Photoionization of Excited Molecular States[1]

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1. Introduction

Rapid advances in laser and detector technologies are making it possible to investigate molecular photophysics and photochemistry in powerful new ways. For example, resonantly enhanced multiphoton ionization (REMPI) measurements, in which the total (or the mass selected) ion current is monitored as a function of laser wavelength, have yielded extensive and often novel information on the spectroscopy of the resonant intermediate states [1]. With the addition of photoelectron spectrometry (PES) to analyze the kinetic energy of the ejected electrons, it is possible to determine the branching ratios into different electronic, vibrational, and rotational levels of the product ion and to focus directly on both the dynamics of the multiphoton ionization process and the photoionization of excited state species [2-9]. In the present paper, we report several REMPI/PES studies of H_2 and N_2. The results reflect both the spectroscopy and the dynamics of photoionization of excited molecular states and are discussed in terms of the selection rules for photoionization and the relative probabilities of photoionization from Rydberg and valence states. In some cases, in accordance with the Franck-Condon principle, the results demonstrate that resonant multiphoton ionization through Rydberg states may be a powerful technique for the production of electronic, vibrational, and rotational state selected ions. However, in other cases, systematic departures from Franck-Condon behavior are observed, which reflect the more subtle dynamics of excited state photoionization.

2. Experimental

The apparatus used to perform these studies consists of a Nd:YAG pumped dye laser (Molectron MY34-10/DL18P), a time-of-flight mass spectrometer, and a hemispherical electron energy analyzer [3,10]. The dye laser output is frequency doubled in a KDP crystal and the resulting UV light is separated from the fundamental by multiple reflections on dichroic beamsplitters, which reduce the visible light by a factor of 10^4. In all of the measurements reported here, the photoelectron spectrometer was operated with 1 mm entrance and exit slits, and with a 2 eV energy of analysis, resulting in an energy resolution of approximately 35 meV. All spectra were recorded

[1] Work supported by the U. S. Department of Energy and the Office of Naval Research.

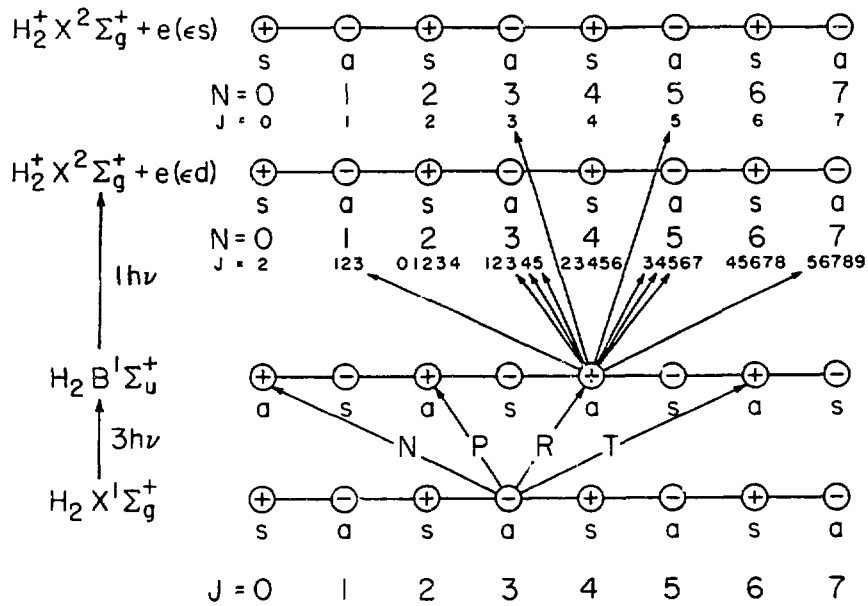

Fig. 1. Schematic diagram of the allowed transitions for (3+1) resonant multiphoton ionization of H_2 via the B $^1\Sigma_u^+$ state. Only those transitions from J"=3 of the ground state and J'=4 of the intermediate state are shown.

along the polarization axis of the laser. The transmission function of the electron spectrometer in the energy range 0.0-3.3 eV was determined by measuring the HeI photoelectron spectrum of the O_2^+ b $^4\Sigma_g^-$ and B $^2\Sigma_g^-$ bands. The estimated error in the relative intensities of the photoelectron peaks in the energy range 0.5-3.3 eV is ~30%. The estimated error for peaks in the energy region 0.0-0.5 eV is greater and is somewhat difficult to assess. However, peaks at energies below 0.25 eV are outside the dynamic range of the analyzer and their intensities are accurate only to within a factor of 2-3.

