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Symmetry and vibrationally resolved absorption spectra near the N K edges of N$_2$O: Experiment and theory

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In this study, angle-resolved energetic-ion yield spectra were measured in the N 1s excitation region of N$_2$O. A Franck-Condon analysis based on ab initio two-dimensional potential energy surfaces of the core-excited Rydberg states, which were calculated by the symmetry-adapted cluster-configuration interaction method, reproduced observed vibrational excitations specific to the individual Rydberg states well and enabled quantitative assignments. Geometric changes in the terminal nitrogen N$_t$ 1s and the central nitrogen N$_c$ 1s excited states with respect to the 3$p\sigma$, 3$p\pi$, and 4$s\sigma$ transitions were analyzed. The coupling of these valence and Rydberg states was examined based on the second moment analysis. Irregular Rydberg-state behavior in the N$_c$ 1s$^{-1}$ 4$s\sigma$ state was observed.

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I. INTRODUCTION

Inner-shell absorption spectroscopy [1,2], which is usually performed today at high-flux and high-resolution synchrotron radiation beamlines that are the successors to those of the original electron-energy-loss spectroscopy (EELS) technique [3], provides important information about the electronic structure and nuclear dynamics of core-excited species. Interpretation of the spectral features observed is often made by comparison with known spectra of related systems within the equivalent core model (ECM) [4], or, if available, based on theoretical calculations. In the case of randomly oriented free molecules, the drawback of traditional angle-integrated EELS and photoabsorption spectroscopy is that these techniques are insensitive to the symmetries of the excited electronic states and information from these states is often vital for making unambiguous assignments, in particular if several electronic states overlap or even coincide.

A breakthrough for gas phase soft x-ray absorption spectroscopy in this respect has been the introduction of angle-resolved yield measurements of fragment ions of inner-shell excited linear molecules [5–7]. Within the validity of the axial-recoil approximation [8,9], symmetry information can be extracted for linear molecules from this technique according to the following principle: For absorption transitions of $\Delta \Lambda = 0$ (i.e., $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, etc.), fragment ions are preferentially detected parallel to the direction of the electric field vector of the linear polarized light, whereas for absorption transitions of $\Delta \Lambda = \pm 1$ (i.e., $\Sigma \rightarrow \Pi$, $\Pi \rightarrow \Sigma$, etc.), fragment ions are detected preferentially perpendicular to the direction of the electric field vector [10]. This method is therefore often referred to as “symmetry-resolved” x-ray absorption spectroscopy [10].

The N$_2$O molecule, with its two nonequivalent nitrogen atoms, the terminal N$_t$ and the central N$_c$, has a linear geometry in the neutral ground state and the related electronic configuration can be denoted as [11]

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

where 1$\sigma$, 2$\sigma$, and 3$\sigma$ correspond to the O 1s, N$_c$ 1s, and N$_t$ 1s core orbitals, respectively.

Several studies on core-excited N$_2$O have been reported previously. Promoting one of the core electrons into the lowest unoccupied molecular orbital $\pi^*$ leads to the O 1s$^{-1}$ $\pi^*$, N$_c$ 1s$^{-1}$ $\pi^*$, and N$_t$ 1s$^{-1}$ $\pi^*$ $\Pi$ states, respectively, as observed in the pioneering EELS studies of Wight and Brion [12] and Tronc et al. [13] in the 1970s. At about the same time, the first nitrogen K-shell photoabsorption spectrum of N$_2$O was recorded at Stanford [14], which agreed well with the EELS measurements and confirmed the assignments made based on the ECM. In the early 1990s Ma et al. [15] succeeded in recording a substantially improved, high-resolution photoabsorption spectrum of N$_2$O at the nitrogen K edges, which revealed many more electronic states than seen before and readily suggested that vibrational fine structures were present, but their assignments were only tentative.

Adachi et al. [16] presented the first high-resolution angle-resolved energetic-ion yield (ARIY) absorption spectra of the N 1s and O 1s excited states of N$_2$O, and investigated them with the help of ab initio self-consistent-field (SCF) calculations with explicit consideration of the core hole. They paid special attention to the O 1s, N$_c$ 1s, and N$_t$ 1s $\rightarrow \pi^*$ excitations and showed conclusively that Renner-Teller
coupling is present in all three excitations, which breaks the degeneracy of these states by bending the linear molecule. This is fundamental for an understanding of related coincidence experiments on N₂O performed at the corresponding photon energies [17–20]. As some studies have recently shown, the Renner-Teller effect in these three I₁ states is generally even more pronounced in a hot target gas [21] compared with N₂O molecules at room temperature. The work of Adachi et al. [16] further demonstrates that no Renner-Teller effect is present in any of the 1s → Rydberg excited states, which suggests that the axial-recoil approximation is fully valid in these cases and allows reliable symmetry information from ARIY measurements in the corresponding spectral regions to be obtained. Based on the symmetry information available from their data, in combination with ab initio calculations and spectral features readily observed by Ma et al. [15], several new assignments were made by Adachi et al. [16].

Later, Prince et al. [22] recorded near-edge total-yield x-ray absorption fine-structure spectra without symmetry resolution, but with high statistics and unprecedented higher energy resolution at the N 1s and O 1s edges of N₂O. They obtained assignments of the spectral features via analysis of the quantum defects of the Rydberg states, the use of the ECM and by comparison to previously published photoabsorption and fragment ion spectra. In particular, several new Rydberg states converging to the oxygen K edge, including spectral features that could be assigned to certain vibrational modes, were revealed in their study.

