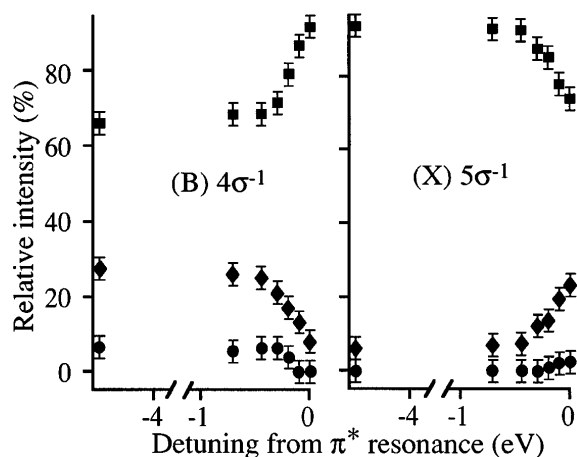
FIG. 3. Variation of relative intensities for the vibrational levels of the X and B states upon frequency detuning. Squares display $\nu' = 0$, diamonds $\nu' = 1$, and circles $\nu' = 2$.

character of the corresponding direct transitions. There is both a *trivial* and a *nontrivial* origin behind this collapse. For large detuning frequencies the ratio between resonant and direct transition amplitudes becomes small, so the vibrational profile *trivially* resumes the character of that for direct photoemission. However, as seen in Figs. 2 and 3, even at a small detuning frequency, starting from about -300 meV, the profiles have practically resumed the character of the direct photoemission. At such a small detuning frequency the resonant amplitudes are more than 6 to 7 times higher than those for the direct transitions. This *nontrivial* cause for vibrational collapse can thus refer only to the resonant contribution. As can be seen from Fig. 2, the simulated spectra strongly resemble the experimentally obtained spectra. This indicates that the direct contribution has a negligible impact on the decay spectra and that the collapse of vibrational structure observed for a small detuning frequency is due to the resonant contribution only. This close resemblance is true for all detuning frequencies between 0 and -700 meV, showing that the collapse effect can be understood within the time independent description based upon Eq. (3). In particular, the collapse of the X state to nearly just one single vibrational component already at -300 meV detuning is well reproduced in the simulated spectra.

While the A state of CO^+ shows complex vibrational profiles at both resonant and nonresonant frequencies, the

TABLE I. Spectroscopic constants used for calculations of the Morse potential curves.

	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	$R_e/\text{Å}$
CO (ground state)	2169.813	13.288	1.1283
CO C1s-π^*	2083.550	15.320	1.1529
$CO^+(X^2\Sigma^+)$	2214.240	15.160	1.1151
$CO^+(A^2\Pi)$	1562.060	13.530	1.2437
$CO^+(B^2\Sigma^+)$	1734.180	27.927	1.1687

X and B states show very simple features, which can be used to illustrate the vibrational collapse. As seen in Figs. 2 and 3, the X state has a second vibrational level excited at resonance, but collapses to a single line for large detuning. The B state shows a reverse behavior, i.e., a single line at resonance but additional vibrational levels off-resonance. These remarkable features can be traced to the short and long resonant duration times and to the matching of potential energy surfaces. The final X state refers to ionization of the nonbonding 5σ orbital, and so the minimum of its potential curve is very close to that of the ground state (GS), whereas the potential energy curve of the B state is very close to that of the core excited state [15,19]. As easily inferred from the Franck-Condon principle, the latter situation leads to only one strong band for the GS-core-B resonant process (the 0-0 and 1-1 transitions between the core and B states have almost the same energies), while the GS-core-X band still shows a distinct vibrational excitation at resonant energy. A dynamic, wave packet illustration is included in Fig. 1, which also shows the case for detuned frequency (or short duration times). For the X band a short duration time means that the wave packet has no time to propagate on the shifted core excited state potential, but is transferred instantaneously on the unshifted final X state potential. It will accordingly not deform at all and the band profile collapses to a single line. For the B state detuning has the implication that the wave packet deforms to a new equilibrium on the shifted B state potential, and a vibrational envelope will develop. In the resonant B case the wave packet was already deformed by the shifted core excited potential, and no further deformation occurred for emission to the equally shifted B state.