3. Photoionization of the B $^1\Sigma_u^+$ and C $^1\Pi_u$ States of H_2

Our (3+1) REMPI/PES studies on H_2 via the B and C states[2] [4,7] both illustrate the power of the method for the study of photoionization dynamics of excited molecular states [4,7] and demonstrate the possibility of producing ions in single electronic, vibrational, and rotational states using selective multiphoton ionization [7]. Figure 1 summarizes the selection rules for both the excitation and ionization steps for REMPI of H_2 via the B intermediate state. For the transition from the ground electronic state to the B state, the three photon selection rules based on symmetry properties are identical to those for single photon transitions (g↔u, +↔-, and

[2] Molecular term symbols are abbreviated according to the following example -- B $^1\Sigma_u^+$, v' = 0 is written B, v' = 0. A double prime on the vibrational quantum number (v") denotes the ground state, a single prime (v') denotes the resonant intermediate state, and a plus (v^+) denotes the ion.

s↔/↔a) [11]. In addition, for a three photon transition, $\Delta J \leq 3$; however, transitions having $\Delta J=3$, i.e., the N and T rotational branches shown in Fig. 1, have been found to be weak or absent in a number of cases [12].

The determination of the rotationally resolved photoelectron spectra obtained by pumping individual rotational transitions will yield important information on the dynamics of the photoionization process from the B excited state, just as the analogous single photon studies have yielded important information on the dynamics of the photoionization process from the ground state of molecular H_2 [13]. The selection rules governing this transition are illustrated in the upper half of Fig. 1. Owing to the g↔u selection rule, the outgoing electron must have an even value of ℓ. Only s and d partial waves need be considered, since higher partial waves will be excluded by their large centrifugal barrier. It is seen that the ionizing transition must obey the selection rule $N(H_2^+ X)-J(H_2 B)=\pm1,\pm3$. It should be noted that, in the angular momentum transfer (j_t) formulation [14-16], the ejection of an s electron can lead only to a j_t value of 1, while the ejection of a d electron can yield j_t values of 1, 2, and 3. The j_t value of 2 is parity unfavored, and only values of 1 and 3 are important. The photoelectron spectra obtained by pumping the P(3) and R(3) rotational transitions of the B, v'=7, ↔ X, v"=0 band are shown in Fig. 2. These spectra show partially resolved rotational structure and clearly demonstrate that higher angular momentum transfers are not observed. One of two conclusions may be drawn from these observations -- either the ejection of a d-wave or an angular momentum transfer of 3 is strongly discriminated against. From various considerations, we believe the latter is more likely to be correct, although this has not been rigorously demonstrated. Experiments such as this are of great fundamental importance, since the quantum state at each of the three stages of the overall process is precisely specified in terms of electronic, vibrational, and rotational degrees of freedom.

