

Vibration-induced suppression of valence-Rydberg mixing in the $O\ 1s \rightarrow ns\sigma$ Rydberg series in N_2O

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Symmetry-resolved ion-yield spectroscopy of vibrationally excited N_2O in the vicinity of the $O\ 1s$ ionization threshold has been carried out using an angle-resolved ion detection technique. The spectral intensity of the $O\ 1s \rightarrow ns\sigma$ Rydberg series, which has σ^* valence character, is significantly reduced by the excitation of the bending vibration in the electronic ground state. Using an *ab initio* analysis of the electronic part of the second moment (r^2), this suppression is interpreted as being due to a decrease in the mixing of the valence character in the $ns\sigma$ Rydberg states with decreasing bond angle.

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I. INTRODUCTION

In most studies of molecular photoabsorption it is assumed that nuclear motion is independent of electronic motion, i.e., that the Born-Oppenheimer approximation is valid. If, however, some of the electronic excited states are degenerate or nearly degenerate, nonadiabatic effects cannot be neglected [1]. In the core excitation region, angle-resolved ion yield spectroscopy is an effective method for studying this vibronic coupling [2–4].

The vibrational wave function of a molecule is spatially more spread out when the molecule has one or more quanta of vibrational excitation. Thus spectroscopic studies of vibrationally excited molecules can be used to probe different regions of the potential surfaces of electronically excited states. In molecules which have high degrees of symmetry, some vibrational modes cannot be observed in the single-photon absorption spectrum. However, some symmetry-forbidden vibrational modes can be observed by making use of symmetry breaking due to vibrational excitation. For example, Page *et al.* [5] found some symmetry-forbidden vibrational modes in the benzene molecule using an infrared-ultraviolet double resonance technique. Also, autoionizing Rydberg states of acetylene, which cannot be observed in conventional vuv absorption, have been studied using vuv synchrotron radiation to ionize state selected rovibrationally excited molecules prepared using ir laser excitation [6,7]. In our previous work [8,9], we have succeeded in observing dramatically enhanced vibronic coupling effects in the x-ray absorption spectra of vibrationally excited triatomic molecules, successfully demonstrating that x-ray absorption spectroscopy of vibrationally excited molecules can provide a benchmark test for probing vibronic coupling.

In this study, we demonstrate that vibrational excitation of the electronic ground state significantly affects the amount of

valence character observed in the Rydberg series in the x-ray absorption spectrum of the linear triatomic molecule N_2O . This change in character is a result of the changing character of the excited states as a function of bending angle. The ground state electronic configuration is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^4 ({}^1\Sigma^+),$$

where 1σ , 2σ , and 3σ are, respectively, the $O\ 1s$, $N_c\ 1s$, and $N_t\ 1s$ core orbitals, and the c and t subscripts label the “central” and “terminal” N atoms. In the $O\ 1s$ x-ray absorption spectrum of ground state N_2O molecules, the $ns\sigma$ Rydberg series appears with significant intensity due to a mixing of σ^* valence character in the Rydberg states [2,10,11]. In this work we show that excitation of the Rydberg states is significantly suppressed for ground state molecules in excited bending-mode vibrational states. Making use of *ab initio* calculations of the relevant potential surfaces and second moments we attribute this suppression to a decrease in the σ^* mixing due to a decrease in bond angle. We discuss this purification of the Rydberg character in terms of the vibronic coupling effect.

II. EXPERIMENT

The experiment was carried out at beam line 27SU [12] at SPring-8 in Japan, using the high-resolution varied line-spacing plane grating soft x ray monochromator [13]. The radiation source is a figure-8 undulator that can provide either horizontally or vertically linearly polarized soft x rays by setting the undulator gap appropriately [14,15]. Two identical ion detectors with retarding potentials of +6 V were orientated at 0° and 90° to the E vector of the horizontally polarized incident light [16,17]. The high-temperature sample gas was produced using a resistively heated molecular beam source. Angle-resolved ion yield (ARIY) spectra were recorded at source temperatures of 300 and 700 K. The

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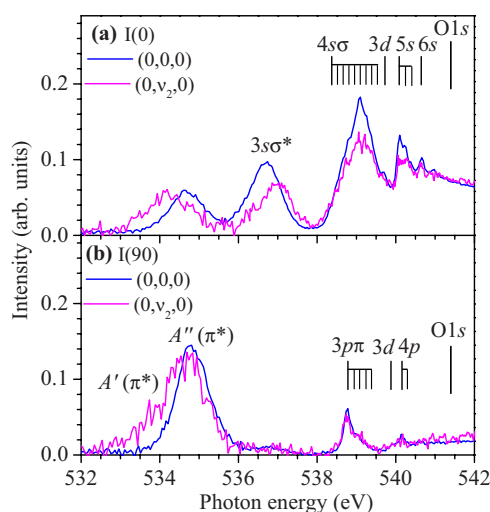