Previously, we investigated the O 1s excited states of N₂O using ARIY spectroscopy [23,24]. Vibrationally resolved spectra were examined by Franck-Condon (FC) analysis based on ab initio calculations and revealed geometric changes in these states. The symmetry-adapted cluster-configuration interaction (SAC-CI) method [25,26] was used within the ECM approximation. The SAC-CI method has been established for investigating excited states of molecules in the fields of chemistry and physics, and in particular it has been successfully applied to various types of core-electronic processes [27–29]. Noticeably, in our previous work [23], the irregular behavior in the Σ−symmetry spectrum of O 1s excited states of N₂O was interpreted by coupling of the valence and Rydberg states using the electronic part of the second moments. The thermal effect on the coupling of the valence and Rydberg states in the O 1s excited states of N₂O was also studied [24].

In this work we examine state-of-the-art symmetry-resolved soft x-ray absorption spectra of N₂O measured with high-photon energy resolution in the vicinity of the two N K edges and analyze them with accurate SAC-CI calculations. Having symmetry resolution and high-photon energy resolution at hand enables us to disentangle spectral features observed previously in high-resolution angle-integrated measurements, and to reveal new spectral lines, some of which can be attributed to regular vibrational progressions of previously identified Rydberg states and some of which are proposed to belong to hitherto unobserved Rydberg states. FC analysis based on ab initio two-dimensional (2D) potential energy surfaces (PESs) explains the detailed vibrational structure and geometry changes in these spectra.

II. EXPERIMENT

The experiments were performed at the c branch of the photochemistry beamline 27SU at SPring-8, Japan, which was equipped with a high-resolution soft x-ray monochromator with a varied-line-space grating [30,31]. The radiation source was a figure-8 undulator, which provided horizontally or vertically linear polarized light after the undulator gap was set appropriately [32,33]. Two ion detectors, each of which had a retarding potential of 6 V for detecting ions with kinetic energies higher than 6 eV, were mounted at 0° and 90° with respect to the electric field vector E of the synchrotron light [34]. The ion detectors were used for recording the symmetry-resolved near-edge x-ray absorption fine-structure spectra. The acceptance angle for fragment ions in the detectors was ~±9°. The ratio of the detection efficiencies of the two detectors was determined by comparing the ARIY spectra recorded using horizontal and vertical linear polarized light. The ratio was close to unity after careful alignments of the two detectors and careful settings of the high voltages on the two detectors. A 4π-sr time-of-flight (TOF) ion detector was placed 250 mm away from the other two detectors and was used to record the total ion yield (TIY) simultaneously with the ARIYs. The photon energy bandwidth of the monochromator was set at 50 meV. The monitor of the photon flux for normalization was made by a drain current after the gas sample. All spectra were normalized to the data acquisition time, gas pressure, and photon flux. The photon energy scale was calibrated using the EELS spectra of Wight et al. [12] as a reference. N₂O gas was commercially obtained with a stated purity <99.99%.

III. COMPUTATIONAL DETAILS

Two-dimensional PESs of the ground and the N 1s core-excited states were calculated along the direction of the normal coordinates q₁ and q₃ corresponding to the quasi-symmetric (ν′₁) and quasi-antisymmetric (ν′₃) stretching vibrational motions, respectively, in the ranges $R_{NN} = 1.00–1.30$ Å and $R_{NO} = 1.00–1.55$ Å. The basis sets were correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis sets without f function, as proposed by Dunning, namely [4s3p2d] [35], plus Rydberg functions [5s5p] [36] placed on the N₃ atom for describing $n = 3, 4, 5$ ($s$ and $p$).

The ground- and core-excited states of N₂O were calculated by the SAC and SAC-CI methods, respectively. Ground-state geometry was obtained as $R_{NN} = 1.122$ and $R_{NO} = 1.184$ Å by the SAC method, in good agreement with the experimental values of 1.127 and 1.185 Å [23,37], respectively. The N 1s core-excited states were calculated by two approaches of the SAC-CI SD-R method in which single (S) and double (D) excitations were adopted for the R operators. One approach calculated the core-excited states directly (without ECM) and the other adopted the ECM approximation. Both approaches have advantages and disadvantages. The SAC-CI method, which calculates the core-excited states directly, describes the orbital relaxation of the core-electron process as it is and solves the N 1s and Nc 1s excited states simultaneously while including the interactions between them. The core-excited states, however, usually have large orbital relaxation for
which higher excitation operators are required to give an accurate description. Therefore, the SAC-CI SD-R calculation is sometimes not sufficient to calculate core-excited states. In such a case, the inclusion of higher excitation operators in the expansion, the SAC-CI general-R method, is necessary; however, we note that the general-R method is computationally expensive in the present implementation. The SAC-CI method using the ECM approximation, in contrast, calculates the $N_1$s and $N_1$ 1s excited states separately. It is usually stable even for the higher Rydberg states and is computationally cost effective, although it describes the orbital relaxation of the core-electronic processes by the ECM approximation. To this end, we conducted both types of SAC-CI calculations and interpreted the results by comparing them with the experimental spectra. In what follows, we denote the latter method as SAC-CI ECM.

In comparing the SAC-CI and SAC-CI ECM results, the PESs were similar to each other except for the $N_1$ 1s$^{-1}$ 3s$^0$ state as discussed later. Therefore, to calculate the 2D PESs of the core-excited states and theoretical vibrational spectra, we used the SAC-CI ECM method which is stable and cost effective. For the $N_1$ 1s and $N_1$ 1s core-excited states, the excited states of ONO and NOO, respectively, were calculated by the SAC-CI ECM method [25,26]. The excited states of the neutral radicals, ONO and NOO, were calculated by an electron attachment scheme of SAC-CI applied to the closed-shell ONO$^+$ and NOO$^+$ ions, respectively. In the SAC-CI SD-R calculations, we used an algorithm that calculates $\sigma$ vectors directly and includes all the $S_2R_1$ and $S_2R_2$ nonlinear terms [38], namely the direct SAC-CI method. All the $S$ and $R$ operators were included without perturbation selection in the SAC-CI calculations. We also adopted the nonvariational method for solving the SAC-CI equations. The equilibrium geometries of each state were obtained from the analytic energy gradients of the SAC-CI method. The optimized structures were also confirmed to be local minima by calculating the PESs in the bending coordinate.