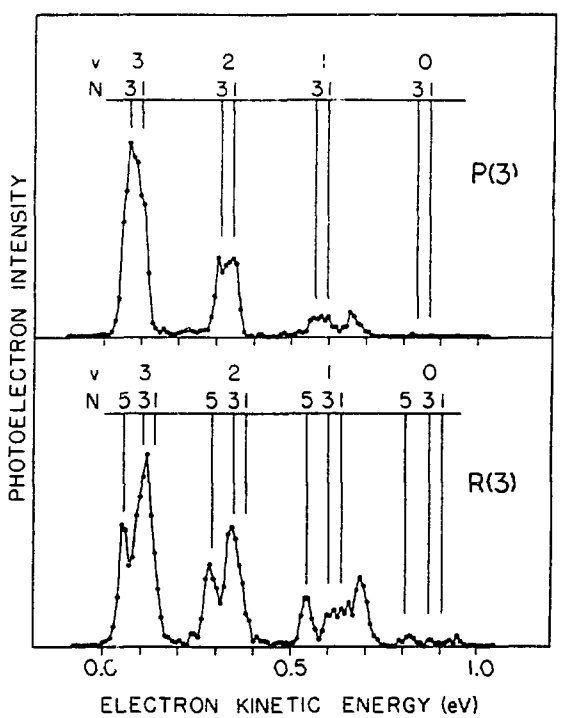

Fig. 2. Photoelectron spectra of H_2 following (3+1) ionization via the B $^1\Sigma_u^+$, v'=7, J'=2 [P(3)] and J'=4 [R(3)] levels. The unassigned peaks at 0.69 eV in the R(3) spectrum and at 0.67 eV in the P(3) spectrum are believed to result from photoionization of H(2ℓ) formed by photodissociation of B $^1\Sigma_u^+$.

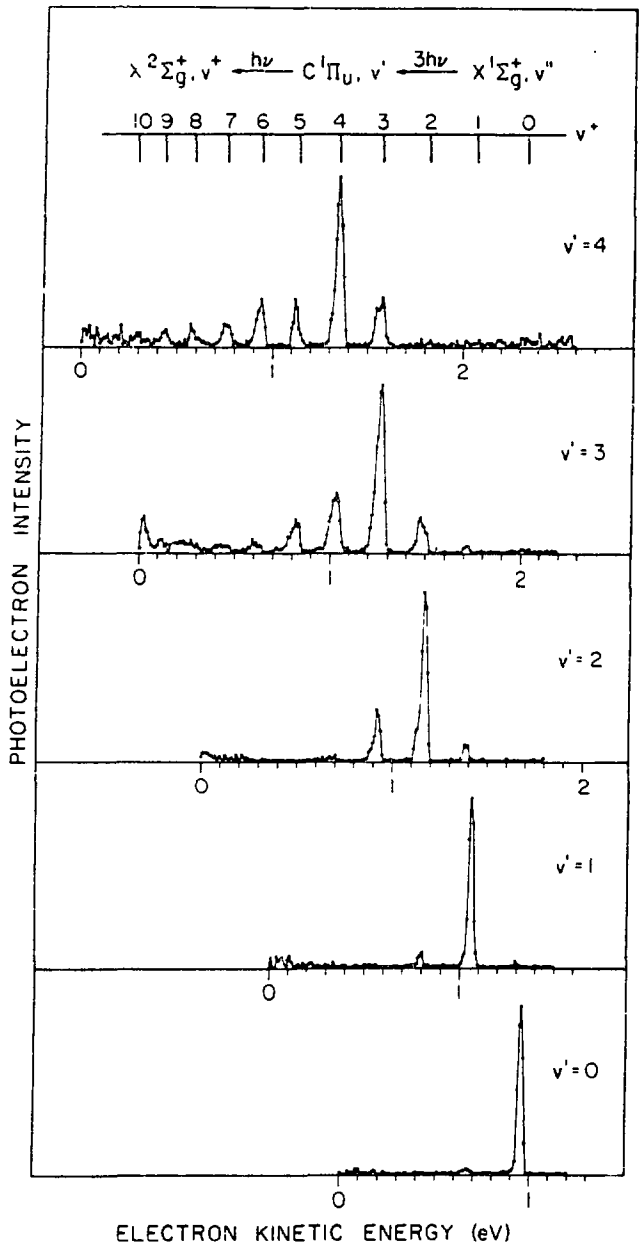

Fig. 3. Photoelectron spectra of H_2 following (3+1) ionization via the C $^1\Pi_u$, v'=0-4 levels.

