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One- and two-color two-photon resonance enhanced multiphoton ionization spectroscopy of the $d\ ^1\Sigma^+$ state of NH

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The ionization and dissociation processes occurring after two-photon excitation of the $d\ ^1\Sigma^+$ state of NH have been investigated using one- and two-color multiphoton ionization spectroscopy in combination with mass-resolved ion and kinetic energy-resolved electron detection. The photoelectron spectra obtained for ionization of the molecule via the $d\ ^1\Sigma^+$ state ($v'=0,1$) reveal a one-photon ionization process to all energetically accessible vibrational levels of the $X\ ^2\Pi$ ground ionic state, at variance with a one-configuration description of the two states. Moreover, electrons are observed that derive from a one-photon ionization of excited neutral nitrogen and hydrogen atoms. Two-color excitation experiments of the $d\ ^1\Sigma^+$ state show that the influence of discrete states at the overall three-photon level on the dissociation dynamics is insignificant. Using the results of *ab initio* calculations it is concluded that these experimental observations can be interpreted consistently if two competing processes are assumed to take place from the $d\ ^1\Sigma^+$ excited state: a molecular one-photon ionization which is forbidden in zeroth order, and a two-photon nonresonance enhanced excitation to neutral (pre)dissociative states.

I. INTRODUCTION

Resonance enhanced multiphoton ionization in combination with photoelectron spectroscopy (REMPI-PES) has in the past been shown to provide a powerful tool for the study of the electronic character of excited states, and its consequences for subsequent photoionization dynamics. The studies performed recently on the imidogen radical (NH) may in this respect be considered as exemplary.^{1,2} In these studies two-photon excitation spectroscopy has led to the identification of several hitherto unobserved Rydberg states, while the application of photoelectron spectroscopy via these Rydberg states enabled a detailed characterization of their electronic nature and the determination of accurate ionization energies, electronically as well as vibrationally. Moreover, the possibility to perform photoelectron spectroscopy with ionic rotational resolution has highlighted several fundamental aspects of the photoionization process itself.^{1,3} The fruitful combination of REMPI-PES experiments with state-of-the-art *ab initio* calculations ultimately elucidated the importance of such effects as Cooper minima in the photoionization channels, orbital evolution, and l mixing in the electronic continuum.³

In the present study we shall be concerned with the electronic nature of a high-lying excited valence state of NH, the $d\ ^1\Sigma^+$ state, and the photoionization and photodissociation processes following absorption of photons from this state. Previous REMPI studies with ion detection,⁴⁻⁶ in which the $d\ ^1\Sigma^+$ state was excited by a two-photon excitation from the $a\ ^1\Delta$ state, have given rise to a number of intriguing ques-

tions. Two key observations are of importance in this respect. First, in a single-configuration picture the $d\ ^1\Sigma^+$ state and the $X\ ^2\Pi$ ground ionic state are described at their equilibrium geometries by the configurations $1\sigma^22\sigma^23\sigma^01\pi^4$ and $1\sigma^22\sigma^23\sigma^21\pi^1$, respectively.^{7,8} Since the two configurations differ by three electrons, a direct one-photon ionization would be forbidden, but NH^+ ions are nevertheless observed. Second, two-photon REMPI via the $d\ ^1\Sigma^+$ state not only produces NH^+ ions, but N^+ and H^+ ions as well.^{5,6} The excitation spectra for forming these fragment ions exactly match the excitation spectrum of the $d\ ^1\Sigma^+$ state, but their yields, relative to the yield of NH^+ ions, are highly dependent on the rotational transition considered.⁶ Furthermore, it is important to note that such fragment ions are not produced in REMPI studies via the nearby $f\ ^1\Pi$ and $g\ ^1\Delta$ Rydberg states.^{6,9} Previously, it has been proposed that a possible mechanism capable of accounting for these observations would be a doubly resonance enhanced ionization, in which resonance not only occurs at the two-photon level by the $d\ ^1\Sigma^+$ state, but also at the three-photon level by "superexcited" autoionizing Rydberg states.⁶

It is clear that in order to achieve a fundamental understanding of the ionization and dissociation dynamics observed after excitation of the $d\ ^1\Sigma^+$ state, studies of the photoelectron kinetic energy release are of crucial importance. Such studies would show at which energy levels ionization of the molecule occurs and might indicate how the fragment ions are produced. In this spirit we have therefore applied two-photon resonance enhanced multiphoton ionization in combination with kinetic energy-resolved electron detection and mass-resolved ion detection on the $d\ ^1\Sigma^+(v'=0,1) \leftarrow a\ ^1\Delta(v''=0)$ transitions. The photoelectron spectra clearly demonstrate that ionization from the

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$d\ ^1\Sigma^+$ state results from a *one*-photon absorption process, in which the vibrational levels associated with the $X\ ^2\Pi$ ionic ground state are populated with strong deviations from the expected Franck–Condon branching ratios. Also important, the photoelectron spectra unambiguously show electrons which are associated with a one-photon ionization process of excited neutral fragments, thereby revealing the presence of neutral dissociation channels. Experiments in which the $d\ ^1\Sigma^+$ state is excited by two photons of different frequencies show no evidence for a possible superexcited state at the overall three-photon level which has previously been suggested to explain the ionization and dissociation dynamics.

In order to rationalize the observed molecular one-photon ionization multireference single and double configuration interaction (MRD-CI) calculations have been performed on the $d\ ^1\Sigma^+$ and $X\ ^2\Pi$ states. From these calculations it becomes clear that the ionization process can only be understood if configuration interaction effects are taken into account. The observed fragmentation into excited neutral atoms will be seen to arise from a two-photon absorption process from the $d\ ^1\Sigma^+$ state, exciting neutral (pre)-dissociative states at the four-photon level. Although such a process would normally not be very probable, it is precisely by virtue of the forbidden nature of the direct one-photon ionization pathway that this absorption process becomes competitive.

II. EXPERIMENTAL DETAILS

The experimental setup has been described in detail previously.¹⁰ Briefly, the laser system consists of a XeCl excimer laser (Lumonics HyperEx 460) operating at 30 Hz. In the one-color experiments this laser pumps a Lumonics HD500 dye laser (bandwidth 0.06 cm^{-1}) operating on Coumarin 540. In the two-color experiments the pump beam is split by a 50:50 beamsplitter and is used to pump the Lumonics HD500 dye laser, as well as a Lumonics HD300 dye laser (bandwidth 0.08 cm^{-1}) operating on Coumarin 540. The output of these dye lasers is frequency-doubled using a Lumonics Hypertrak 1000 unit with a BBO crystal and an Inrad Autotracker II system with a KDP crystal. The linearly polarized laser output is focused into the ionization region of a “magnetic bottle” spectrometer by a quartz lens with a focal length of 25 mm. When two dye lasers are employed, the two beams are led into the spectrometer in a counter-propagating configuration, and are focused by separate lenses mounted on opposite sides of the spectrometer.

In the present experiments REMPI spectroscopy was performed using kinetic energy-resolved electron detection as well as mass-resolved ion detection. In the case of electron detection (REMPI-PES), the magnetic bottle spectrometer allows for a collection efficiency of 50% and an optimum energy resolution of about 10 meV. Although primarily designed for electron detection, this spectrometer can also be employed as a time-of-flight mass spectrometer, enabling mass-resolved ion detection, albeit with a lower collection efficiency. To this purpose voltages of 130 and 90 V are applied to two grids that are mounted on the pole faces of the electromagnet. Of importance is the observation that the ion collection efficiency is mass-dependent. In the present ex-

periments the ions of interest are H^+ , N^+ , and NH^+ . For these ions we have observed that the collection efficiency of H^+ ions can be influenced to a considerably larger extent than those of N^+ and NH^+ ions, which are nominally equal under all circumstances. We therefore conclude that N^+ and NH^+ ions are collected with the same collection efficiency, which is probably smaller than the collection efficiency of H^+ ions.

