

VIBRATIONAL STATE SELECTION OF AMMONIA IONS USING RESONANT 2 + 1 MULTIPHOTON IONIZATION

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Photoelectron kinetic energy spectra are presented for the 2 + 1 multiphoton ionization of NH₃ via the vibronic levels of the \tilde{B} and \tilde{C}' Rydberg states of the neutral. The contribution from $\Delta v = 0$ state-selected ionization is greater than 80% through the \tilde{C}' state and over 70% through the \tilde{B} state. This allows for the production of large densities of NH₃⁺(ν) ions with a high degree of vibrational selectivity.

1. Introduction

Multiphoton ionization (MPI) offers an attractive method for preparing state-selected ions for studying the dynamics of ion-molecule reactions [1]. However, to realize this goal it is necessary to establish the internal energy distribution of the ions formed. We report here a study of the 2 + 1 resonance-enhanced multiphoton ionization of ammonia via the \tilde{B} and \tilde{C}' Rydberg states. These two Rydberg states show long interleaved progressions in the ν_2 umbrella-bending mode. Since the \tilde{B} and \tilde{C}' excited states of the neutral and the \tilde{X} state of the ion have a planar equilibrium geometry, one expects from the Franck-Condon principle that the $\Delta v = 0$ transition should be strongly favored in the ionization step. Thus, ammonia is an excellent candidate for vibrational state selection through resonance-enhanced multiphoton ionization.

Colson and co-workers [2] have pioneered MPI studies of ammonia using a 3 + 1 resonance-enhanced ionization scheme. They investigated the spectroscopy of several new Rydberg states, in particular the NH₃ \tilde{C}' state. This work has been supplemented by Ashfold, Dixon, and Stickland [3] who have examined the \tilde{C}' state predissociation dynamics. In addition, two separate photoelectron spectroscopy (PES) studies have

shown that the 3 + 1 multiphoton ionization of ammonia via the \tilde{C}' state produces vibrationally state-selected ions [4, 5].

In general, the ion yield for 2 + 1 MPI exceeds that of 3 + 1 MPI by one to three orders of magnitude. Hence, the 2 + 1 multiphoton ionization of NH₃ is the preferred method for producing the large number of ions required for reaction studies. Two investigations of the two-photon resonant ionization have been published. A cursory study in a room-temperature static gas of neat ammonia has been performed by Grimley and Kay [6]. A pulsed molecular beam study by Stanley, Echt and Castleman [7] is more detailed, but they note in proof that the degree of cooling obtained in their spectra is far less than that estimated for their supersonic beam conditions.

We have carried out MPI and PES studies of the 2 + 1 resonant-enhanced ionization of a molecular beam of ammonia seeded in argon. By expansion-cooling the ammonia, the accidental overlaps between vibronic bands can be avoided, thus simplifying the resulting spectrum so that rotational assignments can readily be made. Cooling also concentrates molecules in the lowest rotational levels so that the number of ions produced at a given wavelength is increased. The populations derived from the photoelectron kinetic energy distributions demonstrate that the NH₃⁺ \tilde{X} state can be prepared in essentially a single vibrational level by simply selecting the 2 + 1 MPI process to be resonant with different vibrational levels in either the \tilde{B} or \tilde{C}' Rydberg states.

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2. Experimental

The time-of-flight photoelectron spectrometer has been described in detail [8] and will only be discussed briefly here. Ammonia (Matheson 99.99%) at 10 psi backing pressure is admitted through a pulsed nozzle (Lasertechnics) and ionized by the focused doubled output (280–320 nm) of a Nd^{3+} :YAG pumped dye laser (Quanta-Ray DCR-1A and PDL-1). A portion of the ejected electrons traverse a 50 cm magnetically shielded field-free drift tube and are detected by a channel electron multiplier array (Galileo Electronics FTD2003). A fast transient digitizer (Tektronix 7912AD) is used to record the time-of-flight distribution of the photoelectron signals. Typical count rates in these experiments are 5–10 photoelectrons per laser shot. The resolution is limited in most cases by the pulse width of the laser and amounts to about 3% of the electron kinetic energy.