In a companion (3+1) REMPI/PES study of H_2 via the resonant intermediate C state [7], two issues were addressed. First, to what degree can vibrational state selected ions be prepared by photoionization of a Rydberg state. Second, what can we learn about the more subtle dynamical effects in excited state photoionization from a comparison of the observed vibrational branching ratios with accurate Franck-Condon factors. The photoelectron spectra obtained at the wavelengths of the three photon Q(1) transitions of the C, v'=0-4 ← X, v"=0 bands are shown in Fig. 3. The most striking aspect of the photoelectron spectra is the dominance of the photoelectron peak corresponding to the X, v^+ = C, v' transition, indicating that the Rydberg electron is ionized while the vibrational state of the

ionic core remains largely undisturbed. In addition, the weaker peaks with greatest intensity are those adjacent to the $v^+=v'$ peak. This agrees with expectations based on Franck-Condon factor calculations. However, while the qualitative agreement with the calculations is very good, the quantitative agreement is poor. For example, in the spectrum obtained via the C, $v'=4$ level, the relative intensities of the $v^+=3$, 5, and 6 peaks are too large by factors of 3, 2, and 23, respectively, and the intensity of the $v^+=4$ peak accounts for only 43% of the total, rather than the predicted 90%. The most likely causes of such deviations are: (1) a kinetic energy dependence of the electronic transition matrix element, which must be taken into consideration even within the Franck-Condon approximation [17]; (2) an R-dependence of the same electronic transition matrix element, which, by definition, constitutes a breakdown of the Franck-Condon approximation; and (3) a v^+-dependence of the photoelectron angular distribution [2h]. Further experimental studies on this system that will help determine which of the above points is of major importance include determinations of the angular distributions of the photoelectrons and the wavelength dependence of the vibrational branching ratios. In addition, these data represent a well defined case for theoretical investigation of excited state photoionization. DIXIT and McKOY [18] have recently made significant progress in assessing the importance of the dynamical effects mentioned above for the present data.

4. Photoionization of $^1\Sigma_u^+$ and $^1\Pi_u$ Rydberg and Valence States of N_2

Since the first excited state of the N_2^+ ion can be accessed in the ionization step of the REMPI process, electronic as well as vibrational and rotational branching ratios may be determined. Furthermore, since the neutral excited states of N_2 have been very well characterized both experimentally and theoretically [19], N_2 is a particularly attractive system for study using REMPI/PES techniques. The recent vibronic analysis of the $^1\Sigma_u^+$ and $^1\Pi_u$ states by STAHEL et al. [20] provides a useful framework for understanding photoelectron spectra from these levels by providing a breakdown of the strongly perturbed intermediate vibronic levels in terms of deperturbed diabatic states with well defined Rydberg or valence character. However, in some instances, the situation is complicated further by strong local perturbations and predissociations that affect the rotational structure of these bands, as well as the photoelectron branching ratios. These cases require going beyond the vibronic approximation.

Photoelectron spectra have been obtained by single-color (3+1) REMPI via the b $^1\Pi_u$, c $^1\Pi_u$, c' $^1\Sigma_u^+$, and o $^1\Pi_u$ states. The relevant N_2 and N_2^+ potential energy curves are shown in Fig. 4. The c and c' states are the $3p\pi_u$ and $4p\sigma_u$ Rydberg states, both of which converge to the X $^2\Sigma_g^+$ ground state of the ion; the o state is the $3s\sigma_g$ Ryberg state that converges to the A $^2\Pi_u$ state of the ion; and the b state is a valence state having two primary electron configurations, both of which differ from the X and A states of N_2^+ by two orbitals [19]. In this energy region, the b and c states are strongly mixed by a homogeneous perturbation, as are the b' and c' states (the former is also a valence state). Hence, it is possible to study photoionization from Rydberg states (including core-excited Rydberg states), valence states, and certain perturbed levels that are complex mixtures of these.