The vibrational analysis was performed using the SAC-CI ECM 2D PESs of the $N_1$ 1s and $N_1$ 1s excited states of N$_2$O. To calculate the FC factors of the vibrational spectrum, the vibrational wave function was obtained by the grid diagonalization. The 2D PESs of the N$_2$O molecule were described in the binding coordinates where the bond distances were $r_1$ and $r_2$, and the bond angle was fixed at 180°. In this coordinate, the kinetic energy ($T$) part of the Hamiltonian of the vibrational motion was given by:

$$ T = \frac{p_1^2}{2\mu_{N_1N_1}} + \frac{p_2^2}{2\mu_{N_2O}} + \frac{p_3^2}{m_{N_2}}, \quad p_k = -i \frac{\partial}{\partial r_k}, \quad k = 1, 2, $$(1)

where $\mu_{N_1N_1}$ ($\mu_{N_1O}$) is the reduced mass of the $N_1$ and $N_1$ ($N_2$ and O) atoms. The coordinates $r_1$ and $r_2$ were represented by the Hermite discrete variable representation (DVR). The 2D PESs were fitted to the analytic functions of the fifth-order 2D Morse expansion:

$$ V(r_1, r_2) = \sum_{i,j=0}^{5} B_{ij}(1 - e^{-a_1(r_1 - r_{1e})})(1 - e^{-a_2(r_2 - r_{2e})}), $$

where $r_{1e}$ and $r_{2e}$ are equilibrium distances and are determined by the analytic energy gradients of the SAC method or the SAC method with CI. $B_{ij}$ are expansion coefficients of the PESs, and $a_1$ and $a_2$ denote the parameters in the 2D Morse function. The vibrational spectra were calculated in the framework of the FC approximation.

SAC-CI calculations were performed with the GAUSSIAN 09 suite of programs [39] with some changes for calculating core-excited states. For calculating the vibrational states and FC factors, the multiconfiguration time-dependent Hartree (MCTDH) program package [40] was used.

### IV. RESULTS AND DISCUSSION

#### A. $N_1$ 1s excitation

Figure 1 shows a high-resolution TIY photoabsorption spectrum (upper panel) of N$_2$O in the 399–407-eV photon energy region, together with the corresponding ARIY spectra measured at angles of 0° (middle panel) and 90° (lower panel), respectively. The assignments were mainly based on the present calculations and partially based on previous works, in particular the ab initio calculations of Adachi et al. [16] and the ECM-based study of Prince et al. [22], as well as on the analysis of the quantum defects for the various series. They are summarized in Table I where the assignments of Adachi et al. [16] and Prince et al. [22] are also included for comparison.

Figure 2 represents the 405.5–408.5-eV photon energy region of the high-resolution TIY photoabsorption spectrum (upper panel) of N$_2$O together with the corresponding ARIY
spectra measured at angles of 0° (middle panel) and 90° (lower panel), respectively. The Ni 1s ionization threshold, located at 408.43 eV, in accordance with the work of Alagia et al. [41], is included as a reference mark for assignment of the spectral features observed. Figure 3 displays the PESs of the N 1s excited states of σ and π symmetries, which were obtained by the SAC-CI method calculating the core-excited states directly, where a one-dimensional cut was made at \( R_{NN} = 1.10 \) Å. The 2D PESs were calculated with the equal grid of 0.1 Å for \( R_{NN} \) and the cut was selected as it is close to the equilibrium N–N bond length. In this figure, the PESs of the Ni 1s and Nc 1s ionized states are also shown for reference. We also present the corresponding PESs of the Ni 1s excited states obtained by the SAC-CI ECM method shown in Fig. 4. The equilibrium geometries of the ground and low-lying N 1s excited states calculated from the analytic energy gradients of the SAC-CI method are summarized in Table II, which gives a comparison of the results for the SAC-CI and SAC-CI ECM calculations. In the SAC-CI calculations (without ECM), we also obtained the σ^+ states regarded as shape resonances and nonphysical discrete continuum states with the character of the Ni 1s excitation above the Ni (Nc) 1s ionization threshold. These are not included in Fig. 3. Furthermore, we present in Table III the oscillator strength obtained by the SAC-CI method calculating the core-excited states directly.

First, we discuss the PESs obtained by the SAC-CI and SAC-CI ECM calculations. As seen in the comparisons in Figs. 3 and 4, the nature of the PESs of Ni 1s excited states calculated by the two methods is similar except for the Ni 1s\(^{-1}\) 3σσ state. In the SAC-CI PESs of Ni 1s excited states shown by the diabatic representation (Fig. 3), some Ni and Nc
excited states cross each other because the Nc 1s−1 3sσ and Nc 1s−1 4sσ states have a repulsive character whose picture cannot be obtained by the SAC-CI ECM method. It should be noted that, at the crossing points, configuration interaction occurs and the Nt 1s and Nc 1s intermediate core-excited states exist at the potential seam. The PESs of the Nc excited states calculated by the two methods are also similar, as shown later.