FIG. 1. (Color online) ARIY spectra in the N_2O $\text{O } 1s^{-1} \pi^*$ and Rydberg excitation region: (a) Initial state specific 0° ARIY spectra for the vibrational ground state and vibrationally excited states. (b) Initial state specific 90° ARIY spectra for the vibrational ground state and vibrationally excited states.

bandwidth of the monochromator was set to 90 meV for the $\text{O } 1s$ excitation region (resolving power $h\nu/\Delta h\nu \sim 6000$). To compensate for changes in density in the source volume (due to temperature difference) the angle-resolved spectra are normalized to the areas of the combined spectra $I(54.7^\circ) = I(0^\circ) + 2I(90^\circ)$ over the whole energy range at both 300 and 700 K [8,9].

The lowest vibrationally excited state of the electronic ground state of N_2O is at 73.0 meV above the vibrational ground state and belongs to a bending vibration. Assuming a Boltzmann distribution, we estimate the population of the vibrational ground state to be 93.7% at 300 K and 65.8% at 700 K. The ARIY spectra recorded at 300 and 700 K can be assumed to be linear combinations of two “initial-state specific” ARIY spectra, one corresponding to excitation from the vibrational ground state and one to excitation from all vibrationally excited states. The populations estimated using the Boltzmann distribution can then be used to extract these initial-state specific spectra. At 700 K the population of the first excited state is estimated to be 19.7%, with the remaining 7.7% of the molecules in higher excited states. Thus the vibrationally excited ARIY spectrum is due to excitation from molecules with one or more quanta of bending vibration excitation. Based on these assumptions, two *pure* ARIY spectra for the vibrational ground and vibrationally excited states were extracted from the ARIY spectra recorded at 300 and 700 K, for each of the two detection angles of 0° and 90° .

III. RESULTS AND DISCUSSION

Figure 1 shows the initial-state specific ARIY spectra recorded in the vicinity of the $\text{O } 1s$ ionization threshold. Let us briefly review what is already known for the vibrational ground state ARIY. In the π^* excitation region, the axial-recoil approximation is violated due to the Renner-Teller ef-

fect, and energetic fragment ions are observed in both the 0° and 90° ARIY spectra. The detection of fragment ions in the 0° detector is due to the bending motion of the molecules in the bent A' state (in the C_s point group), whereas the 90° spectrum includes both the linear A'' and bent A' states [2,3,10]. The broad structure centered around 536.7 eV in the 0° ARIY spectrum is due to excitation to the $\text{O } 1s^{-1}3s\sigma$ Rydberg state. This state exhibits no vibrational structure, indicating its dissociative nature [11]. It is also known that the $ns\sigma$ Rydberg series appears with significant intensity and shows varying vibrational structure along the series. This is a result of σ^* valence character being strongly mixed in the $ns\sigma$ Rydberg states [2,10,11].

Let us now compare the ground and excited state ARIY spectra. The spectra in the π^* excitation region have been discussed elsewhere [9], and only a brief account is given here. The Franck-Condon region is defined by a zero-point distribution around the 180° bond for the vibrational ground state, with a shift to smaller bond angles for the vibrationally excited states. As a result, the π^* absorption profile in the 0° spectrum, which reflects solely the bent A' state, is broader for excitation from vibrationally excited states and exhibits an energy shift of ~ -0.5 eV. The Renner-Teller energy splitting between the bent A' state and the linear A'' state increases with the decrease in the bond angle. This can be clearly seen in the 90° vibrationally excited spectrum, where a long low-energy tail is observed, which mimics the low-energy part of the 0° spectrum. This is a contribution from the bent A' state, whereas the main peak comes from the linear A'' state.

A key finding that we report here is that the intensity of the $ns\sigma$ Rydberg series and A' state are significantly suppressed and increased for excitation from vibrationally excited states, respectively, whereas the intensity of the $np\pi$ Rydberg series is unchanged. These observations suggest that the decrease in the bond angle causes a decrease in the mixing in of valence character that enhances the transition probability to the Rydberg states. It is worth noting that the rotational distribution also changes upon heating. In contrast to the vibrational excitation, however, the rotational excitation does not cause any significant change to the molecular structure and thus cannot be expected to contribute to the change in transition probability observed here.