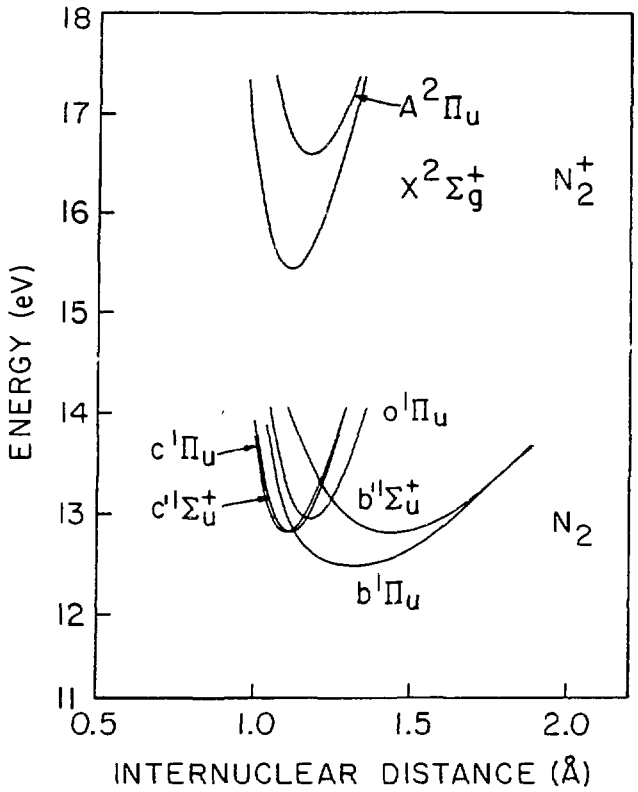

Fig. 4. Potential energy curves of N_2 and N_2^+.

Two of the simplest photoelectron spectra are shown in Fig. 5 and were obtained following (3+1) multiphoton ionization of N_2 via the o, v'=1,2 levels [6], which are relatively unperturbed. This photoionization process leads to the production of N_2^+ A, v^+=1,2, respectively, with greater than 90% purity. Hence, the ionizing transition strongly favors the removal of the outer $3s\sigma_g$ electron, preserving both the electronic and vibrational levels of the ion core. This is the first experimental evidence in a molecular system showing the degree to which the electronic excitation of the ion core is retained following photoionization of a Rydberg state. Similar effects have been observed in the photoionization of the rare gas atoms (i.e., in all of the observed transitions, the spin-orbit state of the ion core was preserved) [21].

Photoelectron spectra obtained following photoionization from various vibrational levels of the b state are more complicated and are shown in Fig. 6. According to the analysis of STAHEL et al. [20], the b, v'=0-2 vibronic levels contain very little c character, and are therefore relatively unpertubed. As is expected, photoionization from these levels populates a broad distribution of vibrational levels, in qualitative although not quantitative agreement with the calculated Franck-Condon factors [8]. Beginning with the b, v'=1 photoelectron spectrum, the A, v^+=0 state of N_2^+ becomes energetically accessible and is observed with a large intensity, as it is in the b, v'=2 photoelectron spectrum. Unfortunately, relative intensities in this (near zero) electron kinetic energy region are not reliable, making it difficult to accurately compare the intensities of the A, v^+=0 ← b, v'=1 and X, v^+=0 ← b, v'=1 ionizing transitions.

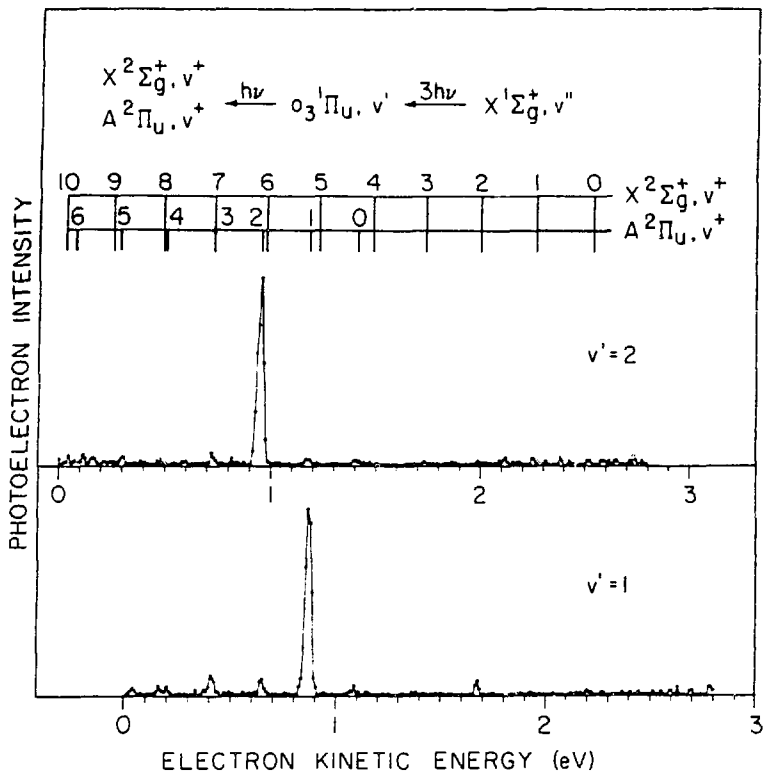

Fig. 5. Photoelectron spectra of N_2 following (3+1) ionization via the $o\ ^1\Pi_u$, v'=1,2 levels.