In addition to these calculations, we performed a geometry optimization of low-lying Nt 1s and Nc 1s excited states. The optimized structures are again similar between the SAC-CI and SAC-CI ECM calculations. For example, in the Nt 1s−1 3pσ state, the optimized bond distances, r_{NN} = 1.109 Å and r_{NO} = 1.102 Å, calculated by SAC-CI, are similar to those

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<th>Table II. Equilibrium bond lengths of the N 1s excited states of N2O optimized by the SAC-CI and SAC-CI ECM methods.</th>
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Two broad features centered around 400.98 eV and 404.6 eV photon energy (cf. Fig. 1) in the TIY spectrum are the well-known Nt 1s−1 π∗ and Nc 1s−1 π∗ resonances, respectively [10,12–16,21,22]. They are also present in the 0° measurements where their maxima are shifted by ∼0.1 eV towards lower photon energy because of the Renner-Teller effect, as discussed in detail previously [10,16]. Note that the PES of the Nc 1s−1 π∗ state is bound in the N–O coordinate as in the O 1s−1 π∗ excited states [23], whereas that of the Nc 1s−1 π∗ state is repulsive in this coordinate as discussed further later in this paper. The oscillator strength of the Nt 1s−1 π∗ transition was f = 0.050, which was smaller than the corresponding value for the Nc 1s−1 π∗ transition, f = 0.062, which is in good agreement with the experimental spectra.

The comparatively sharp line located at 403.88 eV (s2) in the ARIY [I(0°)] spectrum (cf. Fig. 1), which is also discernible in the TIY spectrum as a shoulder (see also Ref. [22]) but which is completely absent in the ARIY [I(90°)] spectrum, has been identified previously as the Nt 1s → 3sσ Rydberg state [10].
The SAC-CI results show that the PES of the $N_t$ states in the higher energy region of the vibrational band is broader than the $N_t$ state. The oscillator strength of this transition was calculated to be $f = 0.0042$, which is one order of magnitude smaller than that of the $\pi^*$ transition.

The spectral region above 405.6 eV photon energy is quite complex because of the presence of several states of $\Sigma$ and $\Pi$ symmetry, which partially overlap or even coincide in the TIY recording, as seen from the angle-resolved measurements (middle and lower panels of Fig. 2). In particular, the line at ~404.23 eV, which might be due to the $\nu_3$ excitation of the $3\sigma$ state ($N_t$ 1$s^{-1}$) Rydberg state. Such an excitation may not be totally unexpected because the mixing of the Rydberg and valence states, as discussed previously [10], may result in distortion of the PES along the $q_1$ and/or $q_3$ normal coordinates. Furthermore, we also noticed that the peak width of the $3\sigma$ excitation appeared to be broader than the $ns\sigma$ ($N_t$) peaks, which might further support this interpretation. The SAC-CI results in Fig. 3 show that the PES of the $N_t$ 1$s^{-1}$ $3\sigma$ state is bound; however, the SAC-CI ECM results in Fig. 4 suggest that the PES of this state is quasibound and distorted. A possible explanation for this finding is that the repulsive character of this PES is underestimated in the SAC-CI ECM calculations. The difference between the calculated equilibrium bond distances is large between these methods: $R_{NN} = 1.113$ Å and $R_{NO} = 1.109$ Å by SAC-CI and $R_{NN} = 1.554$ Å and $R_{NO} = 1.138$ Å by SAC-CI ECM. According to the SAC-CI results, the additional broad band observed in the higher energy region of the vibrational structure may be attributed to the component of the $\pi^*$ transition. The SAC-CI ECM calculations, in contrast, suggest the possibility of the transition occurring within the flat FC region of the PES of this state. The oscillator strength of this transition was calculated to be $f = 0.0042$, which is one order of magnitude smaller than that of the $\pi^*$ transition.

For the $N_t$ 1$s^{-1}$ 3$\pi$ Rydberg state, the SAC-CI ECM calculations result in a large geometry change of the $R_{NO}$ distance, and the calculated equilibrium bond distances of this state are $R_{NN} = 1.117$ Å. A direct comparison between the SAC-CI ECM spectrum of the $N_t$ 1$s^{-1}$ 3$\pi$ state and the ARIY [$I(90^\circ)$] spectrum is made in Fig. 5; the (000) vibrational level of the theoretical spectrum is set to the experimental level because the absolute excitation energy is not obtained in the ECM approximation. As can be seen, the theoretical spectrum reproduces the ARIY spectrum well and the vibrational structure is predominantly attributed to the $\nu_3$ progression; in particular, the $p_3$, $p_4$, and $p_6$ peaks are assigned to transitions to (010) levels, and $p_5$ and $p_7$ to the (100) and (011) levels, respectively. The calculated vibrational spacings of the $\nu_3$ and $\nu_5$ modes were ~180 and ~290 meV, respectively, which are well in accordance with the experimental values of ~180 and ~300 meV, respectively. The oscillator strength of this transition is calculated to be $f = 0.0028$, which is reasonable compared with other transitions.

Returning to the TIY spectrum, a high intense band centered around 406.29 eV (s6) occurs in the photon energy region between ~406 and ~406.8 eV, which gets substantial contributions from states of $\Sigma$ symmetry, as seen from the ARIY [$I(I^0\times)$] recording. To date, the shoulder at 406.13 eV to the (100) component of the $N_t$ 1$s^{-1}$ 3$\pi$ Rydberg state. This assignment is also supported by the present calculations as discussed below. Additional lines towards the higher photon energy side of the (100) line are nicely revealed in the present ARIY [$I(90^\circ)$] spectrum with about the same spacing and an intensity distribution typical for a vibrational band. They are assigned accordingly as higher vibrational components of the ($\nu_1$ 00) mode (cf. Table I). Clearly, the experimental data also give room to infer the $\nu_3$ mode to be excited, as indicated in the lower panel of Fig. 2 and summarized in Table I.