The photoelectron spectra are calibrated using atomic iron [8] produced from the photodissociation of $\text{Fe}(\text{CO})_5$. Photoelectrons from the iron in the energy range 1.0–1.8 eV can be produced by resonant transitions in the UV originating from the $a^5\text{F}$ level, which is ≈ 1 eV above the $a^5\text{D}$ ground state. The multiplicity of these transitions provides numerous photoelectron peaks of known energy for calibrating the flight times during the experiment. An ionization potential of 7 870 eV was used for calculating the Fe photoelectron energies [9].

The portions of the 2+1 MPI wavelength spectrum presented here were recorded by detecting the positive ion current in a separate apparatus capable of mass discrimination of the ion signals [1]. For these experiments, the mass spectrometer was tuned to $m/e = 17$ ($^{14}\text{NH}_3$) and the signal detected with a current amplifier and boxcar integrator. Cooling of the ammonia was achieved by 5% seeding in argon

3. Results and discussion

3.1. Appearance of the 2+1 MPI spectrum via the $\tilde{\text{B}}$ and $\tilde{\text{C}}'$ states

Representative bands from the 2+1 MPI wavelength spectrum recorded in the region 280–320 nm are shown in fig 1. These spectra illustrate the greatly simplified

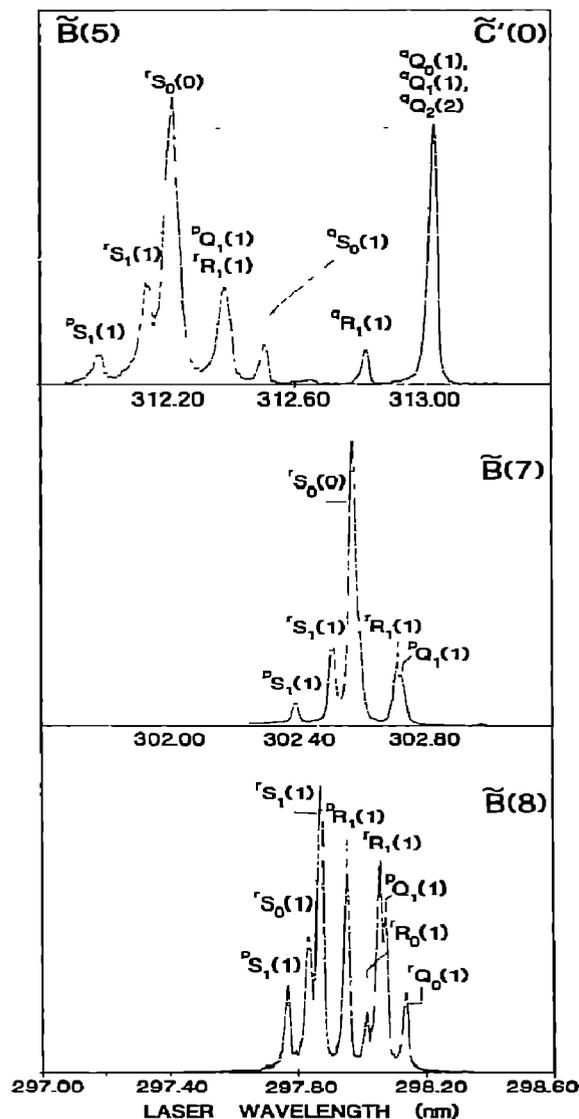


Fig 1. Rotational assignments for several representative vibronic bands in the 2+1 MPI spectrum of ammonia. A rotational temperature of 20 K is found from the rotational analysis.