Unlike the b, v'=0-2 photoelectron spectra, which exhibit a number of intense peaks, the b, v'=3-5 photoelectron spectra each display a single intense X, v^+=0 peak, with very little intensity in any of the other peaks. This is somewhat surprising since the Franck-Condon factors predict a number of other moderately intense peaks [8]. The single intense v^+=0 peak suggests that photoionization from these levels may be dominated by a v'=0 Rydberg state component in the wavefunction of the intermediate state, since photoionization from a Rydberg level is expected to preserve the vibrational quantum number of the intermediate state. The analysis of STAHEL et al. [20] shows that the b, v'=3-5 wavefunctions contain 5.8%, 16.0%, and 22.1% c, v'=0 character, respectively, and this admixture could account for the intense v^+=0 peak observed in the b, v'=3-5 photoelectron spectra.

The c, v'=0 photoelectron spectrum shown in Fig. 7 can be understood by assuming that photoionization from a Rydberg level preserves the vibrational quantum number and the electronic state of the ion core; however, the c, v'=1 photoelectron spectrum cannot be understood in this way. Although the latter spectrum does display a prominant X, v^+=1 peak, the A, v^+=0 peak is equally intense. The appearance of the strong A, v^+=0 peak can be rationalized by the existence of 7% o, v'=0 state character in the c, v'=1 wavefunction [20]. Similarly, the appearance of the A, v^+=1 peak in the photoelectron spectrum may be due to the existence of 2% o, v'=1 character in the c, v'=1 wavefunction. However, the large relative

