

Vibrationally resolved resonant Auger spectroscopy of formaldehyde at the $CI s^{-1} \pi^*$ resonance.

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INTRODUCTION

Resonant Auger (RA) spectroscopy has benefited greatly from advances in both light sources and electron spectrometer techniques in the past decade. Transitions to molecular orbitals are particularly interesting to study using RA spectroscopy due to the dynamics induced in the excited state. When it is not dissociative, changes in the molecular geometry induced by the excitation allow the RA decay process to sample different parts of the potential energy surface of the molecule that can not be accessed directly by single photon absorption and extensive vibrational structure is often observed in the participator decay. Such studies have been performed with vibrational resolution for a number of simple diatomic or triatomic [1,2] molecules and start being explored for larger molecules. In this work, vibrationally resolved RA spectra of gaseous formaldehyde have been measured under resonant Raman conditions at several photon energies on the $CI s^{-1} \pi^*$ resonance. Utilizing high-resolution photoexcitation, specific vibrational states of the $CI s^{-1} \pi^*$ resonance were selectively populated. Participator Auger decay of the excited state populates mainly the A-D ionic states, without any discernable increase in the intensity of the X state. The vibrational manifold of the A state band was examined in details for resonant and non-resonant photoionization. The observations are attributed to changes in the potential energy surfaces.

EXPERIMENT

The experiments were carried out on beamline 10.0.1, which delivers more than 10^{12} photons/sec in 0.1% bandwidth. The photoelectron spectra were measured with a GammaData Scienta SES-200 hemispherical analyzer in a spectrometer system developed exclusively for gas phase experiments. Monomeric formaldehyde in the gas phase was obtained by heating to 70°C the sample cell containing the dimerized form paraformaldehyde (Aldrich, 96% purity). The presence of monomeric formaldehyde and its purity were verified by measuring the outer valence photoelectron spectrum.

RESULTS

A low-energy electron yield spectrum of the $CI s^{-1} \pi^*$ resonance shown in Fig.1 was first measured with the present apparatus to provide good calibration of the energy scale for the subsequent RA measurements. This spectra gives also an idea of the extent of excitation for each normal mode ν_1 mostly C-H stretching, ν_2 C=O mostly stretching, ν_3 mostly HCH bending (Table 1). Vibrationally resolved RA spectra were recorded at the energies corresponding to the positions indicated on Fig.1 and are shown of Fig.2. RA spectra a-c were measured at photon energies corresponding to the excitation of primarily ν_2 quanta in the excited state. The position of the peak intensity steadily increases through higher vibrational levels in the ionic state as higher ν_2 vibrational levels are accessed in the core excited state. The trend continues for spectra d-f although the vibrational levels populated in the excited state become less clear due to the probability of exciting mixtures of quanta ν_1 and ν_3 . This behavior can be qualitatively explained: the change from spectrum a to c is mainly due to the excitation of the higher levels of the ν_2 manifold of the A state, as the vibrational transitions originate from the $\nu_2=0,1,2$ levels of the core excited state respectively. Consequently, the maximum intensity shifts from the $\nu_2=0$ (spectrum a) to the $\nu_2=2$ level (spectrum c) of the final ionic state A. The spectrum has quite different appearance, as now the vibrational transitions originate from the $\nu_1=1$ level, but the $\nu_2=2$ manifold again comes from the ground level of the core excited state (as for spectrum a). Thus the $\nu_2=0$ final state is again populated strongly, but the intensity is shifted to the higher levels in the ν_1 final state manifold. The next spectra e and f again display changes due to the intensity moving to the higher levels of the manifold. The vibrational states populated in the B state band are less obvious owing to the band's lower intensity, but similar trends are discernable. The dispersion of the vibrational intensity A and B state can be attributed to geometric changes in the potential energy surfaces (PES). Geometric changes in the H_2CO molecule upon excitation were reported by analysis of photoabsorption spectrum [3]. The C=O bond increases, while the

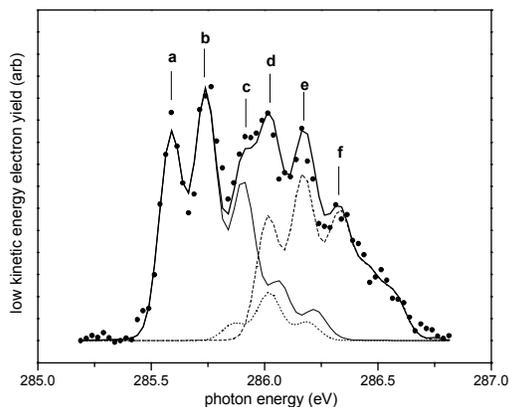


FIG.1 : Low energy electron yield of the $CI s^{-1} \pi^*$ resonance in formaldehyde measured with 75 meV photon resolution. The experimental data has been deconvoluted into contributions from different vibrational states using parameters from [3]. The positions where resonant Auger spectra were measured are indicated by the letters a-f.

C-H bond contracts. The A RA final state, results from the removal of a C=O bond in the ionic state and as such, the resonant decay occurs between two states with similarly displaced PES. Hence the v_2 vibrational quantum number of the excited state is preserved in the ionic state and reflected in the vibrational populations in the participator Auger decay lines. The v_1 progression is very strong, however, indicating that there is a large change in the C-H bond distance between the core excited and A ionic state

TABLE 1: Photon energies of the positions indicated of Fig. 1, where resonant Auger spectra were measured, and relative contributions of different vibrational levels to the $CI s^{-1} \pi^*$ band at those energies.

Label	Photon Energy	Vibrational State Contribution (total = 100)
a	285.59	(0,0,0) – 100
b	285.74	(0,1,0) – 100
c	285.89	(0,2,0) – 82 (0,0,1) – 10 (1,0,0) – 8
d	286.02	(1,0,0) – 52 (0,1,1) – 20 (0,3,0) – 14 (0,4,0) – 14
e	286.17	(1,1,0) – 76 (0,4,0) – 8 (0,5,0) – 8 (0,2,1) – 8
f	286.32	(1,2,0) – 78 (1,0,1) – 14 (1,1,1) – 8

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FIG. 2 : Vibrationally resolved resonant Auger spectra of the participator decay states of formaldehyde measured at the positions indicated on Fig.1 and in Table1.

