

Photoelectron spectra of N_2^+ : Rotational line profiles studied with He I-excited angle-resolved spectroscopy and with synchrotron radiation

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We have recorded angle-resolved He I photoelectron spectra of the three outermost valence states in N_2^+ , with high enough resolution to observe rotational line profiles. For the two Σ states, the $X^2\Sigma_g^+$ and the $B^2\Sigma_u^+$, we found that the rotational branches corresponding to different changes in rotational quantum number can differ dramatically in β value. The well-known difference in β value for the $\nu=0$ and $\nu=1$ vibrations of the $X^2\Sigma_g^+$ state was found to be due to different rotational branching ratios and also different β values of the rotational branches. For the $\nu=0-2$ vibrations of the $A^2\Pi_u$ state, the β value difference between rotational branches is much less pronounced than in the X and B states. We have also recorded synchrotron-radiation-excited photoelectron spectra of the $\nu=0$ vibrational peaks of the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states where rotational line profiles are resolved. The intensities of the rotational branches were studied as function of photon energy, the X state between 23 and 65 eV, and the B state between 23 and 45 eV. The results for the X state have recently been presented in a Letter [G. Öhrwall, P. Baltzer, and J. Bozek, Phys. Rev. Lett. **81**, 546, 1998]. The rotational branching ratios of the two states have very different behaviors as functions of photon energy. The relative intensities of the rotational branches in the X state change significantly over the studied energy range. The $3\sigma_g \rightarrow k\sigma_u$ shape resonance apparently gives rise to a non-Franck-Condon-like behavior for the rotational branching ratio of the X state. In the B state, the rotational branching ratios remain essentially constant over the studied energy range. [S1050-2947(99)07903-2]

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I. INTRODUCTION

Significant insight into the dynamics of valence shell photoionization in molecules can be gained by studying the influence of photon energy on photoelectron line intensities and photoelectron angular distributions. Many photoelectron studies have been performed on different systems to give information about shape resonances, Cooper minima and other phenomena (see, for instance, Refs. [1] and [2] for reviews). Until now, these studies have at best been vibrationally resolved, due to the fact that the energy resolution of conventional photoelectron spectroscopy is usually not capable of resolving rotational fine structure, which is of the order a few meV or less. By achieving rotational resolution, details of the partial photoelectron wave composition can start to be discerned, which would be a great advantage in understanding these photoionization phenomena.

Historically, the linewidth of the exciting synchrotron radiation has been too large to allow rotational resolution. At best, with normal-incidence monochromators, resolving powers of $\approx 10^4$ have been possible to achieve, and these monochromators have an energy cutoff around 35 eV. With high brilliance third generation synchrotron radiation sources, this has been possible to improve dramatically [3]. For instance, at beamline 9.0.1 at the Advanced Light Source in Berkeley, where the experiments presented in this paper were done, a resolving power of more than 10^4 can be achieved between 25 and 300 eV [4], with a maximum of 6.4×10^4 at 64.1 eV [5]. Even higher resolving powers have been presented for other beamlines at lower photon energies [6].

This development, together with advances in photoelectron spectrometer design [7,8], has made it possible for us to study the influence of photon energy on rotational populations. Recently, we presented photoelectron spectra of the $\nu=0$ vibration of the $X^2\Sigma_g^+$ state of N_2^+ , where rotational line profiles were resolved, recorded with photon energies ranging from 23 up to 65 eV [9]. The present paper is an extension of that work, including the $B^2\Sigma_u^+$ state.

Previously, Poliakoff and co-workers studied the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ fluorescence of N_2^+ and the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ fluorescence of CO^+ with rotational resolution, with the molecules photoionized with a wide range of photon energies [10–14]. These experiments clearly showed that rotational populations were affected by Cooper minima and shape resonances, and that further insight into photoionization can be gained by achieving rotational resolution. In these studies, the resolution problem is less severe than for photoelectron spectroscopy, since the fluorescence technique decouples the excitation from the detection. This means that radiation with moderate resolution can be used, and that the energy of the ionizing photons does not influence the resolution of the spectra, barring changes in photoionization cross section and hence intensity.

Lasers have extensively been used in experiments where photoelectrons have been detected with rotational resolution, such as resonantly enhanced multiphoton ionization photoelectron spectroscopy (REMPE-PES) and zero-kinetic-energy pulsed-field ionization (ZEKE-PFI) spectroscopy. For the type of experiment reported in this paper, the use of laser radiation would be problematic. While lasers may have very small linewidths, easily small enough to resolve rotational

structure, their effective range of tunable photon energies is today limited. Also, the lasers available for studies in the vacuum ultraviolet–extreme ultraviolet vuv/xuv energy region are pulsed. This causes large and fast variations of the plasma potentials in the ionization region, which makes accurate energy analysis of the kinetic photoelectrons difficult. If the radiation is continuous (as for discharge lamps), or has a very high repetition rate (as synchrotron radiation), the plasma potential will not vary to the same degree, and can be compensated for.

The first photoelectron experiment where N_2^+ was studied with some sort of rotational resolution was probably the threshold spectroscopy experiments of Peatman *et al.* [15]. They found some structure in the the threshold photoelectron peaks that was attributed to either rotations or to overlapping Rydberg series. The peaks look very different from what was presented in Ref. [16] or the present work, which would indicate that if it was rotational structure, it must have been severely perturbed by auto-ionizing resonances.

With the ZEKE-PFI technique, several rotationally resolved studies of the valence states of N_2^+ have been made, both xuv laser excited [17–20] and synchrotron radiation excited [21]. These experiments can yield quite different rotational branching ratios than conventional photoelectron spectroscopy for this system. Merkt and Softley [17] investigated some of the threshold effects that occurs for the X state of this system in ZEKE studies.

We are not aware of any REMPI-PES studies of N_2^+ that have had high enough resolution to discern even the rotational line profile, let alone rotational states. Such low-energy photoelectron spectra could be interesting to compare with to establish possible threshold effects in the photoelectron spectrum of N_2^+ .