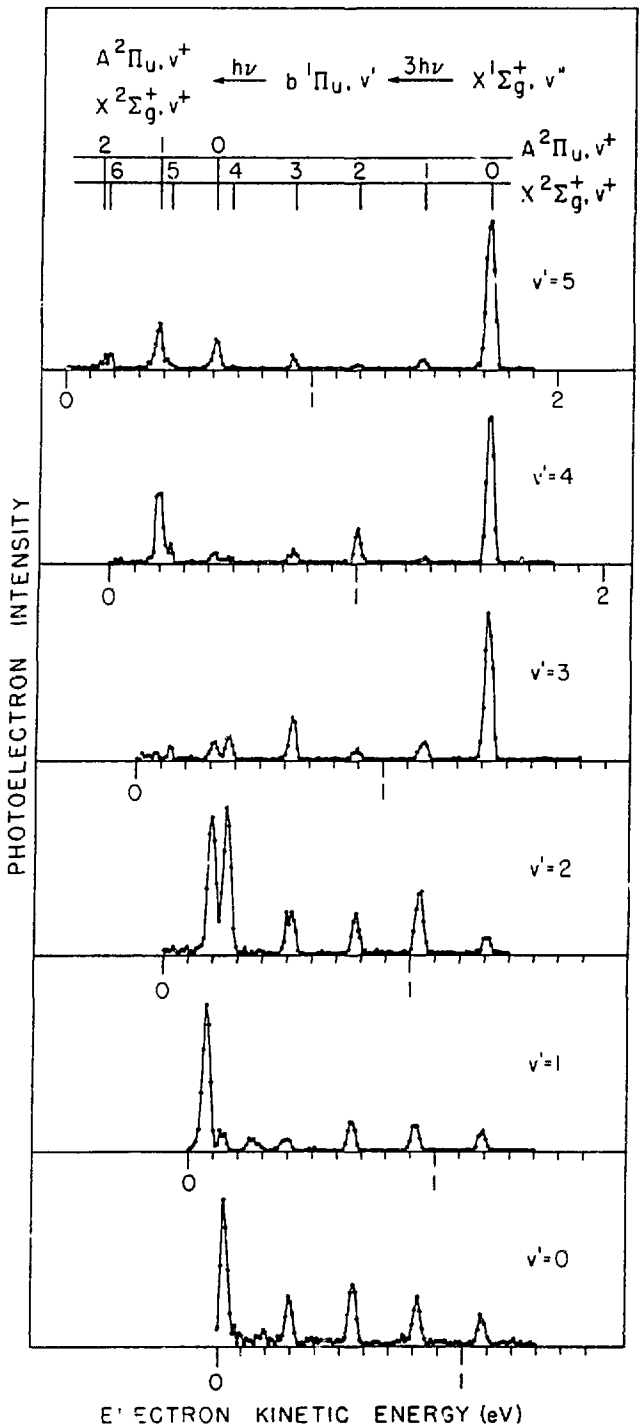

Fig. 6. Photoelectron spectra of N_2 following (3+1) ionization via the $b\,^1\Pi_u$, v' = 0-5 levels. The impurity peaks at 0.26 eV and 0.50 eV in the v'=1 spectrum are due to (2+1) ionization of O_2.

intensity of the A peaks with respect to the X peaks is more difficult to understand, since production of the A electronic state from the c state requires a two electron transition in the ionization step.

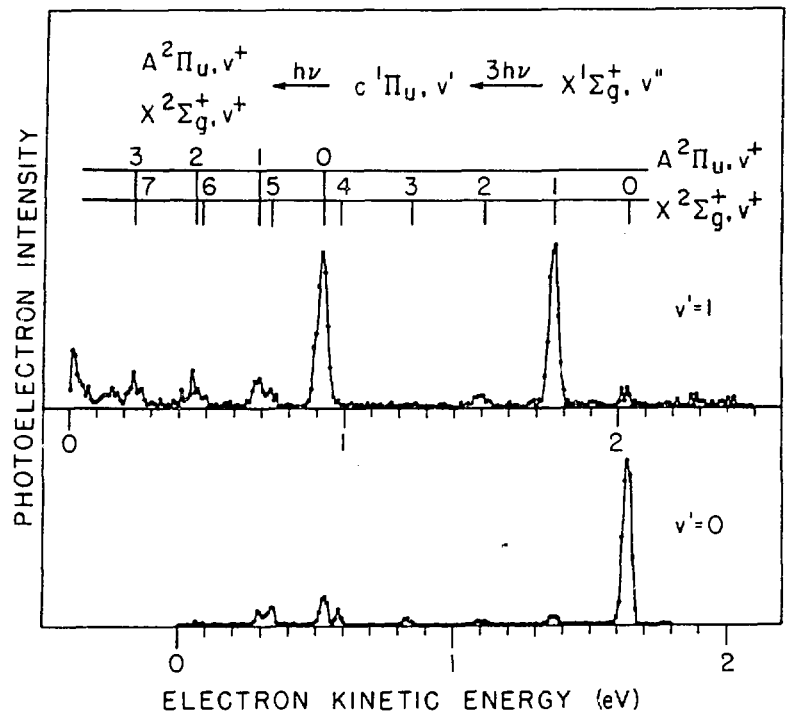

Fig. 7. Photoelectron spectra of N_2 following (3+1) ionization via the $c\,^1\Pi_u$, v'=0,1 levels.