Let us now outline shortly the key steps of the collapse effect in the framework of the time-independent representation. The spectral properties of the ARR scattering are guided by the double differential cross section

$$\sigma(\epsilon, \omega) = \sum_{f, n_f} |F_{n_f}|^2 \Phi(\Omega' - \Omega + \omega_f n_f, \gamma) \quad (1)$$

convoluted with the unit normalized spectral function of the exciting radiation Φ having the width γ. We consider here the case of narrow band excitation to the i*th* core excited electronic state. The amplitude $(F_{n_f} = F_{n_f}^R + F_{n_f}^{NR})$ of absorption of x-ray photon of frequency ω with subsequent emission of an Auger electron of energy ϵ consists of nonresonant and resonant contributions

$$F_f^{NR} = \alpha_f \langle n_f \mid o \rangle, \quad (2)$$

$$F_{n_f}^R = \beta_f \sum_{n_i} \frac{\langle n_f \mid n_i \rangle \langle n_i \mid o \rangle}{\Omega' + \omega_f n_f - \omega_i n_i + \iota\Gamma}, \quad (3)$$

where all unessential constants are collected in α_f and β_f. $\Omega = \omega - [E_i - E_o + (\omega_i - \omega_o)/2]$ and $\Omega' = \epsilon - [E_i - E_f + (\omega_i - \omega_f)/2]$ are the detuning of the

photon frequency and photoelectron energy from the resonant frequencies of adiabatic (0-0) absorption and emission transitions, respectively. E_j, ω_j, and n_j denote the equilibrium electronic energy, vibrational frequency, and vibrational quantum number of the electronic state, $j = o, i, f$. The present simulations are based on Eqs. (1) and (3). In the general case the resonant amplitude F_f^R must be summed over all close lying core excited electronic states $|i\rangle$. But for the CO molecule, the carbon core excited state $|i\rangle = |1s^{-1}\pi^*\rangle$ is well separated from higher levels (~ 5 eV), and we can restrict ourselves to a single electronic resonance approximation (3).

According to Eq. (3) the ARR spectral profile is broadened with vibrational structure determined both by the core excited and the final states. Let us tune the incoming photon frequency away from resonance with absorption transition C1$s \rightarrow \pi^*$: $\tau_c \ll \tau$. Here $\tau_c = 1/\sqrt{\Omega^2 + \Gamma^2}$ is the duration time and $\tau \sim 1/\Delta$ the time of deformation of the nuclear wave packet [11], and Δ is the effective vibronic broadening (second moment) of the ARR profile. The narrowing of the ARR spectral profile will take place for $|\Omega| > \Delta \sim 0.2$ eV, since $\tau_c/\tau \sim \Delta/|\Omega| < 1$. In the case of narrowband excitation, this means that the summation in F_f^R over intermediate vibrational levels $|n_i\rangle$ can be made complete ($\sum_{n_i} |n_i\rangle\langle n_i| = 1$) and the scattering amplitude takes the form of fast ARR scattering: $F_f = \langle n_f | o\rangle[\alpha_f + \beta_f/(\Omega + \Gamma)]$. The ARR cross section (1) collapses to a single resonance (Fig. 1(b))

$$\sigma(\epsilon, \omega) = \Phi(\Omega' - \Omega, \gamma)\rho \qquad (4)$$

when the potential surfaces of ground and final states coincide: $\langle n_f | o\rangle = \delta_{n_f,o}$. The quantity $\rho = \sum_f |\alpha_f + \beta_f/(\Omega + \iota\Gamma)|^2$ describes the interference of resonant and nonresonant contributions, which thus is unimportant for the collapse effect at large detuning, and for this particular CO case unimportant also for small detuning, as follows from the simulation. For the rather particular structure of the C1$s \rightarrow \pi^*$ band, with one strongly dominating vibronic transition, we thus expect to observe collapse at a detuning of ~ 0.2 eV based on estimations from the duration time, whereas the simulations together with experimental data show that this collapse occurs at ~ 0.3 eV.

In summary, we have experimentally verified, through detuning the photon frequency from the resonance, that the vibrational structure of spectral bands of the Auger resonant Raman (or equivalently the resonant photoemission) process is strongly frequency dependent when a narrow-bandpass excitation is used. We have demonstrated that detuning leads to a quenching, even collapse, of vibrational structure. We have applied simple arguments based on scattering theory to explain the effect. The theory shows that the frequency detuning effectively shortens the duration time of the ARR process and that in the limit of large detuning the transitions between the

initial ground state and the final states can be regarded as sudden. The results presented here are of great significance also to resonant x-ray emission studies, and are also of relevance for resonant photoemission experiments involving solids.

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