With conventional single-photon He I excited photoelectron spectroscopy, Allen and Grimm [22] managed to obtain spectra of the X , A , and B states where the rotational line shape could be discerned. With a complex deconvolution technique, they could enhance these spectra to show the rotational branches with some clarity. Morioka *et al.* [23] tried to derive the rotational branching ratios for the X state of N_2^+ from He I excited spectra. The resolution for these spectra were around 20 meV, so no clear rotational lineprofile could be discerned. Ogata *et al.* [24] tried to establish the β value and the branching ratio for the rotational branches of the $\nu=0$ and 1 vibrations of the X state of N_2^+ from He I excited photoelectron spectra. Their resolution was similar to that of Morioka *et al.*, so the rotational line profiles were not discernible. Our group in Uppsala published spectra of the $\nu=0$ vibrations of the X and B states some years ago [16], where the rotational line profiles were clearly visible. We have now recorded the same peaks, plus the $\nu=1$ vibration of the X state and $\nu=0-2$ vibrations of the A state, with improved resolution, and with the angle resolved.

This is an interesting addition to the rather meager amount of investigations into the photoelectron angular distribution of rotational states in molecules. With resonance lamp ionization, only the angular distribution of photoelectrons of the $X^2\Sigma_g^+$ state in H_2^+ has been studied [25–29]. With laser excitation, some angle-resolved studies off the $X^1\Sigma^+$ state of NO^+ have been performed [30–37]. In both these cases, NO^+ and H_2^+ , the ionic state had Σ symme-

tries, and large differences in angular distribution were found for different rotational branches. In the present study, states with both Σ and Π symmetries were investigated, and the results for these symmetries could be interesting to contrast.

II. EXPERIMENT

The synchrotron radiation experiments were performed at the beamline 9.0.1 at the Advanced Light Source synchrotron facility in Berkeley, California. This is an extremely high resolution undulator beamline with a spherical grating monochromator, capable of resolving powers of up to $E/\Delta E = 64\,000$ [5]. It is equipped with three interchangeable gratings for different energy ranges. A 380 line per mm grating was used for the photon energy range 23–45 eV, with a linewidth of the exciting radiation varying between 2 and 4 meV. At 65 eV, a 925 lines per mm grating was used, with slits set to give a linewidth of around 5 meV. The spectra taken with synchrotron radiation were recorded at the magic angle $55^\circ \pm 3^\circ$ to the direction of polarization. The uncertainty in angle may introduce a β dependence of the rotational branching ratios, which also may change with photon energy. However, the error can be estimated to be of the order of at most 5–10%, and will not affect the qualitative result of the present study.

The He I excited spectra were recorded with radiation generated by a microwave-powered electron cyclotron resonance source. This source produces extremely intense radiation with a measured linewidth of 1.2 meV [8,38]. The light was polarized by a simple arrangement with two gold-plated mirrors. After passing through the polarizer, the light was reflected in a grating monochromator which is ordinarily used for monochromatization of He II radiation. This was set for zero order light, i.e., only reflecting, and polarized the light further. Light source, mirror arrangement and monochromator swing around the ionization region on a rotating feedthrough. During the recording, the spectra were swept alternating between 0° and 90° to the main direction of polarization. The size of the polarizing mirrors limited the light, giving it a rectangular cross section. When the angle between the major polarization axis and the acceptance of the spectrometer was changed from 0° to 90° , the size of the ionization volume seen by the spectrometer decreased. The intensity of the measured spectrum was then decreased by a geometrical factor. This factor had to be determined by measuring intensities of a substance with a known β parameter. The polarization also has to be determined experimentally. To do this, we measured the intensities of the outermost valence p orbitals of Ar, Kr, and Xe, for which the β parameters are well known from literature [39,40]. Measuring two substances simultaneously is sufficient to obtain both the geometrical factor due to the rectangular shape of the ionization region, and the degree of polarization. This was done before and after the experiment. The degree of polarization was found to be $P=0.92$, and not to deteriorate measurably during the time the experiment was conducted.

The photoelectron spectrometer used in both the He I and synchrotron excited work is a truncated hemispherical analyzer with 144-mm mean radius which has been described elsewhere [7]. The angle in the dispersive direction accepted into the analyzer was less than 20 mrad. Two of the major

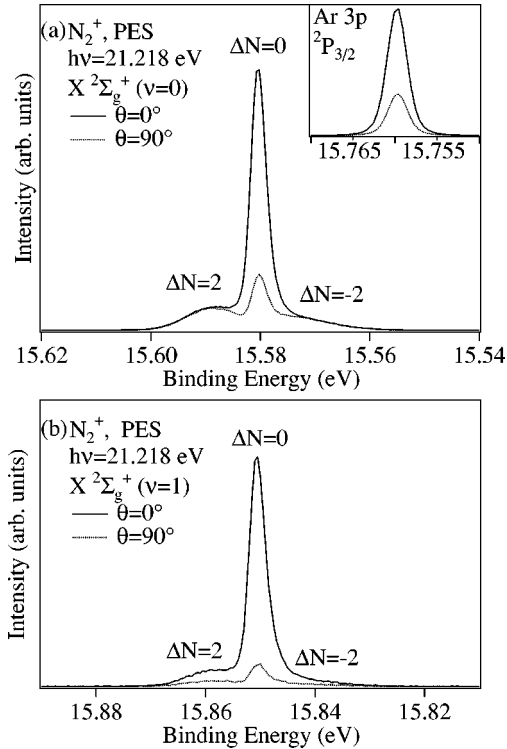


FIG. 1. He I excited spectrum of the $\nu=0$ [(a), top] and $\nu=1$ [(b), bottom] vibrational peaks in the $X^2\Sigma_g^+$ state of N_2^+ , recorded with $\theta=0^\circ$ (solid line) and $\theta=90^\circ$ (broken line). The insert shows the Ar $3p^2P_{3/2}$ peak. The full width at half maximum of the Ar peak is 2.8 meV, corresponding to a spectrometer broadening of around 2.5 meV.