In order to confirm this interpretation we have performed *ab initio* calculations for the energies and the second moments of the $\text{O } 1s$ excited states, varying the bond angle. The bond lengths were held at the experimentally deduced values [18] of $R_{\text{NN}} = 1.127 \text{ \AA}$ and $R_{\text{NO}} = 1.185 \text{ \AA}$. The calculations were performed using the symmetry-adapted-cluster-expansion configuration-interaction (SAC-CI) method [19–22] within the equivalent core approximation (ECA) [23–26]. In the ECA, the $\text{O } 1s$ ionized single-hole state of N_2O is approximated by the ground state of the NNF^+ ion. Thus, the $\text{O } 1s$ excited states of N_2O were approximated by the states in which one electron is attached to NNF^+ . The SAC-CI SD-R method, in which single (S) and double (D) excitations are adopted for R operators, is known to be useful for calculating the one-electron processes we are concerned with here. The employed basis sets consisted of a correlation-consistent polarized valence $[4s3p2d]$ triple zeta

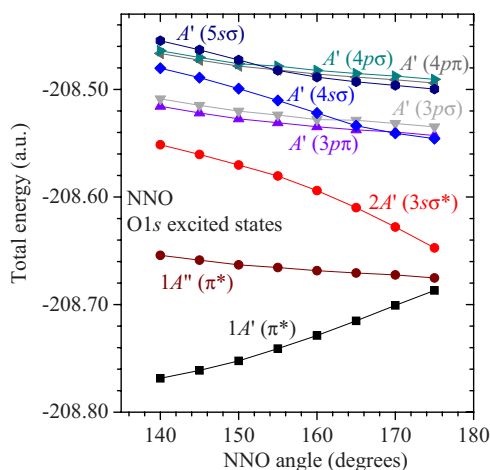


FIG. 2. (Color online) Diabatic potential energy curves of the low-lying O 1s excited states at $R_{\text{NN}}=1.127$ Å and $R_{\text{NO}}=1.185$ Å.

(cc-*p*VTZ-*f*) basis (as proposed by Dunning [27]) combined with Rydberg [6s6*p*] functions [28] located on the central N atom for describing the $n=3,4,5(s,p)$ Rydberg states. We employed an algorithm for calculating the σ vectors directly, including all the nonlinear terms [29]. All the R operators were included without selection in the SAC-CI calculations, while the perturbation selection procedure was adopted for the SAC calculations with an energy threshold set at $\lambda_g=10^{-6}$ a.u. to reduce the computational requirements [30]. The SAC-CI calculations were performed with the development version of the GAUSSIAN03 suite of programs [31].

Figure 2 shows cuts at $R_{\text{NN}}=1.127$ Å and $R_{\text{NO}}=1.185$ Å of the calculated potential energy surfaces of the O 1s excited states of A' symmetry. The curves are shown in the diabatic representation to allow analysis of the Rydberg-valence coupling of each state. The $1A'$ state is correlated to the π^* state and stabilizes along the bending coordinate. The $1A''$ state that is also correlated to the π^* state is plotted for comparison. All other states including the $1A''$ state are stable in the linear structure. A characteristic curve crossing occurs between the s and p Rydberg states along the bending coordinate. The $4s\sigma$ and $5s\sigma$ states destabilize relative to $3p\pi/3p\sigma$ and $4p\pi/4p\sigma$ states, respectively, as the molecule becomes bent. This curve crossing occurs in the region of 160° – 170° for the $4s\sigma$ state and 150° – 155° for the $5s\sigma$ state. From these potential curves, it is clear that the $1A'(\pi^*)$ and $ns\sigma$ Rydberg series change in character along the bending coordinate.

In order to analyze the mixing of the valence character in the Rydberg states, we have analyzed the electronic part of the second moment $\langle r^2 \rangle$, which is anticorrelated to the amount of valence character [11]. The second moments of the low-lying s and p Rydberg states along the bending mode are shown in Fig. 3. The second moments of the $3s\sigma$, $4s\sigma$, and $5s\sigma$ states become large as the molecule becomes bent. This indicates that the mixing of the valence character in these states becomes less as the bond angle decreases. Consequently, the absorption oscillator strength to the $ns\sigma$ Rydberg states becomes small. An analysis of the vibrational wave functions (in the normal coordinate) shows that in the