The NH radical was generated *in situ* by one-photon photolysis of the precursor HN_3 , which was produced from a NaN_3 /stearic acid mixture with a weight ratio of 1:3, heated to about 380 K. Such a photodissociation results in NH radicals almost exclusively in the excited $a\ ^1\Delta$ state, 12 688.4 cm^{-1} above the $^3\Sigma^-$ ground state.¹¹

III. COMPUTATIONAL DETAILS

The potential energy surfaces and associated wave functions of the $d\ ^1\Sigma^+$ state of NH and the $X\ ^2\Pi$ state of NH^+ were calculated using the Wuppertal Bonn self-consistent field (SCF) plus multireference single and double excitation configuration interaction (MRD-CI) package of programs¹² for 16 internuclear distances ranging from 1.5 to 20 bohr. For these calculations a Gaussian atomic orbital basis set was employed for the nitrogen atom which consisted of the $(9s,5p)$ basis of Huzinaga¹³ contracted to a $[5s,3p]$ basis according to Dunning,¹⁴ augmented with two diffuse uncontracted s functions with exponents of 0.028 and 0.010, one diffuse p function with exponent of 0.025, and two polarization d functions with exponents of 1.082 and 0.343. For the hydrogen atom the Huzinaga ($5s$) basis¹³ in the Dunning $[3s]$ contraction¹⁵ was used with a scale factor of $\sqrt{2}$, augmented with one polarization p function with an exponent of 0.75. With this basis set an SCF energy of $-54.535\ 754$ hartree for the $X\ ^2\Pi$ state of NH^+ at the experimental equilibrium bondlength of 2.05 bohr was found.

The SCF and CI calculations to be described were performed in C_{2v} symmetry, the highest Abelian subgroup of $C_{\infty v}$. In the former symmetry group Σ^+ corresponds to A_1 and Π to B_1 and B_2 . For the CI calculation on the $X\ ^2\Pi$ state of NH^+ at a given internuclear distance R a molecular orbital set derived from an SCF calculation on this state at that particular distance was used. In these calculations the nitrogen $1s$ orbital was always kept doubly occupied, while the two virtual orbitals of highest orbital energy were discarded. The set of reference configurations was generated by performing trial calculations at various internuclear distances, and by retaining those configurations that contributed to the CI wave function of the $X\ ^2\Pi$ state by more than 0.05, or to the CI wave functions of the next two states of $^2\Pi$ symmetry by more than 0.1. With this set of 10 reference configurations about 11 000 configurations were generated. Using a threshold of 5 microhartree for configuration selection on the lower three roots resulted in CI expansions in the order of 5000 configurations. The sum of c^2 for the reference configurations in the final CI vector of the $X\ ^2\Pi$ state was always larger than 0.95. In order to estimate the full CI energies the generalized Davidson correction was applied.¹⁶

The CI calculations on the $d\ ^1\Sigma^+$ state of NH were performed in a similar way using the SCF molecular orbitals of

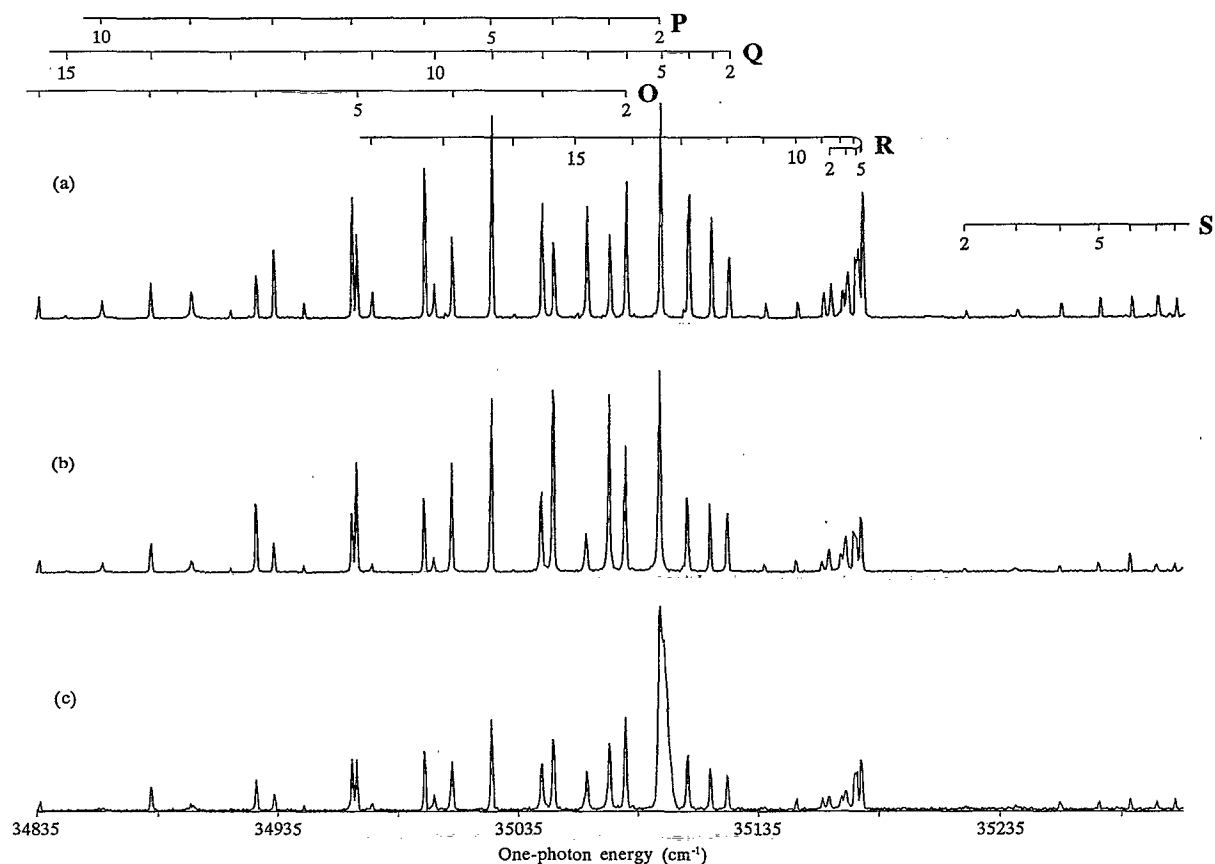


FIG. 1. Two-photon resonant multiphoton ionization excitation spectrum of the $d^1\Sigma^+(v'=0) \leftarrow \leftarrow a^1\Delta(v''=0)$ transition in NH obtained using mass-resolved ion detection. In (a), (b), and (c) the spectra are shown when monitoring the $\text{NH}^+(m/e=15)$, $\text{N}^+(m/e=14)$, and $\text{H}^+(m/e=1)$ channels, respectively.

the $X^2\Pi$ state. Here a list of 37 main configurations was employed in order to ensure that the sum of c^2 for the reference configurations in the final CI vector of the $d^1\Sigma^+$ state was always larger than 0.95 for all internuclear distances considered in the present calculations. About 38 500 configurations were generated from these configurations, from which about 8000 were selected by setting the threshold for configuration selection and energy extrapolation at 5 microhartree.

The vibrational energies and wave functions for the two states have been determined from numerical intergration of the nuclear Schrödinger equation with the Numerov method. For this integration procedure electronic potential energy curves constructed by a cubic spline interpolation between potential energy values calculated for fixed internuclear distances were used.