appearance of the parallel $\tilde{\text{C}}'$ bands ($\Delta K = 0$) and the perpendicular $\tilde{\text{B}}$ bands ($\Delta K = \pm 1$) when they are observed under conditions of significant rotational cooling. The rotational contour of the $\tilde{\text{C}}'(0)$ band, shown in the top panel of fig. 1, is typical of what is observed

for members of the \tilde{C}' progression*. For each band, an intense Q transition is seen and two much weaker R and S lines appear slightly to the blue. Even-numbered vibrational bands originate from the inversion component of A_1' vibronic symmetry of the doubly degenerate NH_3 ground state. No transitions are observed from the level $K'' = 0, J'' = 0$, and indeed all even J for this K level in both the \tilde{X} and \tilde{C}' states are missing due to nuclear spin statistics. For the odd-numbered members of this progression, however, transitions occur from the \tilde{X} state inversion component having A_2'' symmetry. In this case, the odd J for $K = 0$ are missing in both the lower and upper states. Although all the \tilde{C}' bands appear similar, the features which correspond to ${}^9Q_0(1)$ and ${}^9S_0(1)$ for even v correspond to ${}^9Q_0(0)$ and ${}^9S_0(0)$ for odd v . The spectra show that only the levels $K'' = 0, J'' = 0$ or 1 and $K'' = 1, J'' = 1$ of the ammonia ground state are appreciably populated in the supersonic expansion. It is also because of this very restricted initial rotational distribution that we fail to observe any O and P transitions. As can be seen in fig. 1, we achieve more than sufficient rotational cooling to distinguish clearly the $\tilde{C}'(0)$ and $\tilde{B}(5)$ bands, which are severely overlapped in the room-temperature spectrum.

The very low rotational temperature obtained here (≈ 20 K) manifests itself in an interesting manner for the vibrational bands of the \tilde{B} state. While a simple pattern of four features is observed for all the odd vibrational bands, the even vibrational bands show a more complex eight-peak pattern (see fig. 1). The explanation for this difference can again be traced to the presence of only odd J for $K'' = 0$ in the A_1' inversion component, and of only even J in the A_2'' inversion component. In the \tilde{B} state, the vibronic symmetry is either E'' or E' , according to whether v is even or odd, and two-photon transitions connect lower and upper states according to the schemes $A_1' \rightarrow E''$ and $A_2'' \rightarrow E'$. Thus the rotational levels which contribute intensity to the observed spectra are $K'' = 0, J'' = 1$ and $K'' = 1, J'' = 1$ for even v , but $K'' = 0, J'' = 0$ and $K'' = 1, J'' = 1$ for odd v . The two levels in the former case are nearly equal in energy and thus are approximately equally populated, giving rise to the more complicated pattern of lines. In the latter case, the level $K'' = 0$,

$J'' = 0$ dominates, and a simpler band contour is observed in which the transition ${}^1S_0(0)$ carries the major fraction of the intensity. The positions of the lines assigned in fig. 1 are in good agreement with their calculated positions based on the \tilde{C}' state constants reported by Colson and co-workers [2] and on the \tilde{B} state constants reported by Douglas and Hollas [10].

3.2. Photoelectron energy distribution: NH_3^+ vibrational selectivity

Figs. 2 and 3 present our 2 + 1 resonant MPI photoelectron spectra for the \tilde{B} and \tilde{C}' states of ammonia. The conversion from the time-of-flight domain into energy space is performed by using photoelectrons produced from known MPI resonances in atomic iron. This energy calibration is sufficiently accurate to make unambiguous vibrational assignments of the ammonia photoelectron peaks. The vibrational ladders in the figures indicate the photoelectron kinetic energies corresponding to the 0–13 vibrational levels in the NH_3^+ \tilde{X} state. These are determined from the difference of the three-photon energy of the resonance and the energies of the vibrational states of the ammonia ion [11]. Final energy determinations are performed by internal calibration using the known energies for the $v = 0$ and $v = 5$ ionic levels. This procedure is found to be accurate to within ± 10 meV for all vibrational levels.