The $N_t$ 1$s^{-1}$ 3$\pi$ Rydberg state is identified as the $N_t$ 1s $3\pi$ Rydberg state, as identified in previous studies [16,22]. The neighboring line (p4) at 406.01 eV photon energy, also well resolved in the TIY and the ARIY [$I(I^0\times)$] spectra, has been proposed to be a higher vibrational component of the $N_t$ 1$s^{-1}$ 3$\pi$ Rydberg state [22], and was recently assigned as the $N_t$ 1$s^{-1}$ 3$\pi$ (001) line [22]. The vibrational assignment for $N_t$ 1$s^{-1}$ excitations made by Prince et al. [22] was generally guided by the vibrational energy spacing from valence band photoemission data of the ECM molecule NO$_2$ [42]. We would rather use the frequency values of the N$_2$O neutral ground state as a guide for the vibrational assignment. According to a previous study [43], the ground-state vibrational spacing of the symmetric stretching mode ($\nu_3$, primarily N–O stretch), the bending mode ($\nu_2$), and the asymmetric stretching mode ($\nu_1$, primarily N≡N stretch) is 159.3 meV, 73.0 meV, and 275.7 meV, respectively. Regarding the energy difference of 180 meV of the two lines under consideration, which is closest to the $\nu_1$ value, we assigned the spectral line at 405.96 eV to the (100) component of the $N_t$ 1$s^{-1}$ 3$\pi$ Rydberg state. This assignment is also supported by the present calculations as discussed below. Additional lines towards the higher photon energy side of the (100) line are nicely revealed in the present ARIY [$I(90^\circ)$] spectrum with about the same spacing and an intensity distribution typical for a vibrational band. They are assigned accordingly as higher vibrational components of the ($\nu_1$ 00) mode (cf. Table I). Clearly, the experimental data also give room to infer the $\nu_3$ mode to be excited, as indicated in the lower panel of Fig. 2 and summarized in Table I.
also arises from a state of $\Sigma$ symmetry. Regarding the most intense line located at 406.29 eV, which is the $N_1 1s^{-1} 4\sigma$ Rydberg state [16,22], and the two adjacent shoulders on the higher photon energy side, which have recently been attributed to vibrational excitations of the same state [22], we performed a least-squares curve-fitting analysis on this band of the ARIY $[I(0)]$ spectrum. The results of this analysis strongly support the interpretation that the most intense line at 406.29 eV photon energy and the two shoulders ($s_7, s_8$) on the higher photon energy side most likely represent the vibrational progression of the $(\nu_1 00)$ mode of the $N_1 1s^{-1} 4\sigma$ Rydberg state. Again, the experimental data allow for inferring the $\nu_1$ mode to be excited, as indicated in the middle panel of Fig. 2. The shoulder at 406.13 eV ($s_5$), however, is more likely to belong to a separate electronic state. A suitable candidate for the latter with respect to the quantum defect is the $N_1 1s^{-1} 3\sigma$ Rydberg state, which is also in accordance with the calculated oscillator strengths of Adachi et al. [16]. It is worth noting in this context that the unusually high intensity of the $N_1 1s^{-1} 4\sigma$ Rydberg state, in particular, has been rationalized [16] in terms of an underlying mixing of the valence and Rydberg states akin to the prominent $O_2$ case (e.g., [10] and references therein).

Theoretical vibrational spectra of the $N_1 1s^{-1} 4\sigma$ and $N_1 1s^{-1} 3\sigma$ states of $N_2O$.

For evaluating the coupling of the valence and Rydberg states of these core-excited states, the electronic part of the theoretical spectra of the $N_1 1s^{-1} 4\sigma$ and $N_1 1s^{-1} 3\sigma$ states of $N_2O$.
second moment \( \langle r^2 \rangle \) was calculated. The results of the N\(_t\) 1s excited states are shown in Fig. 7. As can be seen, the second moment of the N\(_t\) 1s\(^{-1}\) \( \pi^* \), 3p\(_{\pi}\), and 3s\(_{\sigma}\) states increases as the NO distance is elongated. However, the second moment of the 4s\(_{\sigma}\) state in the diabatic picture shows an irregular behavior; that is, the electronic distribution shrinks as the NO distance becomes larger. This indicates that the coupling of the valence and Rydberg states becomes strong along this coordinate, as was also seen for the O 1s\(^{-1}\) 4s\(_{\sigma}\) state [23]. The calculated value of this state, however, was \( \langle r^2 \rangle = 180–190 \text{ bohrs}^2 \) in the FC region. This indicates that the coupling of the valence and Rydberg states of the N\(_t\) 1s\(^{-1}\) 4s\(_{\sigma}\) state is weak compared with the O 1s\(^{-1}\) 4s\(_{\sigma}\) [23] and N\(_c\) 1s\(^{-1}\) 4s\(_{\sigma}\) states, as discussed later.