IV. RESULTS

In Fig. 1 the two-photon excitation spectrum of the $d^1\Sigma^+(v'=0) \leftarrow \leftarrow a^1\Delta(v''=0)$ transition is shown, employing mass-resolved ion detection and monitoring the $m/e=15$ [NH^+ , Fig. 1(a)], 14 [N^+ , Fig. 1(b)], and 1 [H^+ , Fig. 1(c)] channels. These spectra are in good agreement with the spectra previously reported by Ashfold *et al.*⁶ with respect to the relative intensities of the various rotational transitions. Previously, the relative intensities of the three channels have

been reported as $\text{NH}^+:\text{N}^+:\text{H}^+=19:5:1$ for the strongest transitions in each channel. In the present experiments, on the other hand, an 8:7:2 ratio is obtained, resulting in a significantly better signal-to-noise ratio in the H^+ channel. As outlined in Sec. II the ion collection efficiency of NH^+ and N^+ is the same, though probably smaller than that of H^+ . The $\text{NH}^+:\text{N}^+$ ratio should therefore reflect the correct ratio of ions produced, but the $\text{NH}^+:\text{H}^+$ and $\text{N}^+:\text{H}^+$ ratios are probably underestimated. Figure 1(c) demonstrates a significant broadening of the blended $P(2)/Q(5)$ line in the H^+ channel, which is not observed when lower laser fluxes are used. This broadening is thought to occur as the result of the three-photon resonance of atomic hydrogen from the ground state to the $n=5$ excited states.

Ashfold *et al.* have concluded from their MPI studies that the ratio of NH^+ to N^+ is strongly dependent on the rotational transition considered.⁶ In our study the same phenomenon is observed. When, e.g., the $P(3)$ and $P(4)$ rotational transitions are compared to the neighboring $Q(7)$, $Q(6)/O(2)$, and $Q(8)/O(3)$ transitions, it is clear that there is an enhanced yield of N^+ ions for excitation via $P(3)$ and $P(4)$. Such enhanced yields, on the contrary, do not seem to be present for H^+ ions.

For the $d^1\Sigma^+(v'=1) \leftarrow \leftarrow a^1\Delta(v''=0)$ transition the ion yield ratio $\text{NH}^+:\text{N}^+:\text{H}^+$ is found to be 35:4:1 for the strongest transitions in each channel, which might indicate

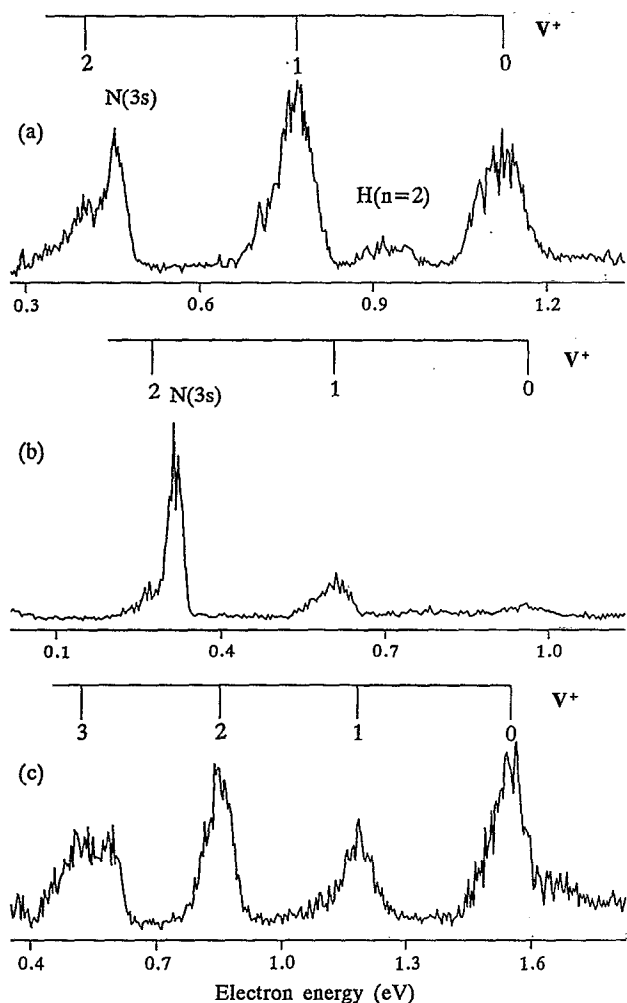


FIG. 2. MPI photoelectron spectra observed following two-photon excitation of (a) the $d^1\Sigma^+(v'=0)$ level via the bandhead of the R branch, (b) the $d^1\Sigma^+(v'=0)$ level via the $P(4)$ rotational transition, and (c) the $d^1\Sigma^+(v'=1)$ level via the $P(7)$ rotational transition.

that the fragmentation probability is smaller than in the case of the $(0,0)$ transition. Within experimental error, which is considerably larger than for the $(0,0)$ transition, the fragment ion yields relative to the molecular ion yield exhibit smaller variations over the excitation spectrum than observed in the excitation spectrum of the $(0,0)$ transition. We emphasize, however, that as the result of the smaller signal intensities, significantly higher laser intensities had to be used for the $(1,0)$ than for the $(0,0)$ transition. A direct comparison between the two transitions should therefore only be made with considerable caution.

In Fig. 2(a) the photoelectron spectrum for photoionization via the bandhead of the R branch of the $(0,0)$ transition is depicted. The electron energies and vibrational spacings observed in this spectrum correspond excellently with the ionization of the $d^1\Sigma^+(v'=0)$ state to the various vibrational levels of the $X^2\Pi$ state by a one-photon absorption process. Photoelectrons deriving from an (auto)ionization process by absorption of more than one photon are not present. Figure 2(a) together with Fig. 2(c), in which the

photoelectron spectrum obtained for photoionization via the $(1,0)$ $P(7)$ transition is shown, reveal that all vibrational levels of the $X^2\Pi$ state, which are energetically accessible in a one-photon ionization process of the $d^1\Sigma^+$ state, are populated with comparable intensity. This is in stark contrast to *a priori* expectations, since the potential energy surfaces of the $d^1\Sigma^+$ and $X^2\Pi$ states are very similar in shape.^{7,8} Franck-Condon considerations, therefore, would have led one to believe that a $\Delta v \approx 0$ propensity would occur.

In Fig. 2(a) two photoelectron peaks are observed which do not derive from the ionization of NH. Careful consideration of their kinetic energies reveals that they are associated with a one-photon ionization process of excited neutral atomic nitrogen and hydrogen, respectively. In the case of nitrogen atoms ionization occurs from the $\dots 2p^2 3s^1, ^2P^e$ state; the hydrogen atoms, on the other hand are ionized from their $n=2$ excited states. The larger width of the latter photoelectron peak can be rationalized by the fact that this light fragment gains a considerable amount of translational energy in the dissociation process, leading to a significant Doppler broadening of the electron signal.

From the mass-resolved excitation spectrum of the $d^1\Sigma^+(v'=0) \leftarrow \leftarrow a^1\Delta(v''=0)$ transition it has been concluded that a number of rotational transitions lead to an enhanced yield of nitrogen ions.⁶ The photoelectron spectrum shown in Fig. 2(a), on the other hand, shows that excited neutral fragments are produced in the excitation process. One might therefore wonder whether the enhanced yield of fragment ions derives only from an enhanced yield of excited neutral fragments, or that other mechanisms, such as fragmentation of the molecule after ionization, are of importance for the production of these ions. Figure 2(b) supports the former assumption. Here the photoelectron spectrum obtained for photoionization via the $(0,0)$ $P(4)$ rotational transition, which gives rise to an enhanced yield of N^+ ions, is depicted. The figure shows that this enhanced yield is the result of an increase in the production of nitrogen atoms in the $\dots 2p^2 3s^1, ^2P^e$ state.

The photoelectron spectra discussed above lead to a scenario in which NH^+ ions are produced from the $d^1\Sigma^+$ state by a one-photon absorption, and the H^+ and N^+ ions derive from the one-photon ionization of excited neutral fragments. This implies that monitoring the appropriate electrons in the photoelectron spectrum as a function of the excitation wavelength should lead to the same excitation spectra as obtained with mass-resolved ion detection in Fig. 1. Such is indeed the case, as is shown in Fig. 3. Because of the overlap of the photoelectron peak associated with the ionization of nitrogen atoms with the one deriving from the ionization of NH to the $X^2\Pi(v^+=2)$ level, slight discrepancies in the relative intensities of the resonances can be observed when compared with the mass-resolved excitation spectra. The fragment enhancement in the nitrogen channel, however, is clearly visible, and for the same transitions as observed with mass-resolved ion detection.