effects that degrade resolution in UV-PES are the field gradients that appear due to plasma potentials in the ionizing region and the drifts in contact potentials that occur during the experiment. To compensate for this, electrodes have been fitted in the ionizing region, which were used for active potential correction of drifts and field gradients during the experiment run [8]. To decrease the Doppler width, another major resolution degrading factor, an effusive beam of gas, perpendicular both to the ionizing radiation and the acceptance of the spectrometer, was used as a sample. The beam was created by passage through a multichannel plate with straight channels. The effusive beam had virtually no cooling effect, so the sample was at room temperature during the experiment. The resolution of the synchrotron radiation excited spectra was degraded by fluctuations in the radiation intensity, that caused fast variations of the plasma potential, which the active potential correction setup could not handle. The energy resolution in the synchrotron-radiation-excited spectra varied from 4 meV at 23-eV photon energy up to 10 meV at 65-eV photon energy. For the He I spectra, the energy resolution was around 2.5 meV (see Fig. 1). The N_2 spectra were recorded simultaneously with a rare-gas line, in order to energy calibrate the spectra and to determine the spectrometer function. For the synchrotron-radiation-ionized spectra, the Ne $2p_{3/2}$ line with a binding energy of 21.5654 eV [41] was used, and for the He I spectra, the Ar $3p_{3/2}$ peak with a binding energy of 15.7596 eV [42] was used.

III. CURVE FITTING

We have curve fitted the spectra to obtain the intensities of the rotational branches. Since the rotational angular momentum couples to the electronic angular momentum in different ways in the final state for the X and B states on the one hand, and the A state on the other hand, different curve-fitting models were used. The description of the initial state was identical for the two cases. The ground state of N_2 is a $1\Sigma_g^+$ state, and can be described by Hund's coupling case (b). The energy of the rotational states in the electronic ground state is given by

$$E_N = E_0 + BN(N+1) - D[N(N+1)]^2, \quad (1)$$

where N is the rotational quantum number, and B and D are rotational constants. The ground-state population is given by a Maxwell distribution, where the nuclear spin degeneration of a homonuclear diatomic molecule has to be taken into consideration. The ^{14}N nucleus is a boson with nuclear spin $s=1$. Therefore, there will be twice as many symmetric as antisymmetric nuclear spin states (6:3) in the N_2 molecule. The electronic ground-state wave function of N_2 is symmetric with respect to interchange of the nuclei, being a Σ_g^+ state. Since the total wave function should be symmetric with respect to the exchange of the nuclei for bosons, rotational states with an even rotational quantum number, i.e., a symmetric rotational wave function, will have twice the degeneration of states with odd quantum number. The modeling of the energy position and the transition probability of the rotational levels in the final state differs for X , A , and B states, and will be described below.

A. X and B states

The X and B states in N_2^+ are both Σ states, and trivially belong to Hund's coupling case (b). The rotational energy levels in these states will be described by the same type of expression as Eq. (1), so the energy position of the rotational states in the photoelectron spectrum will be given by

$$E_{b(N,N^+)} = E_{b(0,0)} + B^+N^+(N^++1) - D^+[N^+(N^++1)]^2 - BN(N+1) + D[N(N+1)]^2, \quad (2)$$

where B^+ and D^+ are the rotational constants in the ionic state, and B and D refer to the initial state. Values for the rotational constants were taken from literature [43].

For transitions in diatomic molecules between states that can be described by Hund's coupling case (b), Xie and Zare [44] have developed a model for rotational line strengths, which is equivalent to the so called BOS model, developed by Buckingham, Orr and Sichel [45]. According to Xie and Zare, the rotational line intensity will be given by

$$I(N, N^+) = (3 + (-1)^N) e^{(-\{BN(N+1) - D[N(N+1)]^2\}/kT)} \sum_k (2N+1)(2N^++1) \begin{pmatrix} N & k & N^+ \\ 0 & 0 & 0 \end{pmatrix}^2 f(k, \theta), \quad (3)$$

where B and D are rotational constants for the ground state, N and N^+ are rotational quantum numbers of ground and ionic states respectively. The function $f(k, \theta)$, with θ being the ejection angle of the photoelectron, describes the angular dependence. This function must fulfill two criteria: at the pseudomagic angle it should equal $|\bar{\mu}(k, 0)|^2$, the square of the reduced multipole moment for angular momentum k , and the transition in total should be described by the familiar formula for the angular dependence for single photon ionization with radiation with degree of polarization P :

$$I \propto 1 + \frac{\beta}{4} (1 + 3P \cos 2\theta). \quad (4)$$

A function that obviously fulfills these two criteria is

$$f(k, \theta) = |\bar{\mu}(k, 0)|^2 \left[1 + \frac{\beta_k}{4} (1 + 3P \cos 2\theta) \right], \quad (5)$$

where the k dependence comes in as different β values for different $|\bar{\mu}(k, 0)|^2$. The angle-resolved data reported in this paper has been analyzed with this model. As mentioned in Sec. II, the synchrotron-radiation-excited spectra were recorded at the pseudomagic angle to the direction of polarization, and the degree of polarization was very high. This

meant that there was no dependence on the β value on the spectra. The discharge-lamp-excited spectra were recorded at $\theta=0^\circ$ and at $\theta=90^\circ$. With the degree of polarization P known, it was possible to determine β_k for the angular momentum k . In the fitting procedure, it is the parameters $|\bar{\mu}(k, 0)|^2$ and β_k that are determined for different k .

Only transitions with even ΔN are allowed for the $X^1\Sigma_g^+ \rightarrow X^2\Sigma_g^+$ transition [46]. As will be seen below, only $\Delta N=0, \pm 2, \pm 4$ branches had a non-negligible intensity, which means that only the reduced multipole matrix elements with $k=0, 2$, and 4 had to be taken into consideration.

For the transition $X^1\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ it is only ΔN odd transitions that are allowed [46]. This means that there is no $\rightarrow 0$ transition, so the term $E_{b(0,0)}$ in Eq. (2) does not correspond to any real transition. Here only the $\Delta N = \pm 1$ and ± 3 branches had non-negligible intensities; hence only the reduced multipole matrix elements with $k=1$ and 3 had to be taken into consideration.