The well-resolved line in the TIY spectrum at 406.99 eV is essentially the N\(_t\) 1s\(^{-1}\) 3d\(_{\pi}\) Rydberg state [16,22], as seen from the ARIY [I(90\(^{°}\))] recording. As indicated in the ARIY [I(90\(^{°}\))] spectrum, there may also be a (100) vibrational component underneath the adjacent spectral feature, the (000) line of the N\(_t\) 1s\(^{-1}\) 4p\(_{\pi}\) Rydberg state centered at 407.25 eV (p11). Furthermore, at least one additional vibrational component of the N\(_t\) 1s\(^{-1}\) 4p\(_{\pi}\) Rydberg state, the (100) line, can be identified at 407.42 eV photon energy (p12) in the ARIY [I(90\(^{°}\))] spectrum. By looking again at the upper panel of Fig. 2, the latter line, however, cannot fully account for the comparatively high intensity in the TIY spectrum at this photon energy. In fact, by comparing the spectral profiles of the TIY, ARIY [I(0\(^{°}\))] and ARIY [I(90\(^{°}\))] recordings around 407.42 eV and above, we can see that particular states of \( \Sigma \) symmetry are rather prominent in this region. Our analysis of the quantum defects of suitable Rydberg states suggests assignments of the various spectral features as included in the middle and lower panels of Fig. 2, respectively, and as summarized in Table I. The presence of the N\(_t\) 1s\(^{-1}\) \( np\_\sigma \) series in this spectral region has been proposed by Prince et al. [22], and the assignment of the N\(_t\) 1s\(^{-1}\) 4s\(_{\sigma}\) and 5s\(_{\sigma}\) states has recently been tentatively proposed by Adachi et al. [16]. The appearance of \( \Sigma \) states at \( \sim 407.85 \text{ eV} \) photon energy and higher, tentatively assigned here as higher N\(_t\) 1s\(^{-1}\) \( ns\_\sigma \) Rydberg members, is perhaps not totally unexpected because the lower members of this series exhibit an extraordinarily high intensity, which is presumably caused by an underlying mixing of the valence and Rydberg states [16].

The corresponding SAC-CI PESs of the N\(_t\) 1s\(^{-1}\) 4p\(_{\sigma}\), 5s\(_{\sigma}\), 4p\(_{\pi}\), and 5p\(_{\pi}\) states are also displayed in Figs. 3 and 4. The calculated energy positions of the N\(_t\) 1s\(^{-1}\) 4p\(_{\pi}\), 4p\(_{\sigma}\), and 5s\(_{\sigma}\) states are consistent with the present ARIY assignments shown in Fig. 2 and Table I, although a detailed vibrational analysis was not performed for these states. The vibrational structure of the N\(_t\) 1s\(^{-1}\) 4p\(_{\pi}\) and 5s\(_{\sigma}\) states in the ARIY spectrum is similar to that of the N\(_t\) 1s\(^{-1}\) 3p\(_{\pi}\) and 4s\(_{\sigma}\) states. In accordance with the ARIY spectra, the PESs of the N\(_t\) 1s\(^{-1}\) 4p\(_{\sigma}\) and 5s\(_{\sigma}\) states interact with each other in a similar way to those of the 3p\(_{\pi}\) and 4s\(_{\sigma}\) states represented in Figs. 3 and 4.

B. N\(_c\) 1s excitation

Figure 8 shows the 409–413-eV photon energy region of the TIY photoabsorption spectrum of N\(_2\)O (upper panel) alongside the corresponding ARIY measurements [I(0\(^{°}\))] middle panel; and I(90\(^{°}\)) lower panel). The N\(_c\) 1s ionization threshold, located...
TABLE III. Vertical excitation energy (\(\Delta E\)) and oscillator strength (\(f\)) of the N 1s transitions calculated by the SAC-CI method at \(R_{NN} = 1.127\ \text{Å}\) and \(R_{NO} = 1.185\ \text{Å}\).

<table>
<thead>
<tr>
<th>State</th>
<th>(\Delta E) (eV)</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_c) 1s</td>
<td>3(\sigma)</td>
<td>405.4 0.0042</td>
</tr>
<tr>
<td></td>
<td>3(\pi)</td>
<td>407.6 0.0073</td>
</tr>
<tr>
<td></td>
<td>4(\sigma)</td>
<td>408.1 0.0022</td>
</tr>
<tr>
<td></td>
<td>4(\pi)</td>
<td>408.8 0.0049</td>
</tr>
<tr>
<td></td>
<td>5(\sigma)</td>
<td>409.0 0.0006</td>
</tr>
<tr>
<td></td>
<td>(\pi^*)</td>
<td>402.2 0.0500</td>
</tr>
<tr>
<td></td>
<td>3(\pi)</td>
<td>407.4 0.0028</td>
</tr>
<tr>
<td></td>
<td>4(\pi)</td>
<td>408.8 0.0008</td>
</tr>
<tr>
<td></td>
<td>5(\pi)</td>
<td>409.3 0.0004</td>
</tr>
<tr>
<td>N(_c) 1s</td>
<td>3(\sigma)</td>
<td>409.4 0.0010</td>
</tr>
<tr>
<td></td>
<td>3(\pi)</td>
<td>412.1 0.0002</td>
</tr>
<tr>
<td></td>
<td>4(\sigma)</td>
<td>411.8 0.0012</td>
</tr>
<tr>
<td></td>
<td>4(\pi)</td>
<td>413.0 0.0000</td>
</tr>
<tr>
<td></td>
<td>5(\sigma)</td>
<td>413.2 0.0004</td>
</tr>
<tr>
<td></td>
<td>(\pi^*)</td>
<td>405.7 0.0623</td>
</tr>
<tr>
<td></td>
<td>3(\pi)</td>
<td>411.6 0.0002</td>
</tr>
<tr>
<td></td>
<td>4(\pi)</td>
<td>412.9 0.0002</td>
</tr>
<tr>
<td></td>
<td>5(\pi)</td>
<td>413.5 0.0002</td>
</tr>
</tbody>
</table>

at 412.44 eV [41], is marked in this figure as a reference for the spectral assignments made. The assignments are summarized in Table IV together with the previous results of Adachi et al. [16] and Prince et al. [22].