Previously it has been suggested that a possible explanation for the strong variations in the fragment yields might be found in the participation of the overall three-photon level on the excitation dynamics from the $d^1\Sigma^+$ state.⁶ In order to

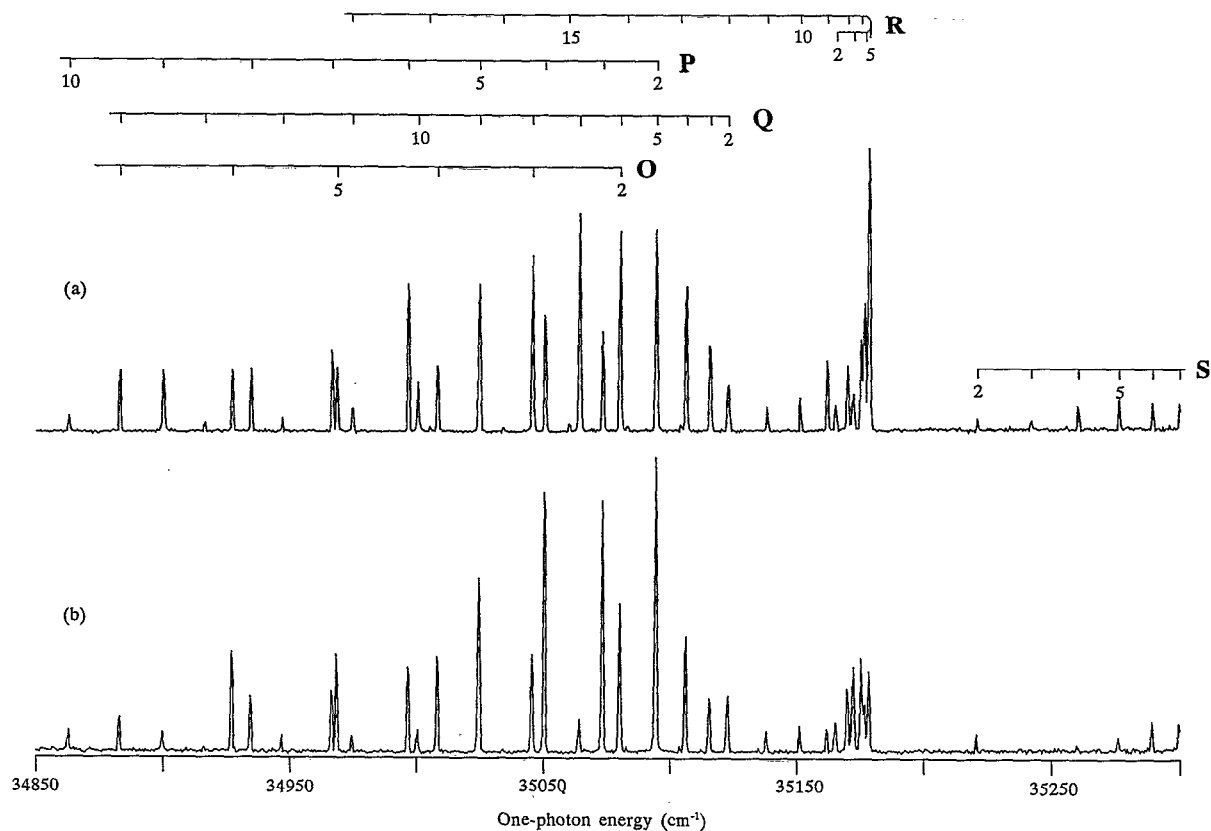


FIG. 3. Two-photon resonant multiphoton ionization excitation spectrum of the $d\ ^1\Sigma^+(v'=0) \leftarrow\leftarrow a\ ^1\Delta(v''=0)$ transition in NH obtained using kinetic energy-resolved electron detection. In (a) the excitation spectrum is shown when only those electrons are monitored which are associated with the one-photon ionization of the $d\ ^1\Sigma^+$ state to the $v^+=0$ level of the $X\ ^2\Pi$ ionic state; in (b) only those electrons are monitored that are derived from the one-photon ionization of nitrogen atoms in the $\dots 2p^2 3s^1, ^2P^e$ state.

investigate such a hypothesis, we have performed excitation studies of the $d\ ^1\Sigma^+(v'=0)$ level using two-color excitation, i.e., two photons of different energy were used to excite this state, instead of the two identical photons used before. Such an excitation scheme is depicted in Fig. 4(a), where it is compared to the one-color excitation scheme. If we suppose, for the moment, that the overall three-photon level is indeed responsible for the enhancement of fragment yields, then Fig. 4(a) shows the consequences of a two-color excitation scheme for these yields. Let us consider a rotational transition, which, using one-color excitation, gives rise to an enhanced yield, and which is now pumped by two-color excitation. Figure 4(a) demonstrates that such enhancements should no longer be present, since the overall three-photon levels accessed with two-color excitation are *per se* different from the one-color excitation level.

An example of a two-color excitation spectrum of the $d\ ^1\Sigma^+(v'=0) \leftarrow\leftarrow a\ ^1\Delta(v''=0)$ transition, obtained using mass-resolved ion detection, is shown in Fig. 5. For this particular spectrum one of the dye lasers was kept fixed at $35\ 076\ \text{cm}^{-1}$, a frequency which in the one-color excitation spectrum is not resonant and consequently does not yield any molecular or fragment ions, while the other dye laser is scanned. Since the fixed frequency is in the middle of the excitation spectrum of the $d\ ^1\Sigma^+(v'=0) \leftarrow\leftarrow a\ ^1\Delta(v''=0)$

transition, scanning the second dye laser will result in an excitation spectrum containing not only resonances deriving from two-color excitation, but also from one-color excitation. When the yields of the N^+ and H^+ ions are compared to the yield of NH^+ ions, it is clear that both one- and two-color excitations give rise to enhancements of equal magnitude at the same rotational transitions. This can be observed particularly well in Fig. 6, where an enlargement is shown of the region containing the rotational transitions, which with one-color excitation give rise to large fragment yields. Similar two-color excitation spectra have been obtained using various nonresonant fixed frequencies. We therefore conclude that at the overall three-photon level there is no evidence for a possible superexcited state influencing the dissociation dynamics.

V. DISCUSSION

A. Molecular signals

The presented photoelectron spectra have unambiguously revealed that a one-photon absorption process is responsible for the ionization of NH from the $d\ ^1\Sigma^+$ state. This conclusion is at odds with the single-configuration descriptions of the $d\ ^1\Sigma^+$ state ($\dots 3\sigma^0 1\pi^4$) and the $X\ ^2\Pi$ state ($\dots 3\sigma^2 1\pi^1$), which would not allow such a process to occur.

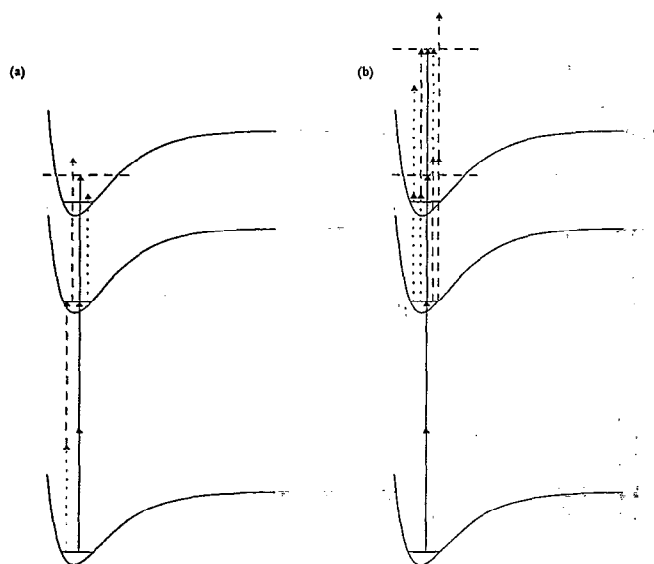


FIG. 4. Comparison between one- and two-color excitation schemes of the $d^1\Sigma^+$ state of NH. The solid arrow represents the photon of energy $h\nu_1$ used in one-color excitation. In the two-photon excitation experiment photons with energies $h\nu_2$ and $h\nu_3$ (represented by dashed and dotted arrows) are employed such that $2h\nu_1 = h\nu_2 + h\nu_3$. From (a) it becomes clear that for excitation via a given rotational transition the overall three-photon levels accessed in one- and two-color experiments are different; in (b) it is shown that for excitation of a certain rotational level in the $d^1\Sigma^+$ state with either one- or two color excitation the same overall four-photon levels can be reached.