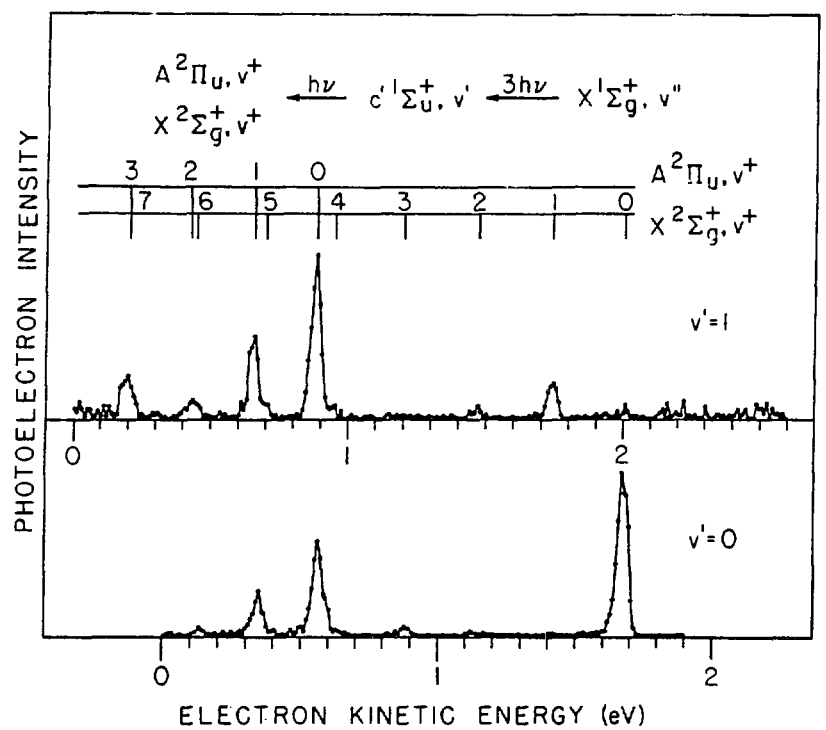

Fig. 8. Photoelectron spectra of N_2 following (3+1) ionization via the $c'\,^1\Sigma_u^+$, v'=0,1 levels.

The c', v'=0,1 photoelectron spectra shown in Fig. 8 also show signficiant complications. The X, v^+=0 peak is the most intense in the c', v'=0 photoelectron spectrum (in agreement with the Franck-Condon factor calculations [8]); however, the A, v^+=0,1 photoelectron peaks are much larger than expected for photoionization from a Rydberg state converging to the X state of N_2^+. This indicates that the c', v'=0 Rydberg state ion core does not act like a spectator in the ionizing transition as it does in photoionization of the o state. The c', v'=1 photoelectron spectrum in Fig. 8 is even more intriguing, as the X, v^+=1 peak is completely overshadowed by the intense A, v^+=0,1 peaks. According to the analysis of STAHEL et al. [20], the c', v'=1 level contains 14% b, v'=4 character and 2% b', v'=3 character, while the c', v'=0 state contains less than 2% total b' character. A large A ← b' electronic transition matrix element would help account for the strength of the A, v^+=0,1 peaks, but it is difficult to imagine that it is so much larger than the corresponding X ← c' matrix element. In addition, the Franck-Condon factors for the A, v^+=1 ← b', v'=3,4 transitions are three and two times larger, respectively, than those for the A, v^+=0 ← b', v'=3,4 transition [8], while the observed A, v^+=0 peak is nearly twice as intense as the A, v^+=1 peak. A second possibility (which may also be applicable to the c, v'=1 photoelectron spectrum) is the presence of autoionizing resonances at the four photon energy. In order to examine this possibility, we determined the photoelectron spectrum from the c', v'=1 state prepared by a two step process. The first laser pumped a two photon transition to the a $^1\Pi_g$, v=1, J=4 level, and a second laser was tuned to the wavelength of the c', v'=1, J'=5 ← a, v"=1, J"=4 transition. Ionization occurred by absorption of one photon of the first laser wavelength. Although the total energy is 140 cm^{-1} removed from the four photon energy in the single laser experiments, the photoelectron spectrum obtained is nearly identical to that of Fig. 8. This indicates that the observed branching ratios are not due to sharp autoionizing resonances, although the effects of a broad autoionizing resonance cannot be ruled out.

5. Summary

The present studies represent some of our early attempts to exploit the technique of resonantly enhanced multiphoton ionization to probe the photoionization dynamics of the excited states of small molecules that are theoretically tractable. Another aspect of REMPI is that it allows the selective ionization of one component of a complex mixture. Thus, state preparation of ions and the study of their subsequent reactions could be performed in the same region of space. This would allow the study of reactions of ions in relatively short-lived electronic states without interference from extraneous ionization products. However, the present studies illustrate that one cannot rely, a priori, on the Franck-Condon principle to predict the vibrational state distributions following REMPI.

6. References

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