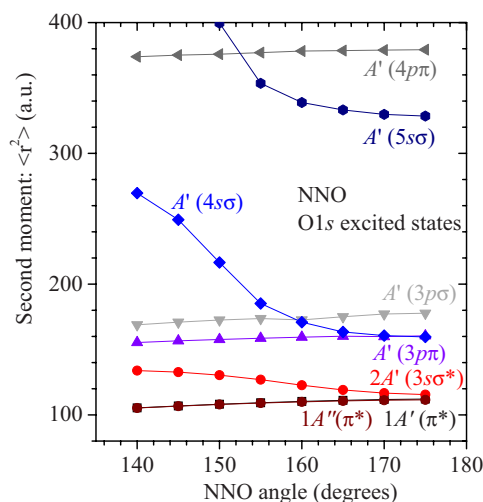


FIG. 3. (Color online) Second moments $\langle r^2 \rangle$ of the low-lying O 1s excited states at $R_{\text{NN}}=1.127$ Å and $R_{\text{NO}}=1.185$ Å. Curves are shown for the diabatic states.

ground state the contribution of molecular geometries with bond angles of less than 166° is only 2.1%, whereas the contribution is 15.1% for the first vibrationally excited state. These results confirm the interpretation of the intensity changes observed for excitation from vibrationally excited molecules. The nd Rydberg series was also examined by adding d functions to the basis set: the second moment for these states does not change significantly along the bending coordinate.

The question now arises as to where the valence character in the Rydberg states goes with the decrease in the bond angle. As seen in Fig. 2, the $1A'(\pi^*)$ state stabilizes along the bending coordinate whereas the $2A'(3s\sigma^*)$ state destabilizes more than the $1A''(\pi^*)$ state. This anticorrelation indicates

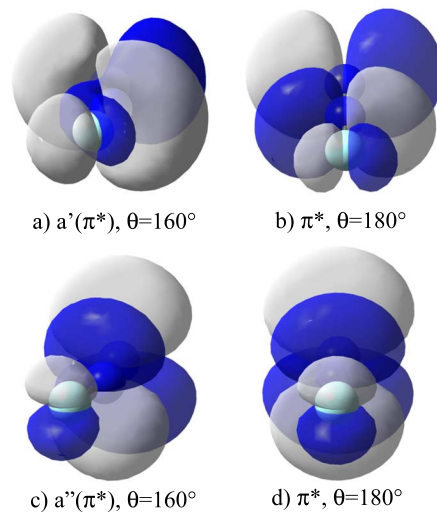


FIG. 4. (Color online) Calculated in-plane $a'(\pi^*)$ and out-of-plane $a''(\pi^*)$ molecular orbitals at bond angles of $\theta=160^\circ$ and 180° . In our experiment, π^* absorption from the vibrationally excited state corresponds to the promotion of an O 1s electron to these orbitals in bent molecules.

that the $1A'(\pi^*)$ and $3s A'$ states are strongly coupled. We speculate that this coupling opens a *flow* of the valence character from the $3s A'$, $4s A'$, and $5s A'$ Rydberg states to the $1A'(\pi^*)$ state. The corresponding increase in the transition probability to the $1A'(\pi^*)$ state can be clearly seen in Fig. 1, especially in the $I(90^\circ)$ spectrum. In order to confirm this speculation, we have analyzed the character of the molecular orbitals (MOs) to which an electron is promoted. Figure 4 shows the in-plane $a'(\pi^*)$ and out-of-plane $a''(\pi^*)$ MOs at bond angles of $\theta=160^\circ$ and 180° . Figs. 4(c) and 4(d) reveal that the out-of-plane $a''(\pi^*)$ MO has 3 $p\pi$ -type lobes independent of bond angle. For the in-plane $a'(\pi^*)$ component, however, it is clear that the $s\sigma$ -type component moves to the central N atomic site with the decrease in bond angle, as can be seen by comparing Figs. 4(a) and 4(b). Thus, we can conclude that the counterpart of the decrease in the mixing of the valence character in the $3s$, $4s$, and $5s$ states is an increase in the $s\sigma$ -type character of the $a'(\pi^*)$ orbital. It is worth noting that the $A'(ns\sigma)$ states gain $A'(\pi^*)$ character in the bent conformation due to back donation as a counterpart to the σ^* character. A quantitative discussion of the transition probabilities thus needs further theoretical study in which all these effects, along with the interference between the different contributions are taken into account.

IV. SUMMARY

We have observed a significant suppression of the spectral intensity of the $O\ 1s \rightarrow ns\sigma$ Rydberg series in N_2O for excitation from bending vibrationally excited ground states. Based on an *ab initio* second moment analysis, this is attributed to a decrease in the mixing of the valence character in the $ns\sigma$ Rydberg states with decreasing bond angle. The study of vibrationally excited “hot” molecules is demonstrated to open new vistas in molecular spectroscopy.

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