One obvious explanation which comes to mind is electronic autoionization. In the energy region reached upon absorption of one photon from the $d^1\Sigma^+$ state, a plethora of rovibronic levels of Rydberg states converging to the ionic $A^2\Sigma^-$, $B^2\Delta$, and $C^2\Sigma^+$ states should be present. These Rydberg states have a $\dots 3\sigma^1 1\pi^2 n l \lambda$ configuration, and might be subject to electronic autoionization into the continuum associated with the $X^2\Pi$ ionic state.

When this explanation is considered more seriously, various problems arise. First, in order to excite these Rydberg states from the $d^1\Sigma^+$ state, a two-electron transition would need to take place by the absorption of a single photon. Such a process is highly unlikely. Second, if this mechanism were indeed to account for the ionization of the $d^1\Sigma^+$ state, ionization would only be possible in the case of an accidental double resonance: both the $d^1\Sigma^+ \leftarrow a^1\Delta$ and the $(A^2\Sigma^-, B^2\Delta, \text{ or } C^2\Sigma^+) n l \lambda \leftarrow d^1\Sigma^+$ would have to be resonant for ionization to occur. This would lead to dramatic variations with wavelength in the yield of NH^+ , which are not observed. On the contrary, the relative intensities of the rotational transitions in the excitation spectrum shown before can be simulated satisfactorily if it is assumed that the ionization step is not wavelength dependent. Finally, the results of the two-color excitation experiments described above would be difficult to interpret if indeed at the three-photon level a bound, resonant autoionizing state would be important.

A second explanation for the observed one-photon ionization behavior of the $d^1\Sigma^+$ state might in principle be

found in the presence of a dissociative autoionizing state at the overall three-photon level. Such a state might give rise to the observed vibrational distribution in the ion and would be accessible over a wide range of excitation energies, making the double resonance condition easy to fulfill. It is, however, difficult to find such a state. The states dissociating to the low-lying atomic fragments $\text{H}(n=1)$ and $\text{N}[(2p^3), ^4S^0, ^2D^0, \text{ or } ^2P^0]$ are all too low, and the associated electronic configurations would not allow autoionization into the $\text{NH}^+(X)$ continuum. States dissociating to higher lying fragments will only come into the Franck-Condon accessible region at much higher energies, making the transition to such states highly improbable.

A more general problem in describing the ionization dynamics on the basis of an autoionizing state at the three-photon level is found in the results of two-photon excitation experiments on the regular $f^1\Pi$ and $g^1\Delta$ $3p$ Rydberg states.^{1,3,9} Excitation of these states leads to overall three-photon energy levels which are close to the levels accessed in the present experiments, e.g., by excitation of the $f^1\Pi(v'=0)$ level a three-photon energy of $110\,600\text{ cm}^{-1}$ [measured relative to $a^1\Delta(v''=0)$] is reached, while excitation of the $d^1\Sigma^+(v'=1)$ leads to three-photon energies of $109\,100\text{ cm}^{-1}$. REMPI-PES experiments on these $f^1\Pi$ and $g^1\Delta$ Rydberg states show photoelectron spectra with a strong $\Delta v=0$ propensity.^{1,3} If an autoionizing state, and certainly a dissociative one, would influence the ionization dynamics, it would be difficult to understand why this influence would be so large for ionization via the $d^1\Sigma^+$ state, and nonexistent for ionization via the $f^1\Pi$ and $g^1\Delta$ states.

We conclude that an explanation of our results based on autoionization runs into serious problems, and return to a possible direct ionization mechanism. As mentioned above, direct ionization from the dominant configuration of the $d^1\Sigma^+$ state to the dominant configuration of the ground state of the ion is not allowed. Theoretical studies of these two states have shown, however, that a one-configuration description of both states is far from adequate. For the $X^2\Pi$ state it has been calculated, e.g., that a significant amount of $\dots 3\sigma^0 1\pi^3$ character ($\approx 10\%$ at the equilibrium bondlength) is mixed into the wave function.⁸ A one-photon ionization process from the dominant configuration of the $d^1\Sigma^+$ state to this particular ionic configuration is an electronically allowed process. Conversely, it has been established that the wave function of the $d^1\Sigma^+$ state changes dramatically as a function of internuclear distance.⁷ It has been shown, e.g., that at larger internuclear distances the $d^1\Sigma^+$ state acquires a significant amount of $\dots 3\sigma^2 1\pi^1 2\pi^1$ Rydberg character. Ionization from this configuration to the main configuration of the $X^2\Pi$ state would be allowed as well.

In order to investigate the role of configuration interaction in the description of the wave functions of the $d^1\Sigma^+$ and $X^2\Pi$ states in more detail, we have analyzed the composition of these states over a large range of internuclear distances by means of the MRD-CI calculations described above. The potential energy surfaces resulting from these calculations are depicted in Fig. 7. In this figure are shown as a function of R the contributions of the $\dots 3\sigma^2 1\pi^2$, $\dots 3\sigma^0 1\pi^4$ and the $\dots 3\sigma^2 1\pi^1 2\pi^1$ configurations to the CI vector of the