B. A state

For the A state, the rotational angular momentum and the electronic orbital angular momentum couple to each other as an intermediate case between Hund's cases (a) and (b). The energy position of the rotational states is well described by the Hill-Van Vleck formula [47,48]. For an inverted doublet like the $A^2\Pi_u$ of N_2^+ , this will be

$$E_{N, J^+, \Omega=3/2} = E_0 + B^+ \left[(J^+ + 1/2)^2 - \Lambda^2 - \frac{1}{2} \sqrt{4(J^+ + 1/2)^2 + Y(Y-4)\Lambda^2} \right] - D^+(J^+)^4 - BN(N+1) + D[N(N+1)]^2, \quad (6)$$

and

$$E_{N, J^+, \Omega=1/2} = E_0 + B^+ \left[(J^+ + 1/2)^2 - \Lambda^2 + \frac{1}{2} \sqrt{4(J^+ + 1/2)^2 + Y(Y-4)\Lambda^2} \right] - D^+(J^+ + 1)^4 - BN(N+1) + D[N(N+1)]^2, \quad (7)$$

where J^+ is the total angular momentum in the ion, Ω is the sum of spin and electronic orbital angular momentum; $\Lambda=1$ is the electronic orbital angular momentum; $Y=A/B^+$, with A being the spin-orbit splitting, and other entities are as above. For the $A^2\Pi_u$ state $A = -9.25$ meV [49], with small (≈ 0.02 cm $^{-1}$) variations between vibrations. Since Xie and Zare's model for the line intensities [44] is developed for Hund's case (b), it does not apply. Buckingham, Orr, and Sichel [45] have considered Hund's case (a), but the fact that the energy positions of

the rotational states are given by an intermediate case between Hund's cases (a) and (b) casts doubts upon whether using a case (a) model for the intensity really is justified. Braunstein, McKoy, and Dixit developed a model for the mixed case [50], but this is rather involved. As a crude model, we have considered the intensities to be given by the ground state population. This is a reasonable approximation, particularly for states with high rotational quantum numbers. The intensity will then be given the formula:

$$I(N, J^+) \propto (C_{\Delta J} (3 + (-1)^N)) (2N+1) \times e^{\{-BN(N+1) - D[N(N+1)]^2/kT\}} \quad (8)$$

$$\times \left[1 + \frac{\beta_{\Delta J}}{4} (1 + 3P \cos 2\theta) \right], \quad (9)$$

where $C_{\Delta J}$ is a constant proportional to the transition probability for the $\Delta J = J^+ - N$ rotational branch, $\beta_{\Delta J}$ is the angular anisotropy parameter for the ΔJ branch, and the rest is as above. In the fitting procedure, it is the parameters $C_{\Delta J}$ and $\beta_{\Delta J}$ that are determined.

IV. RESULTS He I STUDIES

A. X state

Spectra of the $\nu=0$ and 1 vibrations of the $X^2\Sigma_g^+$ state are presented in Fig. 1. Both vibrations exhibit striking differences in β value for different rotational branches. The $\Delta N=0$ branch has a much higher β value than the $\Delta N=\pm 2$ and $\Delta N=\pm 4$ branches. There are also obvious differences between the vibrations. The $\Delta N=\pm 2$ branch of the $\nu=0$ vibration has a β value close to 0, i.e., the angular distribution is isotropic, whereas for the $\nu=1$ vibration it is clearly positive. The relative intensities of the rotational branches also differ between the vibrations.

In the ZEKE spectra presented by Merkt and Softley [17], quite different branch intensities were found. For $\nu=0$ vibration the $\Delta N=-2$ and $\Delta N=0$ branches were strong, the $\Delta N=2$ and $\Delta N=-4$ branches less so, and no $\Delta N=4$ lines were seen. For the $\nu=1$, the $\Delta N=2$ and $\Delta N=4$ branches dominated, the $\Delta N=0$ and $\Delta N=-2$ branches were less strong, and the $\Delta N=-4$ branch was missing. The intensity distortions were shown to be due to rotational autoionization for the $\nu=0$ vibration, and to a so-called complex resonance close to the ionization threshold for the $\nu=1$ vibration. Our spectra are recorded much further from threshold, and should not be affected by the same mechanisms.

Similar results have been found for the $X^2\Sigma_g^+$ state of H_2^+ [25–29]. Here the $\Delta N=2$ branch also exhibits a much lower β value than the $\Delta N=0$ branch. The fact that the relative intensity of the $\Delta N=\pm 2$ branches is much higher, and that the $\Delta N=\pm 4$ branches have non-negligible intensities for the $X^2\Sigma_g^+$ state of N_2^+ , indicates a greater influence of large l components in the outgoing photoelectron wave for the N_2^+ case.

These spectra have been fitted according to the model of Xie and Zare [44], presented above. The relative size of the square of the reduced multipole moment matrix elements obtained from these fits are presented in Table I. The curve fit is presented for $\nu=0$ and $\theta=90^\circ$ in Fig. 2, and as can be seen the modeling with Eq. (3) describes the intensity very well.

In Table I it is seen that $|\bar{\mu}(0,0)|^2$, which only affects the $\Delta N=0$ branch, has a much higher β value than $|\bar{\mu}(2,0)|^2$ or $|\bar{\mu}(4,0)|^2$, which affect all the observed rotational branches. This is expected from theory, and, in the work Ogata *et al.* [24], for theoretical reasons it was set to be equal to 2. The

TABLE I. Anisotropy parameter and relative reduced multipole moment matrix elements of the vibrations $\nu=0$ and 1 for the $N_2^+ X^2\Sigma_g^+$ state. Two different recordings of $\nu=0$ were made. The nomenclature of Ogata *et al.* [24] is different from ours, but the values are equivalent. The numbers in parentheses indicate the errors.

| | Relative size of $ \bar{\mu}(k,0) ^2$ | β , this work | σ_{0k}/σ_{00} , Ref. [24] | β , Ref. [24] |
|---------|---------------------------------------|---------------------|---------------------------------------|---------------------|
| $\nu=0$ | | 0.68 | | 0.77(3) |
| $k=0$ | 1.000 | 1.89 | 1.0 | 2.0 |
| $k=2$ | 1.804 | 0.03 | 1.32(1) | -0.14(4) |
| $k=4$ | 0.076 | 0.15 | 0.04(1) | 0.32(82) |
| $\nu=0$ | | 0.66 | | |
| $k=0$ | 1.000 | 1.88 | | |
| $k=2$ | 1.867 | 0.04 | | |
| $k=4$ | 0.086 | -0.04 | | |
| $\nu=1$ | | 1.45 | | 1.58(36) |
| $k=0$ | 1.000 | 1.89 | 1.0 | 2.23(27) |
| $k=2$ | 0.682 | 0.92 | 0.73(10) | 0.62(66) |
| $k=4$ | 0.057 | -0.05 | 0.10(7) | 2.18(3.36) |

value of $\beta \approx 1.85$ we obtained for $|\bar{\mu}(0,0)|^2$ was also what we found for the $X^2\Sigma_g^+$ state of H_2^+ [29].

