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Selective vibrational excitation in the resonant Auger decay following core-to-π^* transitions in N_2O

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ABSTRACT

In N_2O a detailed study of the vibrational distribution of the $\tilde{X}$ state reached after decay of core-to-π^* excitation of N terminal, N central and O 1*s* core levels is reported. We observe a change in the relative intensity of bending versus stretching modes while scanning the photon energy across all three resonances. While this effect is known to be due to the Renner–Teller splitting in the core-excited states, we could derive that the antisymmetric stretching is excited mainly in the decay of the N terminal 1*s*-to-π^* excitation. An explanation for such selectivity is provided in terms of interplay of vibrational structure on potential energy surfaces of different electronic states involved in the process.

1. Introduction

When a core electron in a molecule is excited, the core hole can relax by electron emission. The core-hole decay takes place within the time scale of few or few tens of femtoseconds. This time scale is of the same order as the period of molecular vibrations and therefore the nuclear motion of the molecule may affect the electronic decay dynamics [1].

An interesting aspect which can be probed by resonant Auger spectroscopy is the nuclear motion taking place in the core-excited state and its interplay with the Auger decay on the same time scale. Within a semiclassical picture, as soon as a wave packet is created on the potential energy surface of the core-excited state by the resonant excitation, this wave packet starts to propagate, exploring details of this surface and, at the same time, decaying to the various final states. The resonant Auger line profile measured will directly reflect the nuclear motion taking place in the core-excited state modulated by its relative shape and position with respect to the potential energy surface of the final state reached by Auger decay [2]. The geometry of the intermediate state can differ from that one of the ground state. As an example, core-excited states of linear molecules can be bent and those of planar molecules can be pyramidal. Such geometry change reflects in the properties of the Auger decay. Good examples of this so-called "dynamical Auger emission" have been reported for BF_3 and BCl_3 [3–5].

In more complex cases, a core-excited linear molecule can undergo Renner–Teller splitting [6–8] to stabilize the intermediate state, and this Renner–Teller effect has visible consequences in the vibrational distribution of the final states reached after resonant Auger decay. In triatomic molecules with a doubly degenerate core-to-π^* excited state, the twofold degeneracy is removed by the vibronic coupling with bending vibrations through the Renner–Teller effect and the core-to-π^* excited state is split into a in-plane and a out-of-plane excited states with bent and linear equilibrium geometries, respectively. Typical examples are OCS, CO_2, CS_2 and N_2O molecules which are linear in the ground state. Many spectroscopic studies were dedicated to the study of such nuclear dynamics induced by core excitation [2,9–18]. In the case of CO_2 and N_2O, the Renner–Teller splitting was found to be large, while it is of medium magnitude in OCS and very small in CS_2 [9,14].

In N_2O a conformational change from linear ($C_{\infty v}$ point group) to bent (C_s point group) takes place when a N 1*s* or O 1*s* core electron is promoted into the π^* (3π) unoccupied molecular orbital. Upon bending the degeneracy of the π^* orbitals in the $C_{\infty v}$ symmetry is lifted, giving rise to in-plane and out-of-plane orbitals in the C_s symmetry, corresponding to bent and linear structures, respectively, the bent being lowered in energy by bending of

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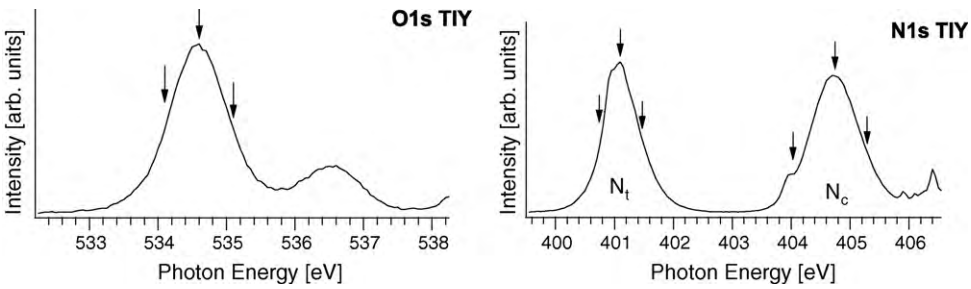

Fig. 1. Total ion yield spectra recorded in the vicinity of the N_t $1s$ and N_c $1s \rightarrow 3\pi$ (right part) and O $1s \rightarrow 3\pi$ (left part) transitions. The arrows mark the photon energies at which RAS spectra were recorded.

the molecule. Due to the linear conformation of the molecule in the ground state, and using the Franck–Condon principle for the core-to-π^* transitions, the bending mode will be strongly excited when the photon energy is tuned below the resonance maximum (negative detuning), while only stretching modes can be effectively excited when the photon energy is tuned above the resonance maximum (positive detuning) [2].