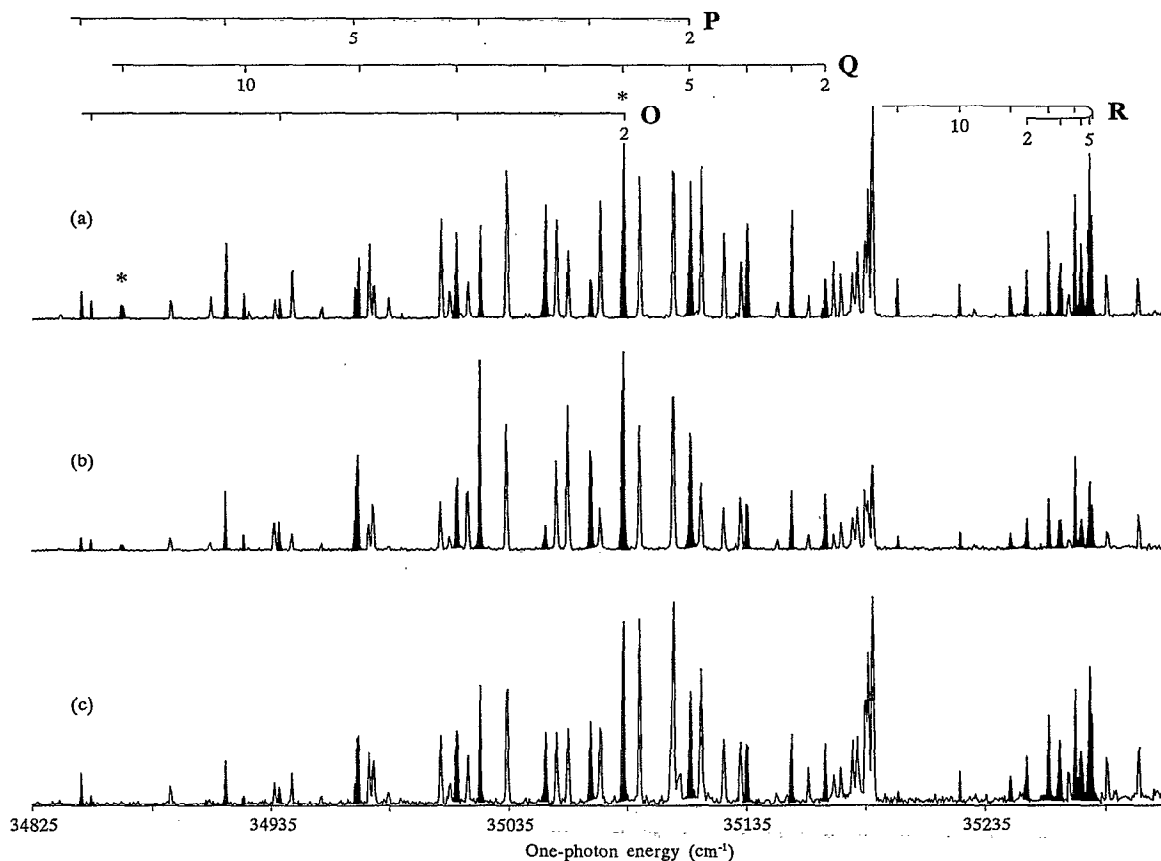


FIG. 5. Two-color two-photon resonant multiphoton ionization excitation spectrum of the $d^1\Sigma^+(v'=0) \leftarrow a^1\Delta(v''=0)$ transition in NH obtained using mass-resolved ion detection. In (a), (b), and (c) spectra are shown when monitoring the $\text{NH}^+(m/e=15)$, $\text{N}^+(m/e=14)$, and $\text{H}^+(m/e=1)$ channels, respectively. In these experiments one of the lasers is fixed at $35\,076\text{ cm}^{-1}$, while the other laser is scanned. The excitation spectrum shows $d^1\Sigma^+$ state resonances associated with the absorption of two identical photons (open resonances) and the absorption of two different photons (shaded resonances). The peaks marked with an asterisk are overlapping one- and two-color resonances. The assignment of the resonances deriving from two-color excitation is indicated by the combs on top of the figure.

$d^1\Sigma^+$ state, as well as those of the $\dots 3\sigma^2 1\pi^1$ and $\dots 3\sigma^0 1\pi^3$ configurations to the CI vector of the $X^2\Pi$ state. The CI wave functions calculated for the $d^1\Sigma^+$ state demonstrate that a good description of this state requires significant contributions ($>10\%$) of several configurations. It then becomes clear that the zeroth-order forbidden $X^2\Pi \leftarrow d^1\Sigma^+$ direct ionization process may acquire significant transition probability through configuration interaction: both processes involving the ionization from a "minor" configuration of the $d^1\Sigma^+$ state to the dominant configuration of the $X^2\Pi$ state, and ionization from the dominant $\dots 3\sigma^0 1\pi^4$ configuration of the $d^1\Sigma^+$ state to a minor configuration of the $X^2\Pi$ state are possible.

This mechanism, in which ionization takes place essentially through configuration interaction, might also explain the observed vibrational branching ratios upon ionization. In an allowed, direct ionization process it is normally assumed that vibrational branching ratios reflect the overlap between the vibrational wave functions of the two states involved. In the present case, however, the ionization process becomes only possible by virtue of the participation of minor configurations, whose contributions may vary rapidly with internu-

clear distance and, consequently, may lead to a strong R dependence of the ionization probability.

An accurate calculation of the $X^2\Pi(v^+) + e^- \leftarrow d^1\Sigma^+(v')$ transition probability is presently not feasible. For such calculations one would need to take the electronic transition moment between correlated wave functions and its dependency on the internuclear distance into account. Similar calculations using uncorrelated wave functions have been performed previously for Rydberg states of NH and have shown the importance of effects such as orbital evolution, l mixing, and Cooper minima.³ Inclusion of such effects may well be of significant importance in the present ionization dynamics.

In order to assess, at least in a very crude manner, the effects of the R dependence of the contributions of electronic configurations on the vibrational branching ratios upon ionization, calculations have been performed, in which the transition probability is assumed to be proportional to $[\int c_d(R)\chi_d(R)c_X(R)\chi_X(R)dR]^2$. In this expression $\chi_d(R)$ and $\chi_X(R)$ are the vibrational wave functions of the $d^1\Sigma^+$ and $X^2\Pi$ states, respectively, and $c_d(R)$ and $c_X(R)$ the coefficients of the two configurations involved in the ionization

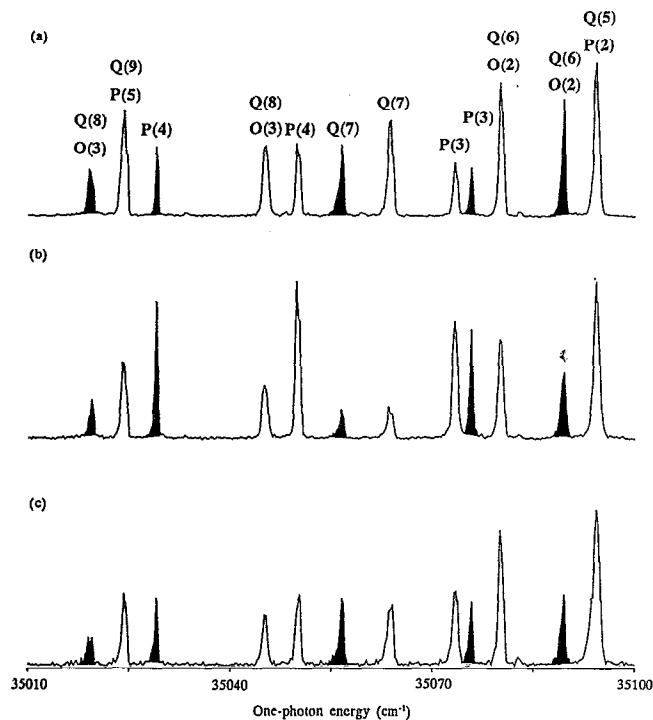


FIG. 6. Detail of the two-color two-photon resonant multiphoton ionization excitation spectrum of Fig. 5. Comparison of the yields of N^+ and H^+ relative to the yield of NH^+ obtained with one- or two-color excitation reveals that with both types of excitation the same enhancements are observed for the same rotational transitions.

process. This approximation assumes that the electronic transition moment is only dependent on the composition of the wave functions, and that the configurations in the wave functions retain the same electronic character over the complete potential energy surface. The results of such calculations are given in Table I, where they are compared with straightforward Franck–Condon factors, i.e., $c_d(R) = c_x(R) = 1$. The latter factors are, as expected, strongly diagonal, with the $\Delta v = 0$ transition carrying over 90% of the transition probability. Table I shows a large influence of the ionization mechanism on the vibrational branching ratios. When ionization is assumed to occur from the $\dots 3\sigma^0 1\pi^4$ configuration of the $d^1\Sigma^+$ state to the $\dots 3\sigma^0 1\pi^3$ configuration of the $X^2\Pi$ state, a $\Delta v = 0$ propensity is observed. The same behavior occurs for ionization from the $\dots 3\sigma^2 1\pi^2$ to the $\dots 3\sigma^2 1\pi^1$ configuration. For ionization from the $\dots 3\sigma^2 1\pi^1 2\pi^1$ Rydberg configuration to the $\dots 3\sigma^2 1\pi^1$ configuration, on the other hand, the vibrational branching ratios exhibit significant deviations from $\Delta v = 0$, although a quantitative comparison with the experimental results still shows considerable differences. Considering the crude assumptions that have been made in these calculations it is, however, encouraging to note that the latter ionization mechanism, at least in a qualitative sense, is capable of predicting non-Franck–Condon behavior.