In terms of squared reduced multipole moment matrix elements, the difference in β value between the vibrations $\nu=0$ and 1 is seen to depend mostly on $|\bar{\mu}(2,0)|^2$. Both the β value and the relative size of $|\bar{\mu}(2,0)|^2$ differ between the vibrations. For $\nu=0$, a lower β value and larger size of $|\bar{\mu}(2,0)|^2$ than for $\nu=1$ was observed, giving the vibration in total a considerably lower β value. This was also the qualitative result of Ogata *et al.* [24], even if their numbers differ from ours. The cause of this is undoubtedly that the resolution in their experiment was lower than in the present work. Furthermore, a theoretical β value for the entity corresponding to $|\bar{\mu}(0,0)|^2$ was used in their analysis, and the other β values were calculated as relatives to this.

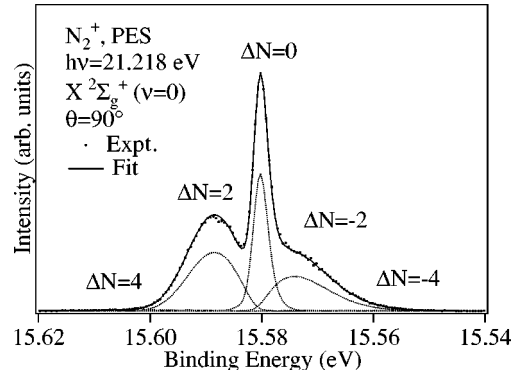


FIG. 2. Experimental (dotted) and fitted (solid line) spectra of the $\nu=0$ vibrational peak of the $X^2\Sigma_g^+$ state of N_2^+ for $\theta=90^\circ$ plotted together. The rotational branches of the fit are also shown in the figure. The $\Delta N=\pm 4$ branches are very weak.

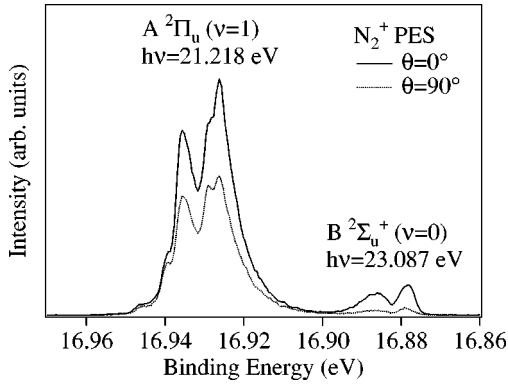


FIG. 3. The $\nu=1$ peak of the $A^2\Pi_u$ state of N_2^+ , recorded with $\theta=0^\circ$ (solid line) and $\theta=90^\circ$ (broken line). The most intense peaks are the $\Delta J=\frac{1}{2}$ branch of the $\Omega=\frac{3}{2}$ component and the $\Delta J=\frac{1}{2}$ branch of the $\Omega=\frac{1}{2}$ component, which lie around 16.925 and 16.935 eV, respectively. The structure at 16.88 eV is the He I β excited vibration $\nu=0$ of the B state (compare Fig. 4).

The reason for this large difference in β value between the vibrations is a long standing question. The shape resonance in the $3\sigma_g \rightarrow k\sigma_u$ ionization channel [52–55] can certainly affect the rotational population, as we have shown in our earlier paper [9], and also the angular distribution, as has been seen in vibrationally resolved work [55]. For the $X^3\Sigma_g^-$ state in O_2^+ , Braunstein and co-workers [50,51] found differing rotational branching ratios for different vibrations, which was presumed to be due to a shape resonance. This may also be the case for the $X^2\Sigma_g^+$ state of N_2^+ , but the actual shape resonance lies around 29–30 eV, i.e., not very close to the present photon energy. Angle-resolved measure-

TABLE II. Relative branching ratio and β values for different rotational branches of the first three vibrations in $N_2^+A^2\Pi_u$. The intensity quoted for the rotational branches is relative to $C_{\Delta J=1/2}$ for the $\Omega=\frac{3}{2}$ component of each vibration. The intensity of the $\Omega=\frac{1}{2}$ component in total is relative to the $\Omega=\frac{3}{2}$ component.

| Rot. branch | Rel. int. | β | Rel. int. | β | Rel. int. | β |
|-------------------------|-----------|---------|-----------|---------|-----------|---------|
| | $\nu=0$ | 0.40 | $\nu=1$ | 0.33 | $\nu=2$ | 0.26 |
| $\Omega=\frac{3}{2}$ | 1.00 | 0.44 | 1.00 | 0.38 | 1.00 | 0.34 |
| $\Delta J=-\frac{5}{2}$ | - | - | 0.07 | -0.38 | 0.12 | 0.39 |
| $\Delta J=-\frac{3}{2}$ | 0.38 | 0.28 | 0.39 | 0.30 | 0.44 | 0.03 |
| $\Delta J=-\frac{1}{2}$ | 0.41 | 0.40 | 0.44 | 0.41 | 0.36 | 0.37 |
| $\Delta J=\frac{1}{2}$ | 1.00 | 0.53 | 1.00 | 0.46 | 1.00 | 0.39 |
| $\Delta J=\frac{3}{2}$ | 0.53 | 0.39 | 0.54 | 0.31 | 0.57 | 0.34 |
| $\Delta J=\frac{5}{2}$ | 0.14 | 0.44 | 0.16 | 0.48 | 0.18 | 0.71 |
| $\Omega=\frac{1}{2}$ | 0.88 | 0.35 | 0.86 | 0.27 | 0.90 | 0.17 |
| $\Delta J=-\frac{3}{2}$ | 0.56 | 0.41 | 0.48 | 0.19 | 0.58 | 0.20 |
| $\Delta J=-\frac{1}{2}$ | 0.53 | 0.28 | 0.61 | 0.34 | 0.52 | -0.17 |
| $\Delta J=\frac{1}{2}$ | 0.73 | 0.44 | 0.71 | 0.34 | 0.76 | 0.39 |
| $\Delta J=\frac{3}{2}$ | 0.25 | 0.11 | 0.29 | 0.07 | 0.34 | 0.03 |
| $\Delta J=\frac{5}{2}$ | 0.08 | 0.16 | 0.11 | 0.24 | 0.14 | 0.23 |
| $\Delta J=\frac{7}{2}$ | 0.01 | 1.45 | 0.02 | 0.17 | 0.05 | 0.83 |