A single prominent photoelectron peak corresponding to the $\Delta v = 0$ transition appears in the two-photon resonant, three-photon ionization of ammonia via the vibrational levels of the \tilde{B} and \tilde{C}' states. Thus, direct state-selected ionization is the dominant mechanism in the 2 + 1 MPI process for these two states. This is in agreement with the separate studies done by Colson and co-workers [4] and by Kimura and co-workers [5] for the 3 + 1 ionization via the \tilde{C}' state. However, state-selected ion production through the \tilde{B} state could not be observed in either of these experiments as the fourth, ionizing photon does not carry sufficient energy to reach the $\Delta v = 0$ level in the ground state of the ion. Only near-zero kinetic energy photoelectrons corresponding to vibrational autoionization were observed for the \tilde{B} state [4]. The role played by vibrational autoionization in the 2 + 1 ionization via the \tilde{B} and \tilde{C}' states in this experiment is difficult to assess because such low-energy electrons are difficult to detect. Autoionization via highly excited Rydberg states is expected

* We note, however, that evidence for predissociation is observed for the vibrational bands $\tilde{C}'(3)$ to $\tilde{C}'(6)$ as has been found in ref. [3].

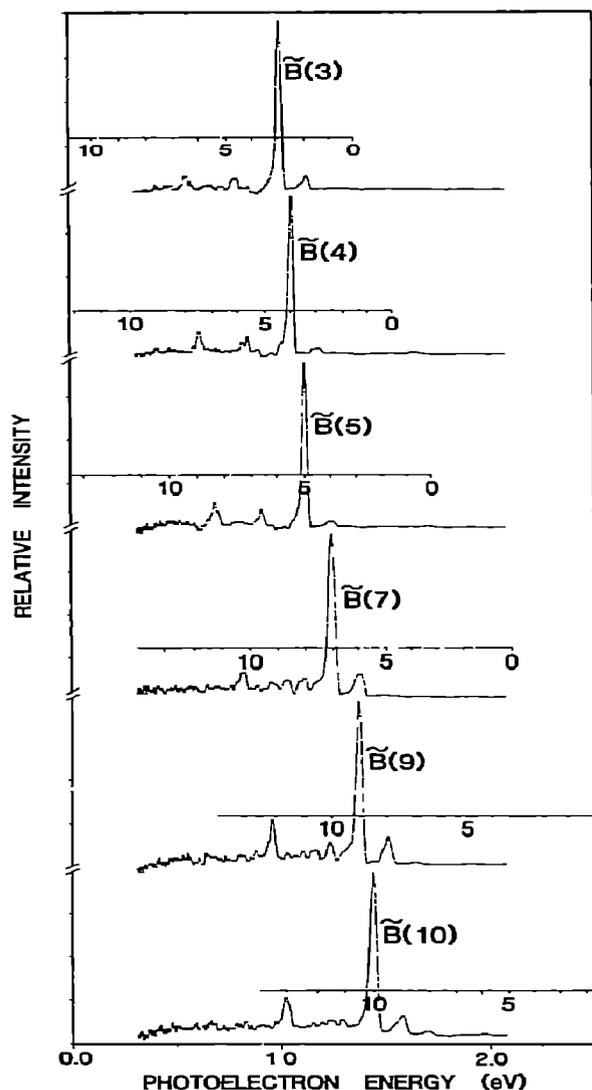


Fig. 2. Photoelectron kinetic energy spectra for 2+1 MPI resonant with different vibronic levels in the NH_3 \tilde{B} state. Assignments are indicated by the vibrational ladders for the ground-state ion. The $\Delta v = 0$ transition accounts for greater than 70% of the photoelectrons produced via the \tilde{B} state.

to differ significantly in the two cases since the single-photon energy used in the two-photon resonant ionization is 50% greater than the photon energy in the three-photon resonant case. For the wavelength region studied here, the 3+1 process exceeds the ionization po-