Finally, Table I contains the branching ratios for an ionization mechanism in which these three pathways are present simultaneously with equal weight, i.e., it is assumed that the

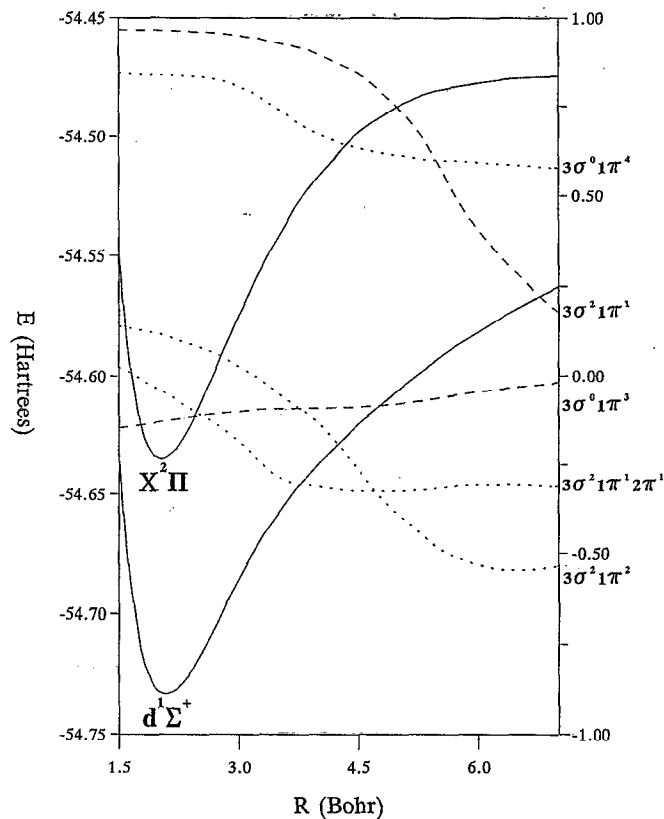


FIG. 7. Calculated MRD-CI potential energy in hartree of the $d^1\Sigma^+$ state of NH and the $X^2\Pi$ state of NH^+ (solid lines and left vertical scale) as a function of the internuclear distance. The dotted and dashed lines show the contributions of the indicated configurations to the CI vectors of the $d^1\Sigma^+$ and $X^2\Pi$ states, respectively (right vertical scale), as a function of the internuclear distance.

electronic transition moment for each of the pathways is the same. In such a mechanism interference between the various Franck–Condon factors is observed, although the resulting vibrational branching ratios still largely reflect the ones calculated on the basis of the $\dots 3\sigma^2 1\pi^1 \leftarrow \dots 3\sigma^2 1\pi^1 2\pi^1$ Rydberg ionization. The calculated CI wave functions of the $d^1\Sigma^+$ and $X^2\Pi$ states show that, apart from the three ionization pathways discussed above, ionization can also occur via many other pathways involving minor configurations in the wave functions of both the $d^1\Sigma^+$ and $X^2\Pi$ states. In an accurate calculation of the ionization cross sections such interference effects may therefore be of crucial importance.

The important conclusion to be drawn from the above arguments is that direct one-photon ionization of the $d^1\Sigma^+$ state is a formally forbidden process, which only becomes allowed when configuration interaction effects are taken into account. As an unusual result of the forbidden nature of this direct process, other processes might now compete effectively with one-photon ionization. In the following it will be shown that the major process competing with ionization is two-photon absorption to (pre)dissociative states.

B. Fragment signals

The analysis of the photoelectron spectra has revealed fragment ion signals which derive from a one-photon ioniza-

TABLE I. Vibrational overlap integrals between vibrational levels of the $d^1\Sigma^+$ and $X^2\Pi$ states calculated for several ionization mechanisms. In (a) the integrals have been calculated on the basis of the bare potential energy surfaces of the two states; in (b)–(e) ionization occurs via the indicated configurations.

(a)		$v^+=0$	$v^+=1$	$v^+=2$	$v^+=3$
	$v'=0$	0.981 104	0.193 033	0.013 074	0.000 241
	$v'=1$	-0.100 977	0.941 661	0.277 862	0.018 678
(b)		$v^+=0$	$v^+=1$	$v^+=2$	$v^+=3$
	$v'=0$	-0.103 176	-0.015 510	-0.000 576	-0.000 055
	$v'=1$	0.024 143	-0.096 711	-0.021 905	-0.000 665
(c)		$v^+=0$	$v^+=1$	$v^+=2$	$v^+=3$
	$v'=0$	0.104 878	0.010 540	-0.001 385	0.000 134
	$v'=1$	-0.029 199	0.094 271	0.013 278	-0.002 868
(d)		$v^+=0$	$v^+=1$	$v^+=2$	$v^+=3$
	$v'=0$	-0.045 083	-0.033 431	-0.001 513	-0.000 836
	$v'=1$	-0.013 207	-0.050 773	-0.048 875	-0.004 980
(e)		$v^+=0$	$v^+=1$	$v^+=2$	$v^+=3$
	$v'=0$	-0.043 381	-0.038 402	-0.003 474	-0.000 757
	$v'=1$	-0.018 264	-0.053 213	-0.057 502	-0.008 512

tion process of excited neutral fragments: for atomic nitrogen ionization occurs from the $\dots 2p^2 3s^1, ^2P^e$ excited state, hydrogen atoms are ionized from their $n=2$ excited states. These two fragments must be produced from two independent dissociation channels, since a simultaneous production from the same channel involves the absorption of at least six photons from the $a^1\Delta$ state.

The lowest dissociation limit leading to $\dots 2p^2 3s^1, ^2P^e$ nitrogen atoms, with hydrogen atoms in the ground state, is located 101 019 cm^{-1} above the $a^1\Delta$ state of NH.¹⁷ With the photon energies used to excite the $d^1\Sigma^+(v'=0)$ state ($\approx 35\,100\text{ cm}^{-1}$) this implies that the overall three-photon level is $\sim 4300\text{ cm}^{-1}$ above this dissociation limit. Dissociation leading to excited nitrogen atoms might therefore occur after a one-photon absorption process from the $d^1\Sigma^+$ state. A number of arguments go against a dissociation process at this energy level. First, the discussion on the possible role of a superexcited state in the ionization dynamics presented above is equally valid here. Second, at a mere 4300 cm^{-1} excess energy with respect to the dissociation limit the Franck–Condon overlap between the bound vibrational wave functions of the $d^1\Sigma^+$ state and the unbound wave functions of a (pre)dissociative state is expected to be rather poor. Finally, in previous two-photon excitation studies of the $f^1\Pi$ and $g^1\Delta$ states, where similar three-photon energy levels are accessed, the parent ions are observed to be the exclusive product of the multiphoton ionization process.⁹ A dissociation channel at the three-photon level would therefore seem unlikely.

The lowest asymptote yielding $\text{H}(n=2)$ atoms is the dissociation limit to $\text{H}(n=2)$ and $\text{N}(^4S^0)$, 109 826 cm^{-1} above the ground state of NH. Similar arguments as presented in the case of the channel leading to excited atomic nitrogen show that this dissociation channel is not expected to be important at the three-photon level. Additionally, it is noted that this $\text{H}(n=2)$ and $\text{N}(^4S^0)$ channel would involve a spin conversion, since the molecular states that can be built from

these atomic states are either triplet or quintet states which are not directly accessible from the $d^1\Sigma^+$ state. The first spin-allowed dissociation limit is found at 129 055 cm^{-1} and results in $\text{H}(n=2)$ and $\text{N}(^2D^0)$ atoms, well above the three-photon energies employed in our experiments.