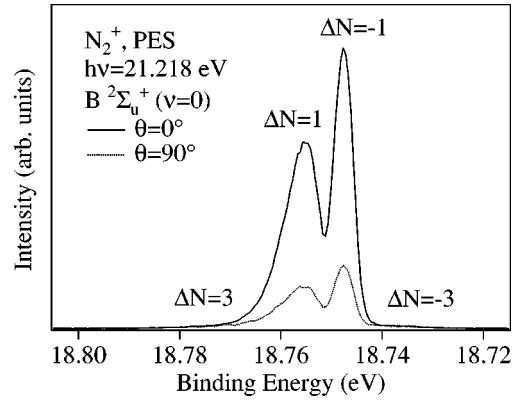


FIG. 4. He I excited spectrum of the $\nu=0$ vibrational peak of the $B^2\Sigma_u^+$ state of N_2^+ , recorded with $\theta=0^\circ$ (solid line) and $\theta=90^\circ$ (broken line).

ments with a rotational energy resolution, performed with a fine photon energy mesh, should be able to shed some light on the process. This is unfortunately not an easy experiment to perform with our present equipment.

The $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(4,0)|^2$ squared reduced multipole moment matrix elements both have approximately the same relative sizes and β values for $\nu=0$ and $\nu=1$. The values of Ogata *et al.* [24] corresponding to $|\bar{\mu}(4,0)|^2$, differed quite dramatically between vibrations, but their uncertainty was very large. The β value for $|\bar{\mu}(0,0)|^2$ was, as stated above, a theoretical one, and not derived from the experiment.

B. A state

We have recorded an angle-resolved photoelectron spectrum of the three first vibrations of the $A^2\Pi_u$ state of N_2^+ , and, as an example of this spectrum, the vibrational peak $\nu=1$ is presented in Fig. 3. Both the $\theta=0^\circ$ and 90° spectra are shown. As can be seen, the He I β ($h\nu=23.087$ eV) excited peak for the $\nu=0$ vibration of the $B^2\Sigma_u^+$ state at 16.88 eV (cf. Fig. 4) overlaps slightly with the $\nu=1$ peak of the A state. The He I β satellite for the $\nu=1$ vibration of the B state lies around 17.18 eV, and overlaps parts of the $\nu=2$ vibration of the A state.

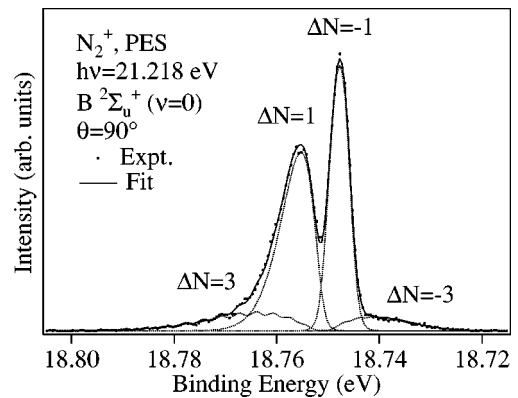


FIG. 5. Experimental (dotted) and fitted (solid line) spectra of the $\nu=0$ vibrational peak of the $B^2\Sigma_u^+$ state of N_2^+ for $\theta=90^\circ$ plotted together. The rotational branches of the fit are also shown in the figure. The wiggles in the $\Delta N=3$ branch correspond to individual rotational states.

TABLE III. Anisotropy parameter and relative reduced multipole moment matrix elements of the $\nu=0$ vibration for the $N_2^+ B^2\Sigma_u^+$ state.

| | Relative size of $ \bar{\mu}(k,0) ^2$ | β |
|---------|---------------------------------------|---------|
| $\nu=0$ | | 1.10 |
| $k=1$ | 1.000 | 1.28 |
| $k=3$ | 0.169 | 0.00 |

The spectra were curve fitted with the simple model described above, and the relative rotational branch intensities and β values are presented in Table II. The difference in β value between vibrations was found to be rather small. According to our measurements, it changes from $\beta=0.40$ to 0.26 from $\nu=0$ to 2, in excellent agreement with Kreile and Schweig [39]. The appearance of the rotational line profile and spin-orbit components within the vibrational peaks is similar for the different vibrations. However, the overlap of the two spin-orbit-split components makes a precise assessment of the intensities of the rotational branches difficult, and hence also the determination of β values. A few observations can still be made. The β value of the $\Omega=\frac{1}{2}$ spin-orbit component is lower than that of the $\Omega=\frac{3}{2}$. The rotational branching ratio is not the same for the two spin-orbit components, and also the total intensity differs. The $\Omega=\frac{1}{2}$ component had 85–90% of the intensity of the $\Omega=\frac{3}{2}$ component. In the ZEKE spectrum of Hepburn [19], a higher intensity was also found for the $\Omega=\frac{3}{2}$ component compared with the $\Omega=\frac{1}{2}$ component. There is a weak asymmetry in the rotational branching ratio, favoring negative and low ΔJ transitions. This was also seen in the ZEKE spectrum of Hepburn [19]. A surprising fact is that the $\Delta J=\frac{1}{2}$ branch of $\Omega=\frac{1}{2}$ spin-orbit component has a lower β value than the branches around it. The difference between the branches was otherwise mostly rather small. In some cases, where the intensity was low or where the overlap between the spin-orbit components was large, which aggravated the determination of the β value, larger differences were found, but the uncertainty was then large. The β value of the $\Delta J=\frac{1}{2}$ of the $\Omega=\frac{1}{2}$ spin-orbit component of $\nu=2$ appears to be substantially higher than the other other rotational branches of the same vibration. This is undoubtedly a result of the overlap from the He I β excited $\nu=1$ vibration of the $B^2\Sigma_u^+$ state.