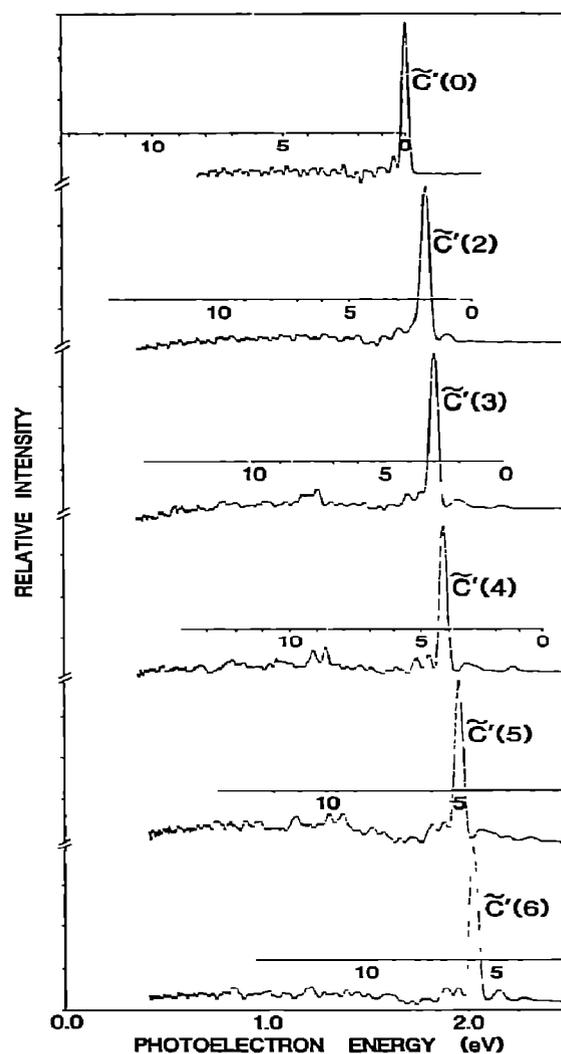


Fig. 3. Photoelectron kinetic energy spectra for 2+1 MPI resonant with different vibronic levels in the NH_3 \tilde{C}' state. State-selected ionization ($\Delta v = 0$) accounts for over 80% of the photoelectrons produced via the \tilde{C}' state.

tential by only 0.1 to 1.3 eV, whereas the 2+1 process exceeds the IP by 1.4 to 2.7 eV.

Tables 1 and 2 list the photoelectron distributions as a fraction of the total number of photoelectrons observed for 2+1 resonant ionization through the NH_3 (\tilde{B}, v) and NH_3 (\tilde{C}', v) states. The $\Delta v = -1$ peak amount to about 5% of the intensity of the $\Delta v = 0$ peak from the \tilde{C}' state and about 10% of the intensity

Table 1
Photoelectron distributions from different vibrational levels of the \tilde{B} state of NH_3

| | $\text{NH}_3^+(\tilde{X}, \nu)$ | | | |
|-----------------|---------------------------------|------------------|-------------------|------------|
| | $\Delta\nu = 0$ | $\Delta\nu = -1$ | other $\Delta\nu$ | unassigned |
| \tilde{B} (3) | 0.83 | 0.06 | 0.00 | 0.11 |
| (4) | 0.82 | 0.04 | 0.00 | 0.14 |
| (5) | 0.78 | 0.04 | 0.00 | 0.18 |
| (6) | — | — | — | — |
| (7) | 0.76 | 0.11 | 0.00 | 0.13 |
| (8) | 0.74 | 0.10 | 0.00 | 0.16 |
| (9) | 0.74 | 0.11 | 0.01 | 0.14 |
| (10) | 0.74 | 0.10 | 0.02 | 0.14 |

Table 2
Photoelectron distributions from different vibrational levels of the \tilde{C}' state of NH_3

| | $\text{NH}_3^+(\tilde{X}, \nu)$ | | | |
|------------------|---------------------------------|------------------|-------------------|------------|
| | $\Delta\nu = 0$ | $\Delta\nu = -1$ | other $\Delta\nu$ | unassigned |
| \tilde{C}' (0) | 1.00 | 0.00 | 0.00 | 0.00 |
| (1) | — | — | — | — |
| (2) | 0.94 | 0.04 | 0.02 | 0.00 |
| (3) | 0.83 | 0.05 | 0.02 | 0.10 |
| (4) | 0.80 | 0.05 | 0.02 | 0.12 |
| (5) | 0.80 | 0.05 | 0.02 | 0.12 |
| (6) | 0.88 | 0.06 | 0.02 | 0.04 |

of the $\Delta\nu = 0$ peak from the \tilde{B} state. Production of $\Delta\nu = -1$ ions is consistent with the expectation that the Franck-Condon overlap be non-zero for the $\nu' = \nu'' - 1$ level in going to the less tightly bound ion. The $\Delta\nu = +1$ transition is less easily distinguished from the background (see figs. 2 and 3). The asymmetric shading of the main peak to longer times (lower energy) and the small amount of ringing in the detection electronics further mask the presence of this peak. This transition is less than 5% of the intensity of the $\Delta\nu = 0$ peak. Other transitions to lower vibrational levels in the ion, notably $\Delta\nu = -2$ and $\Delta\nu = -3$, begin to appear weakly as one proceeds higher in the vibrational manifolds of either state.