The corresponding SAC-CI ECM results of the PESs of the N\(_c\) 1s excited states, where a one-dimensional cut was made at \(R_{NN} = 1.10\ \text{Å}\), and the electronic part of the second moment \(|\langle r^2 \rangle|\) for these states are displayed in Figs. 9 and 10, respectively. As can be seen, the PES of the N\(_c\) 1s\(^{-1}\) 3\(\sigma\) state is repulsive along the NO distance, which differs from that of the N\(_t\) 1s\(^{-1}\) 3\(\sigma\) state. The oscillator strengths of the N\(_c\) 1s transitions are given in Table III. The oscillator strength of the N\(_c\) 1s\(^{-1}\) \(\pi^*\) transition is large, whereas those of other transitions are much smaller. This trend is different from the N\(_t\) 1s transitions, which has also been found in previous work [16].

The measured TIY spectrum essentially consists of three gross features located at \(~409.95\ \text{eV}, 411.31\ \text{eV}, \) and \(411.83\ \text{eV}\) photon energy, respectively, all of which get substantial contributions from states of \(\Sigma\) and \(\Pi\) symmetry; compare ARHY [I(0\(^{\circ}\))] and ARHY [I(90\(^{\circ}\))] spectra. The identification of the spectral features in the ARHY [I(90\(^{\circ}\))] recording is fairly straightforward using the quantum defect as a guide, and we essentially identify the same electronic states as previously reported [16, 22]. Clearly, some of the N\(_c\) 1s\(^{-1}\) \(np\pi\) Rydberg states are broadened. This is most likely because of vibrations of the \(v_{100}\) mode with an energetic spacing of \(~130\ \text{meV},\) as marked in Fig. 8.

The theoretical vibrational spectrum of the N\(_c\) 1s\(^{-1}\) 3\(\pi\pi\) state is compared with the corresponding experimental spectrum in Fig. 11. The calculated bond distances of the N\(_c\) 1s\(^{-1}\) 3\(\pi\pi\) state are \(R_{NN} = 1.119\ \text{Å}\) and \(R_{NO} = 1.243\ \text{Å},\) and the \(v_{1}\) mode is active for the N\(_c\) 1s\(^{-1}\) 3\(\pi\pi\) excitation; the p16 and p17 peaks are assigned to the (000) and (100) levels,
TABLE IV. Energies, assignments and quantum defect $\delta$ for the $N_c$ 1s Rydberg states identified in the angle-resolved ion yield spectrum of Fig. 8.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Expt. (eV)</th>
<th>Theory (eV)</th>
<th>Assignment</th>
<th>$\delta$</th>
<th>Prince</th>
<th>Adachi</th>
</tr>
</thead>
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<tr>
<td>s21</td>
<td>409.65</td>
<td>409.65$^a$</td>
<td>$4s\sigma (N_c)$</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s22</td>
<td>409.81</td>
<td>409.78</td>
<td>$4s\sigma (N_c)$ (100)</td>
<td>0.68</td>
<td>$3\rho\sigma (N_c)$</td>
<td>$3\rho\sigma (N_c)$</td>
</tr>
<tr>
<td>p16</td>
<td>409.93</td>
<td>409.93$^b$</td>
<td>$3\pi\sigma (N_c)$</td>
<td>0.68</td>
<td>$3\rho\pi (N_c)$</td>
<td>$3\rho\pi (N_c)$</td>
</tr>
<tr>
<td>s23</td>
<td>409.95</td>
<td>409.94</td>
<td>$4s\sigma (N_c)$ (200)</td>
<td>1.61</td>
<td></td>
<td>$3\rho\sigma (N_c)$</td>
</tr>
<tr>
<td>p17</td>
<td>410.06</td>
<td>410.05</td>
<td>$3\pi\sigma (N_c)$ (100)</td>
<td>0.68</td>
<td>$3\rho\pi (N_c)$</td>
<td>(001)</td>
</tr>
<tr>
<td>s24</td>
<td>410.07</td>
<td>410.14$^c$</td>
<td>$3\rho\sigma (N_c)$</td>
<td>4.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s25</td>
<td>410.20</td>
<td>410.26</td>
<td>$3\rho\sigma (N_c)$ (100)</td>
<td>4.00</td>
<td>$3\rho\sigma (N_c)$</td>
<td></td>
</tr>
<tr>
<td>s26</td>
<td>410.37</td>
<td>410.39</td>
<td>$3\rho\sigma (N_c)$ (200)</td>
<td>4.00</td>
<td>$3\rho\sigma (N_c)$</td>
<td></td>
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<tr>
<td>s27</td>
<td>410.51</td>
<td>410.51</td>
<td>$3\rho\sigma (N_c)$ (300)</td>
<td>4.00</td>
<td>$3\rho\sigma (N_c)$</td>
<td>+ $\nu$</td>
</tr>
<tr>
<td>s28</td>
<td>410.67</td>
<td>410.56</td>
<td>$3\rho\sigma (N_c)$</td>
<td>4.00</td>
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<td></td>
</tr>
<tr>
<td>s29</td>
<td>410.81</td>
<td>410.81</td>
<td>$3\rho\sigma (N_c)$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>s30</td>
<td>411.25</td>
<td>411.25</td>
<td>$3\rho\sigma (N_c)$</td>
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<td></td>
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<tr>
<td>p18</td>
<td>411.31</td>
<td>411.31</td>
<td>$4\rho\pi (N_c)$</td>
<td>0.56</td>
<td></td>
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<tr>
<td>s31</td>
<td>411.37</td>
<td>411.37</td>
<td>$5\pi\sigma (N_c)$</td>
<td>1.45</td>
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<tr>
<td>p19</td>
<td>411.44</td>
<td>411.44</td>
<td>$4\rho\pi (N_c)$ (100)</td>
<td>1.45</td>
<td></td>
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<tr>
<td>s32</td>
<td>411.50</td>
<td>411.50</td>
<td>$5\pi\sigma (N_c)$ (100)</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s33</td>
<td>411.79</td>
<td>411.79</td>
<td>$6\pi\sigma (N_c)$</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p20</td>
<td>411.83</td>
<td>411.83</td>
<td>$5\pi\pi (N_c)$</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The calculated (000) level of the $N_c$ 1s$^{-1} 4s\sigma$ state is set to 409.65 eV.