C. B state

$\theta=0^\circ$ and 90° spectra of the $\nu=0$ vibration of the $B^2\Sigma_u^+$ state are presented in Fig. 4, along with a presentation of a curve fit in Fig. 5. As can be seen in Fig. 4, the $\Delta N=\pm 3$ branches have a much lower β value than the $\Delta N=\pm 1$ branches. The fitting of these spectra according the model of Xie and Zare [44] yielded the relative squared reduced multipole moment matrix elements presented in Table III.

In Fig. 3 the He I β satellite line of $\nu=0$ of the B state is well resolved, and could possibly be used for determining β parameter and values for the reduced multipole moment matrix elements at $h\nu=23.087$ eV. However, we do not know the degree of polarization of the radiation at this energy, since it was only determined from known β parameters for

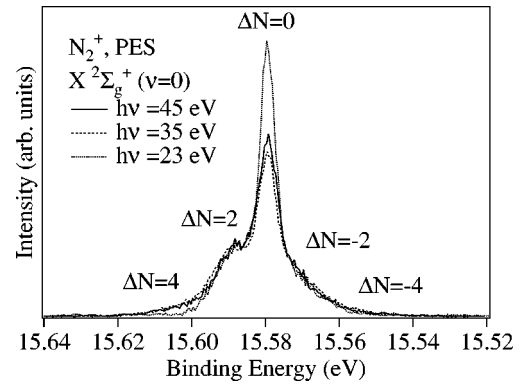


FIG. 6. Synchrotron-radiation-excited spectra of the $\nu=0$ vibration of the $X^2\Sigma_g^+$ state of N_2^+ , recorded $h\nu=23$ eV (short dash), at $h\nu=35$ eV (long dash), and $h\nu=45$ eV (solid line). Note that the central feature (the $\Delta N=0$ branch) is stronger in the $h\nu=23$ eV spectrum than in the $h\nu=35$ and $h\nu=45$ eV spectra. The $\Delta N=0$ branch of the $h\nu=45$ eV spectrum has a greater peak height than the $h\nu=35$ eV spectrum, and is also slightly broader. The relative intensity of the $\Delta N=0$ branch is higher at 45 eV than at 35 eV, and must go through a minimum between 23 and 45 eV.

photoionization with He I α . It can be expected to be rather similar to that at $h\nu=21.218$ eV, and under the condition that is identical, we obtained values when we fitted the spectra that are close to those presented in Table III. This independence on photon energy is very much in line with what we see for the squared reduced multipole moment matrix elements in the synchrotron-radiation-excited spectra.

V. RESULTS SYNCHROTRON STUDIES

A. X state

In Fig. 6, spectra for the $X^2\Sigma_g^+$ state recorded at 23, 35, and 45 eV are presented. As can be seen, the $\Delta N=0$ branch has a higher relative intensity at 23 eV than at 35 and 45 eV. Also, at 45 eV the $\Delta N=0$ branch is slightly more intense than at 35 eV, so the $\Delta N=0$ branch intensity goes through a minimum between 23 and 45 eV. Curve fitting our spectra according to the model of Xie and Zare, mentioned above, yields the relative squared reduced multipole moments pre-

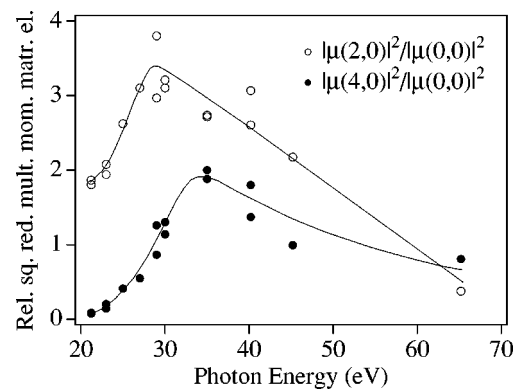


FIG. 7. The relative of the square of the reduced multipole moment matrix elements of the transition $X^1\Sigma_g^+(\nu=0) \rightarrow X^2\Sigma_g^+(\nu=0)$ as a function of photon energy. Unfilled circles, $|\bar{\mu}(2,0)|^2/|\bar{\mu}(0,0)|^2$; filled circles, $|\bar{\mu}(4,0)|^2/|\bar{\mu}(0,0)|^2$. The lines are intended as guides to the eye.

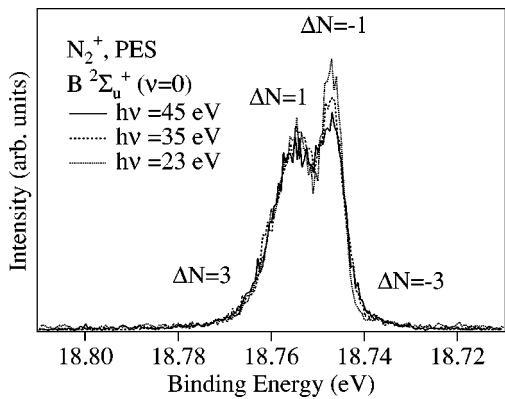


FIG. 8. Synchrotron-radiation-excited spectra of the $\nu=0$ vibration of the $B^2\Sigma_u^+$ state of N_2^+ , at $h\nu=23$ eV (short dash), $h\nu=35$ eV (long dash), and $h\nu=45$ eV (solid line). The rotational branch intensity does not change markedly with photon energy, unlike the case of the $X^2\Sigma_g^+$ state. The differences in peak height are due to differences in energy resolution.

sented in Fig. 7. These data have already been presented in a recent Letter [9]. In the figure, the values from the He I measurement have also been included, and as seen they fit well with the synchrotron excited data.