There are several photoelectron peaks occurring at energies less than the state-selected peak in the series of spectra for both states. These peaks do not appear to fit into the vibrational level spacing of the $\text{NH}_3^+(\tilde{X})$

ground-state ion as do the previously discussed peaks. The combined intensity for these anomalous peaks accounts for about 10% of the photoelectrons produced resonantly through the \tilde{B} state and 0–5% of the photoelectrons produced through the \tilde{C}' state. Presently, the origin of these unassigned peaks is unknown. These represent a significant contamination for state-selective ionization through the \tilde{B} state, but less so for the \tilde{C}' state.

We speculate that these peaks might arise from several different processes. First, they may come from ionization of some species other than NH_3 , such as ammonia clusters [12]. Second, they may arise from a competing non-direct ionization mechanism, such as internal conversion or a radiative transition to another ammonia Rydberg state prior to the ionization step. Third, they may be caused by ionization leaving the ammonia ion in the excited \tilde{A} state. The first excited state of the NH_3^+ ion at 14.94 eV can be reached at the four-photon level in the 2 + 1 scheme. Production of electronically excited ammonia ions may therefore be possible if the laser is focused sufficiently tightly for this process to occur. Because the unassigned peaks represent only a minor contamination for state-selective ionization through the \tilde{B} state, they were not further investigated. Understanding the origin of the unassigned peaks would clear up any remaining questions on the efficiency of the MPI process for state-selective $\text{NH}_3^+(\tilde{X}, \nu)$ ion production.

The "purity" of the ammonia ions produced by 2 + 1 MPI can also be diminished if the $\text{NH}_3^+(\tilde{X}, \nu)$ ion is photodissociated. The appearance potential for this process is 15.80 eV and this channel becomes accessible at the four-photon level in the two-photon resonant process. This process appears as a minor contribution (the order of a few percent) in the MPI mass spectrum [1] for $\tilde{B}(\nu > 4)$ and $\tilde{C}'(\nu > 0)$. The importance of this channel increases with increasing ν , as has been observed in the 3 + 1 multiphoton ionization [4].

4. Conclusions

Rotational analysis of the MPI wavelength spectra indicate that the ammonia is rotationally cooled to ≈ 20 K before ionization. This is sufficient to resolve cleanly all vibronic levels between the overlapping \tilde{B} and \tilde{C}' states. Only the three lowest rotational levels ($K = 0, J = 0, 1$ and $K = 1, J = 1$) in the NH_3 ground

state are populated and this distribution is not expected to change markedly on ionization. Thus, the contribution of rotation to the energetics of the MPI-produced ammonia ions is negligibly small.

Two-photon resonant, three-photon ionization through the \tilde{C}' state is more selective in producing ions in a single vibrational state than ionization through the \tilde{B} state. Although the \tilde{B} state allows for state-selected ion production, the presence of other ionization processes results in a more complicated and ambiguous distribution of ion states. Ionization through the \tilde{C}' state is therefore the preferred method for efficiently producing state-selected NH_3^+ ($\tilde{X}, v = 0-6$) ions by 2+1 multiphoton ionization.

Finally, it is expected that the production of vibrationally state-selected ions using resonance-enhanced multiphoton ionization should be a rather general phenomenon. If the resonant intermediate state has a similar geometry to that of the ion, as is the case for the Rydberg states often accessed in MPI experiments, the Franck-Condon factors will strongly favor this process. Therefore, the dynamics of numerous ion-molecule reactions can now be studied using the MPI technique as the source of vibrationally state-selected reagent ions.

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