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## FLUORESCENCE EXCITATION STUDIES OF MOLECULAR PHOTOIONIZATION IN EXTERNAL ELECTRIC FIELDS

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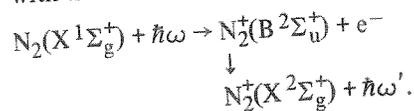
Using molecular nitrogen as an example, we show that fluorescence excitation spectroscopy can be used to measure partial photoionization cross sections of free molecules in external electric fields. The production of the  $N_2^+(B^2\Sigma_u^+)$  state was studied and the threshold for this process was found to shift linearly with the square root of the applied field. This behavior is compared with the hydrogenic case and with previously studied systems.

### 1. Introduction

Studies of atomic and molecular photoionization in external electric fields provide special insight into photoionization dynamics because they allow one to probe the effects of changing the molecule's external field (i.e. the photoelectron's boundary conditions) while leaving the core region practically unaffected [1-10]. This has stimulated extensive theoretical interest [1,2,8,11-14] and recent multichannel quantum defect theory (MQDT) calculations have successfully accounted for the novel features observed in experimental spectra [13,14]. Unfortunately, the types of experimental information available are limited because many standard methods (e.g. photoelectron spectroscopy) are not applicable when external fields are present. In the present work, we demonstrate that fluorescence excitation spectroscopy is useful under

these conditions, and that one may selectively probe photoionization channels which populate individual excited states. In particular, this selectivity is exploited here to study an excited-state threshold which would be masked if total photoabsorption or photoionization methods were to be used.

Molecular nitrogen was studied in the present work with the excitation/fluorescence sequence



The process was carried out in Stark fields with strengths up to 7.64 kV/cm. The undispersed fluorescence intensity from the B state of  $N_2^+$  was monitored as a function of the excitation energy,  $\hbar\omega$ . This system was chosen for a couple of reasons. First, the partial photoionization cross section for the  $N_2^+(B^2\Sigma_u^+)$

state is very small compared with the total photoionization cross section [15–17], underscoring the point that weaker channels in atomic or molecular photoionization in external electric fields may be studied selectively using fluorescence excitation spectroscopy. Second, autoionization structure is very weak in the threshold region for the B state of  $N_2^+$ , and an unambiguous study of the threshold shift as a function of applied field is easily carried out.

The behavior of the shift in the observed threshold is an easily parameterized quantity, and is readily compared to shifts observed in other molecules. Very few of these studies have been carried out, but it appears that a comparison of these shifts among various molecules may provide insight into the dynamics of molecular photoionization in electric fields. A larger collection of data is necessary to broaden the scope of the empirical evidence, and the present study contributes to this by providing the first information on a small diatomic molecule.

## 2. Experimental

The experimental arrangement is shown in fig. 1. Basically, the gas sample was photoionized with an electric field present and the total (non-monochromatized) fluorescence from the B state of  $N_2^+$ ,  $\hbar\omega'$ , was monitored as a function of the excitation energy,  $\hbar\omega$ . The experimental apparatus is similar to the arrangement used for fluorescence polarization studies [18,19]. Vacuum ultraviolet radiation from the Synchrotron Ultraviolet Radiation Facility (SURF-II) at the National Bureau of Standards was the excitation source. The incident VUV radiation was monochromatized with a 2 m monochromator [20] and the experiments were performed with 0.8 Å instrumental resolution. The radiation intersected the gas sample which was formed with an effusive jet.

The electric field was created by applying voltages of equal magnitude and opposite sign to two planar grids that were spaced 0.785 cm apart. The gas jet was attached to one of these grids and was insulated from the chamber ground by a 15 cm length of teflon tubing. The chamber pressure during the measurements was approximately  $10^{-4}$  Torr and the sample pressure in the interaction region was somewhat higher, probably in the range of  $10^{-3}$ – $10^{-2}$  Torr.

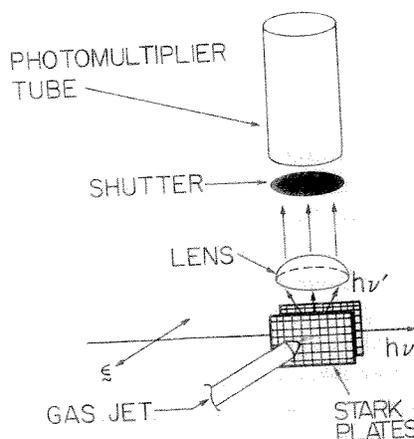


Fig. 1. Schematic diagram of the apparatus.