There are three normal vibrational modes associated with triatomic linear molecules: two stretching (ν_1 and ν_3) and a bending (ν_2) motion which is doubly degenerate in the ground state. In the case of N_2O, ν_1 and ν_3 are called quasi-symmetric and quasi-antisymmetric stretching modes which are associated mainly with the N–N and N–O stretching vibrations, respectively, and ν_2 corresponds to N–N–O bending vibrations.

Resonant Auger spectroscopy is a powerful method to identify the influence of the Renner–Teller splitting on the dynamics of core excitation–deexcitation, in particular in what concerns which vibrational modes in the final states reached after electron emission are affected by the reduced symmetry of the intermediate state.

In N_2O the vibrational structure of the $\tilde{X}$ state reached after participator decay following the excitation of the N terminal (N_t) $1s$ to the π^* virtual orbital has been studied in some detail [2]. In particular, it has been demonstrated that as the photon energy is varied across the resonance the vibrational structure of the final state changes dramatically. The change has been attributed to the fact that for excitations in the low-energy side of the resonance the bent intermediate state is more populated, with consequent increase in the bending vibrational progression in the final state, while for excitations in the high-energy side the stretching mode(s) become prominent in the final state. However, the resolution in [2] was not sufficient to perform a complete analysis of the vibrational distribution of the final state, in particular in what concerns the relative importance of the symmetric and antisymmetric stretching modes.

We present here a detailed analysis of the vibrational structure of the $\tilde{X}$ state in N_2O, reached after decay following the excitation of all three core levels, N terminal (N_t), N central (N_c) and O $1s$, to the π^* orbital. We indeed observe a change in the relative intensity of bending versus stretching modes while scanning the photon energy through the resonances. Furthermore, we were able to distinguish between the vibrational progressions due to the two different stretching modes, and therefore we can assess that the antisymmetric stretching mode is excited mainly in the decay of the high-energy side of the N_t $1s \rightarrow \pi^*$ resonance. An explanation for such selective excitation is provided in terms of interplay of vibrational structure on potential energy surfaces of the ground, intermediate and final states.

2. Experiment

The experiments were performed on the C2-branch of the soft X-ray beamline 27SU at the SPring-8 synchrotron radiation facility in Japan [19]. The radiation source is a figure 8 undulator and provides linearly polarized light: the polarization vector E is horizontal for the first-order harmonic light and vertical for the 0.5-order harmonic light [20]. The measurements were performed with the horizontal linearly polarized light. The monochromator installed on this branch is of Hettrick type [21]. The monochromator resolution was set to be around 50 meV at the N $1s$ edge. For the O $1s$ edge, the monochromator resolution was set to be around 50 meV for the excitation on the low and high photon energy sides of the O $1s \rightarrow \pi^*$ resonance; and to around 100 meV off-resonance and on top of the resonance. The high-resolution electron spectroscopy system employed consists of an SES-2002 hemispherical electron energy analyser, a gas cell and a differentially pumped main chamber [22]. The lens axis of the analyser is in the horizontal direction, and the entrance slit of the analyser is set parallel to the photon beam direction. The analyser resolution was set to be about 78 meV at the N K-edge and about 47 meV at the O K-edge.

The experimental total ion yield and resonant Auger decay spectra are presented in Figs. 1 and 2.

3. Calculations

The geometries of the ground, $\tilde{X}$ final cationic, both linear and bent N_t, N_c and O $1s \rightarrow \pi^*$ core-excited states were calculated with Dalton, a molecular electronic structure program [23], using Restricted Active Space RAS(16,12) wave function and ANO-1 (7s5p3d2f) basis sets for N and O atoms with an additional polarizing g function with exponent 1.43 on nitrogen and exponent 1.85 on oxygen. For all states, the doubly occupied core orbitals were inactive, i.e. not correlated. For ground states of the neutral and singly-ionized molecule were described at the Complete Active Space (CAS) level of theory, correlating 16 and 15 electrons for X and X, respectively. Within CS symmetry, the active space consists of 9 A' and 3 A" orbitals. The core-excited states were described in the RAS formalism, with 18 electrons distributed over the strictly singly-occupied core orbital (making up the RAS1 space) and a RAS2 space equal to the CAS space described for the ground states. Core-excited states were optimized with relaxed core orbital. Vibrational analysis calculations were also carried out for all the above-mentioned states. The results of the calculations are summarized in Table 1.

The minima of the potential energy surfaces were estimated in normal coordinates relative to the ground state for ν_1 and ν_3 vibrational modes.

The calculated $1s \rightarrow \pi^*$ transition energies are in a good agreement with experiment. The measured values of the peak maxima for the N_t, N_c and O $1s \rightarrow \pi^*$ resonances (401.1, 404.7 and 534.6, respectively [24]) fall between the theoretically predicted values of the linear and bent core-excited states of the Renner–Teller pair for all three edges. The calculated N–N–O angles of the bent core-excited states (115.6° (N_t–N_c–O*), 118.6° (N_t–N_c^*–O), 133.6° (N_t^*–N_c–O)) are in a good agreement with the previ-