These considerations allow for the conclusion that at least two photons need to be absorbed from the $d^1\Sigma^+$ state in order to access the dissociation channels leading to excited atomic nitrogen and hydrogen. The two-color experiments can only be interpreted consistently if it is assumed that dissociation occurs at an even-photon level (*vide infra*). It thus seems very likely that the dissociation channels are already excited by two-photon absorption. Since neutral fragments are produced, these dissociation channels should be associated with two superexcited (pre)dissociative states well above the lowest ionization limit of NH. Apart from dissociation, these states can also decay by autoionization to the $C^2\Sigma^+$, $B^2\Delta$, $A^2\Sigma^-$, and $X^2\Pi$ states. The obtained photoelectron spectra do not show photoelectrons deriving from such processes, and thus demonstrate that autoionization does not compete effectively with (pre)dissociation. Analogously, the two-photon absorption process might have led to direct ionization at the overall four-photon level to the $C^2\Sigma^+$, $B^2\Delta$, and $A^2\Sigma^-$ ionic states, since the two-photon transition $\dots 3\sigma^0 1\pi^2 \epsilon l \lambda \leftarrow \dots 3\sigma^0 1\pi^4$ is allowed. Apparently this ionization process does not have a significant cross section, since photoelectrons which can be attributed to such a process are not observed in the photoelectron spectra.

The complete picture of photon absorption after excitation of the $d^1\Sigma^+$ state thus involves the unusual situation of two competing processes. On the one hand, the molecule can be ionized by a zero-order forbidden one-photon ionization process, on the other hand the molecule can be subject to a two-photon absorption leading to dissociation of the molecule into excited neutral fragments. Since different numbers of photons are involved in these two processes, the relative contribution of the two processes should be power

dependent. Although we have not performed a systematic study of this power dependence, we notice that in previous studies⁶ a different $\text{NH}^+:\text{N}^+:\text{H}^+$ ratio has been measured for the $d^1\Sigma^+(v'=0)\leftarrow\leftarrow a^1\Delta(v''=0)$ transition (19:5:1 compared to 8:7:2 in the present study). This would be in line with the aforementioned power dependence, since the power densities employed in the present study are considerably higher than the power densities used previously.

Two-photon excitation multiphoton ionization spectroscopy with mass-resolved ion detection on the analogous $d^1\Sigma^+$ state of PH also exhibits a dramatic dependence of the yields of the molecular and fragment ions on the rotational transition via which ionization takes place.^{6,18} These findings have been rationalized by a (2+2) MPI process terminating at the predissociating $A^2\Delta$ state of the PH^+ ion. In light of the present results it would be of interest to apply the REMPI-PES method on this state of PH as well, in order to investigate whether for this molecule indeed different ionization and dissociation processes occur.

From the results of our two-color excitation experiments we conclude that the overall three-photon level has a negligible influence on the dissociation dynamics, in particular with respect to the enhanced yields which have been observed for a number of rotational transitions in both one- and two-color excitation. At first instance it might seem puzzling that the observed enhancements are independent of our excitation schemes. However, Fig. 4(b) shows that this observation is in agreement with the conclusion that dissociation takes place via excitation of superexcited (pre)dissociative states at the overall four-photon level. For this we consider a four-photon level associated with a rotational transition, which in the one-color experiments gives rise to an enhanced fragment yield. When the same rovibronic level of the $d^1\Sigma^+$ state is populated via two-color excitation, two types of two-photon absorption processes can take place. First, the molecule might absorb two photons of the same color, reaching four-photon levels distinctly different from the one-color four-photon level. Second, it might absorb one photon of one color and one photon of the other color. In the latter absorption process the same four-photon level is excited as in the one-color experiments. Consequently, if superexcited states at this level are responsible for the dissociation dynamics, similar enhancements in fragment yields are indeed to be expected.

From the present experiments the amount of information on the identity and location of these superexcited states is rather limited. The only observation that can be made in this respect derives from the four-photon levels accessed at the rotational transitions for which clear enhancements of excited atomic nitrogen are seen. These levels seem to suggest a superexcited state structure at $\sim 152\,000\text{ cm}^{-1}$ above the ground state of NH. For a detailed investigation of these states one would probably have to resort to a double resonance experiment in which the $d^1\Sigma^+$ state is excited by a two-photon transition, while the superexcited states of the neutral are subsequently probed by a VUV source.

VI. CONCLUSIONS

The application of one- and two-color two-photon excitation spectroscopy in combination with mass-resolved ion and kinetic energy-resolved electron detection has led to a detailed characterization of the electronic structure of the $d^1\Sigma^+$ state of NH, and the consequences of these electronic properties for subsequent photon absorption. One of the important conclusions drawn from the present experiments is that two strongly competing processes can take place after excitation of the $d^1\Sigma^+$ state.

The ionization pathway after excitation of the $d^1\Sigma^+$ state which can normally be assumed to be dominant in subsequent photon absorption processes, is largely forbidden as a result of the intrinsic electronic character of the state. That the molecule is nevertheless ionized by a one-photon absorption can nicely be explained by taking the important role of configuration interaction effects into account, as has been demonstrated by *ab initio* calculations. In addition, the observation of non-Franck–Condon vibrational branching ratios over the ionic vibrational levels in the $X^2\Pi$ state upon ionization can be attributed to the strong dependence of the contributions of the various configurations on the internuclear distance, most notably the $\dots 2\sigma^2 3\sigma^2 1\pi^1 2\pi^1$ Rydberg configuration in the $d^1\Sigma^+$ state.

The observation of electrons deriving from the ionization of excited neutral fragments in the photoelectron spectra obtained for ionization via the $d^1\Sigma^+$ state has ultimately led to the conclusion that a two-photon absorption process from the $d^1\Sigma^+$ state, which for regular states would not be very probable, has now become a significant competing process. By this process superexcited states of the neutral molecule are accessed, which are responsible for the dissociation of the molecule into neutral fragments.

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¹E. de Beer, M. Born, C. A. de Lange, and N. P. C. Westwood, *Chem. Phys. Lett.* **186**, 40 (1991).

²S. G. Clement, M. N. R. Ashfold, C. M. Western, E. de Beer, C. A. de Lange, and N. P. C. Westwood, *J. Chem. Phys.* **96**, 4963 (1992).

³K. Wang, J. A. Stephens, V. McKoy, E. de Beer, C. A. de Lange, and N. P. C. Westwood, *J. Chem. Phys.* **97**, 211 (1992).

⁴R. D. Johnson III and J. W. Hudgens, *J. Chem. Phys.* **92**, 6420 (1990).

⁵J. J. Chu, P. Marcus, and P. J. Dagdigian, *J. Chem. Phys.* **93**, 257 (1990).

⁶M. N. R. Ashfold, S. G. Clement, J. D. Howe, and C. M. Western, *J. Chem. Soc. Faraday Trans.* **87**, 2515 (1991).

⁷A. Banerjee and F. Grein, *J. Chem. Phys.* **66**, 1054 (1977).

⁸M. Guest and D. M. Hirst, *Mol. Phys.* **34**, 1611 (1977).

⁹S. G. Clement, M. N. R. Ashfold, and C. M. Western, *J. Chem. Soc. Faraday Trans.* **88**, 3121 (1992).

¹⁰B. G. Koenders, D. M. Wieringa, K. E. Drabe, and C. A. de Lange, *Chem. Phys.* **118**, 113 (1987).

¹¹H. H. Nelson and J. R. McDonald, *J. Chem. Phys.* **93**, 8777 (1990).

¹²R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.* **35**, 771 (1978); R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33

- (1974); **39**, 217 (1975); P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys. Lett.* **72**, 278 (1980); R. J. Buenker, in *Studies in Physical and Theoretical Chemistry*, edited by R. Carbó (Elsevier, Amsterdam, 1982), Vol. 21, p. 17; R. J. Buenker and R. A. Philips, *J. Mol. Spectrosc.* **123**, 291 (1985).
- ¹³S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ¹⁴T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).
- ¹⁵T. H. Dunning, Jr., *J. Chem. Phys.* **55**, 716 (1971).
- ¹⁶S. T. Elbert and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 857 (1974).
- ¹⁷W. R. Anderson, *J. Phys. Chem.* **93**, 530 (1989).
- ¹⁸M. N. R. Ashfold, R. J. Stickland, and B. Tutcher, *Mol. Phys.* **65**, 1455 (1988).