This photon energy dependence of the rotational branching ratio is most likely due to the $3\sigma_g \rightarrow k\sigma_u$ shape resonance in N_2 [52–55]. Poliakoff and co-workers noticed influences of shape resonances on rotational branching ratios [11,12,56]. In particular, an enhancement of large ΔN transitions at low photon energies was seen in the B state of CO^+ as a result of a $4\sigma \rightarrow k\sigma$ shape resonance [12]. Both for this resonance and the mentioned resonance in N_2 , it is the $l=3$ partial photoelectron wave that has the resonant behavior. The resonant behavior of the $l=3$ partial wave leads to a favoring of larger ΔN transitions around the resonance in both these cases.

We calculated what vibrationally averaged β values we would obtain as a function of photon energy from the measured relative sizes of $|\bar{\mu}(k,0)|^2$, under the condition that the β value of each squared reduced multipole moment matrix element stayed constant with photon energy. We used the β values obtained from the He I study presented above. Mostly due to the minimum of the $|\bar{\mu}(0,0)|^2$ square reduced multipole matrix element, we also obtain a minimum β value of approximately 0.4 at around $h\nu=35$ eV. This is not in good accord with what has been measured before (see Ref. [55]). The only way to reconcile these findings with what has been measured before is that not only the relative size of the reduced multipole moment matrix elements, but also their angular distributions change with photon energy.

B. B state

In Fig. 8, spectra for the $B^2\Sigma_u^+$ state recorded at 23, 35, and 45 eV are presented. As for the X state above, a slight difference in resolution exists for the spectra, but the clear difference in rotational branching ratio seen for the X state does not appear for the B state in this energy region. In Fig. 9, the squared reduced multipole moment matrix element $|\bar{\mu}(3,0)|^2$ relative to $|\bar{\mu}(1,0)|^2$ obtained by curve fitting the

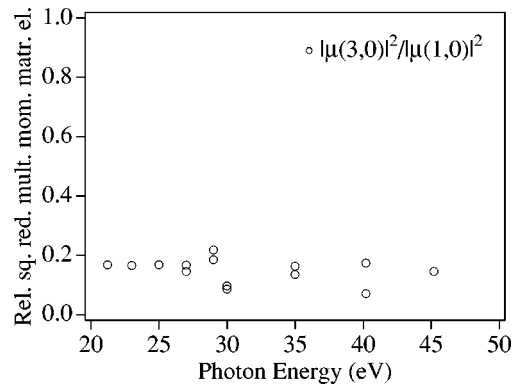


FIG. 9. The relative of the square of the reduced multipole moment matrix elements of the transition $X^1\Sigma_g^+(\nu=0) \rightarrow B^2\Sigma_u^+(\nu=0)$ as a function of photon energy. Unfilled circles, $|\bar{\mu}(3,0)|^2/|\bar{\mu}(1,0)|^2$.

photoelectron spectra for photon energies between 23 and 45 eV is shown. The values from derived from the angle-resolved He I excited spectra are also included. Obviously, the relative size of the squared reduced multipole moment matrix elements of the B state is fairly constant. A slightly decreasing trend may be discerned from the data presented in Fig. 9. This is contrary to what was found by Poliakoff and co-workers [10–14], namely, an increase in $\Delta N \geq 3$ transitions with increasing photon energy. Judging from the data they presented, the increase should be quite small in the energy range we studied, and could be hidden in the statistical scatter of our measurement.

Several effects have been suggested to influence the $X^1\Sigma_u^+ \rightarrow B^2\Sigma_u^+$ transition in this photon energy region. For instance, the $3\sigma_g \rightarrow k\sigma_u$ shape resonance may influence the $2\sigma_u$ photoionization [57,58]. Small deviations from Franck-Condon vibrational branching ratios have been found in the energy region of the $3\sigma_g \rightarrow k\sigma_u$ shape resonance in fluorescence spectra for the transition $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ [59,60], and also effects on the photoelectron angular distribution for the $B^2\Sigma_u^+$ state [61]. Recently, Erman and co-workers [62,63] measured the vibrational branching ratio from fluorescence spectra, and found a structure which was suggested could be due to doubly excited states in the energy region 20 to 35 eV, which autoionize into the $B^2\Sigma_u^+$ state. If there is an effect on the rotational branching ratio from the $k\sigma_u$ shape resonance or from the doubly excited states, it must be small. There is an apparent kink in the curve for the relative size of $|\bar{\mu}(3,0)|^2$ compared to $|\bar{\mu}(1,0)|^2$ between 29 and 30 eV which could be due to any of these effects, but it can well be stochastic. The drastic changes seen for the $X^2\Sigma_g^+$ state in the rotational branching ratio does not happen for the $B^2\Sigma_u^+$ state. Smaller variations may not be ruled out, but experiments with better statistics would have to be performed to determine this.

VI. CONCLUSION

In this paper, we have studied rotational line profiles of N_2^+ with angle-resolved photoelectron spectroscopy. For the X and B states, which are both Σ states, we found the difference in β value for different rotational branches to be dramatic. In the $A^2\Pi_u$ state, the differences between rotational

branches in the β value are much less pronounced, even though there certainly are differences. For the X state, the difference in β value between the $\nu=0$ and 1 vibrations is a compounded effect of different rotational branching ratios and β values for the rotational branches. The $3\sigma_g \rightarrow k\sigma_u$ shape resonance may cause this anomaly, but other effects can also be involved. This shape resonance certainly affects the rotational branching ratio in the X state, as can be seen from the photon energy dependence study presented in this paper and in Ref. [9]. The $B^2\Sigma_u^+$ state is said to be affected by interchannel coupling [57–60] and by autoionizing doubly excited resonances [62,63] in this energy region. Unfortunately, we have some scatter in our values, which makes it

difficult to definitely state more than that the influence of these different processes on the rotational branching ratio must be small in the studied photon energy range. Over an extended photon energy range ($5 \leq E_k \leq 230$ eV), it has been found that Cooper minima affect the rotational population of the B state in N_2^+ [13,14,64]. The smaller energy range we have studied ($2.5 \leq E_k \leq 26$ eV) makes these effects too insignificant to be noticed.

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