$^b$The calculated (000) level of the $N_c$ 1s$^{-1} 3\pi\sigma$ state is set to 409.93 eV.

$^c$The position of the (000) level of the $N_c$ 1s$^{-1} 3\rho\sigma$ state is calculated relative to the $N_c$ 1s$^{-1} 3\rho\pi$ state.

respectively. The energy separation was 120 meV, which compares well with the experimental value of 130 meV. The calculated FC factors show that the geometry change appears to be overestimated in the present calculations; higher $(\nu_100)$ levels are also populated.

The assignment of the peak structures in the ARIY [I(0°)] recording is more ambiguous, in particular because the first band at $\sim 409.95$ eV appears quite broad, as was pointed out in the study by Adachi et al. [16]. Large parts of the recording can certainly be attributed to the $N_c$ 1s$^{-1} 3\rho\pi$ Rydberg state, and the superimposed fine structure, with a spacing of $\sim 160$ meV, suggests excitation of vibrations of the $(\nu_100)$ mode. However, none of the other Rydberg states we observed had such an extended progression, and because the PESs of the excited Rydberg states are usually nearly equal to that of the ionized states, this finding is surprising. Whether or not the $N_c$ 1s$^{-1} 3\rho\sigma$ and/or the $N_c$ 1s$^{-1} 4s\sigma$ Rydberg states, as marked in the figure, contribute to the intensity of this band is difficult to judge, in particular because their excitations are expected to be rather weak due to symmetry reasons [16]. An underlying mixing of the valence and Rydberg states, as proposed by Adachi et al. [16] for other states, could give rise to such an extended vibrational progression, akin to the O 1s$^{-1} 4s\sigma$ Rydberg states in N$_2$O (e.g. [10] and references therein).

In the theoretical results of this energy region, the relative energies of the $N_c$ 1s$^{-1} 3\rho\sigma$ and 4s\sigma states in the FC region are delicate; the $N_c$ 1s$^{-1} 4s\sigma$ state is stable compared with the $N_c$ 1s$^{-1} 3\rho\sigma$ state. The calculated vibrational spectra of these
The excitation energy of the Nc states are compared with the experimental spectrum in Fig. 12. The excitation energy of the Nc states was calculated relative to the Nc state, whereas the excitation energy of the Nc state was shifted by +0.8 eV to fit the calculated (000) peak to the s21 peak in the ARIY spectrum. As can be seen in the calculated Nc state, the higher vibrational levels of the Nc state were excited, which can be understood from the large geometry change of this state. The oscillator strengths of the Nc states were calculated to analyze in detail the spectral features observed and reveal geometry changes in the electronic states studied. The theoretical spectrum reproduced the experimental observations well, which were specific to individual Rydberg states and gave quantitative assignments of the vibrational fine structure in these states. The coupling of the valence and Rydberg states of these states was examined in detail. Regular Rydberg behavior of the Nc and Nc states are consistent with the present experimental assignment.

FIG. 12. The ARIY [I(0-)] and SAC-CI ECM spectra of the Nc 1s" 4σ and Nc 1s" 3σ states of N2O.

The comparatively broad band at 411.23 eV also reflects some fine structure of ~160 meV spacing, suggesting (ν1,00) vibrations of the Nc 1s" 4σ Rydberg state. Some contribution from the Nc 1s" 5σ Rydberg states may also play a role; however, they are expected to be rather weak due to symmetry reasons. The remaining spectral features in the ARIY spectrum, located at 411.23 eV (p18) and 411.79 eV (p20) photon energy, have been revealed for the first time in this study, and can be assigned to the Nc 1s" 4σ and Nc 1s" 5σ Rydberg states, respectively, based on evaluation of the quantum defect. The comparatively broad band at 411.23 eV also reflects some fine structure of ~160 meV spacing, suggesting (ν1,00) vibrations of the Nc 1s" 4σ Rydberg state. Some contribution from the Nc 1s" 5σ Rydberg states may also play a role; however, they are expected to be rather weak due to symmetry reasons. Finally, the PESs of the Nc 1s" 4σ, 5σ, 4π, and 5π states were also computed as shown in Fig. 9. The relative energy positions of the Nc 1s" 4σ and 5σ states are consistent with the present experimental assignment.

V. SUMMARY

We have investigated vibrational fine structure in the Nc 1s and Nc 1s absorption spectra of N2O using high-resolution ARIY spectroscopy and accurate SAC-CI and SAC-CI ECM calculations. The equilibrium structures and the 2D PESs of the Nc 1s and Nc 1s excited states with respect to 3π, 3σ, and 4σ transitions were calculated to analyze in detail the spectral features observed and reveal geometry changes in the electronic states studied. The theoretical spectrum reproduced the experimental observations well, which were specific to individual Rydberg states and gave quantitative assignments of the vibrational fine structure in these states. The coupling of the valence and Rydberg states of these states was examined based on second moment analysis. Irregular Rydberg behavior was found in the Nc 1s" 4σ state.

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