There were no discharge problems with this arrangement. Data were collected with fields of 0.00, 1.27, 2.55, 5.10, and 7.64 kV/cm. Measurements were carried out with the electric field oriented in either direction along the polarization axis of the excitation radiation and the results were independent of this orientation, suggesting the absence of experimental artifacts.

The fluorescence radiation was collimated with a plano-convex lens, and the fluorescence intensity was monitored with a twelve-stage photomultiplier tube cooled to  $-30^\circ\text{C}$ . An electrically controlled shutter was positioned in front of the detector so that dark counts were measured and subtracted from the data. The experiment was interfaced to a dedicated LSI 11/2 microcomputer using standard CAMAC interfaces. The only differences between these measurements and the previous polarization measurements [18,19] were the presence of the Stark plates to generate the electric field and the absence of a polarizer.

An interference filter was placed in front of the detector to ensure that only the desired fluorescence signal was observed by the detector but the results were insensitive to this precaution. This is not surprising, because no other  $N_2^+$  fluorescence occurs in the operational spectral range of the photomultiplier tube. The results are presented for the data obtained with the filter absent, as the statistics are somewhat improved for these data.

### 3. Results

The fluorescence excitation spectra are shown in fig. 2. The thresholds are clear in all cases and they shift systematically to lower energy as the external field is increased. The thresholds have been extracted from these spectra by normalizing the spectra above threshold (as plotted) and taking the wavelength at the half-maximum as the threshold wavelength.

The intensity of the fluorescence signal decreased systematically as the electric field was increased. For the spectrum taken at 7.64 kV/cm, the fluorescence intensity above threshold was roughly half that observed for the field-free spectrum. This is attributed to the extraction of ions from the interaction region by the electric field during the fluorescence lifetime of the B state of the  $N_2^+$  ion. There are two cases where this ion extraction must be taken into account for reliable interpretation of the data. First, extremely long-lived excited states can be fully extracted during the fluorescence lifetime, reducing the signal below usable levels. Second, measurements requiring relative signal levels for different electric fields must be calibrated for this signal loss, which is field strength dependent. For the present study, however, this effect was not important because only the shape of the excitation curve in the threshold region was of interest and the excited-state lifetime was short compared to the extraction time.

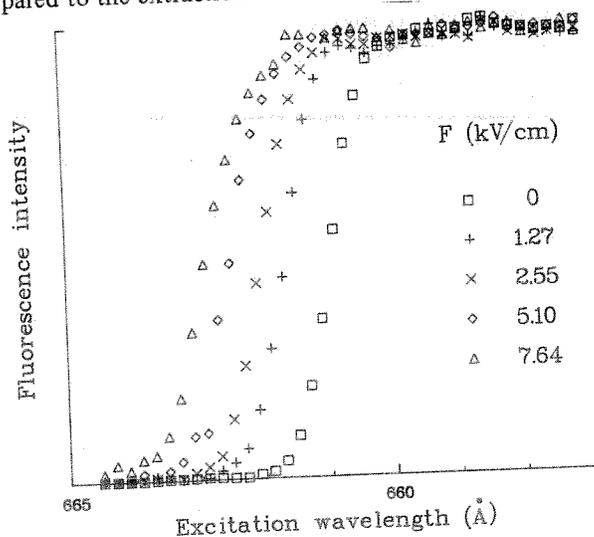


Fig. 2. Fluorescence excitation spectra for different applied electric fields. The states involved are given in eq. (1).

The signal levels were quite high ( $\approx 2000$  Hz) so that the data acquisition time for the spectra shown was less than two hours. It is reasonable to assume that for cases with large signal levels such as this, the experiment might be extended to include the measurement of monochromatized fluorescence.

### 4. Discussion

The threshold shown in fig. 2 is unobservable in photoabsorption or photoionization spectra even in the absence of an electric field [15,16]. The present results clearly define the ionization thresholds and the dependence of these thresholds on the electric field. Thus, they demonstrate that fluorescence excitation spectroscopy can be used to select a channel of interest and to investigate its behavior systematically in the presence of an electric field.

It is straightforward to estimate the energy shift of the ionization threshold on the basis of electrostatic considerations. In the absence of an external field, the long-range potential for the photoelectron is purely Coulombic, i.e.  $E = -1/r$ . Introduction of a uniform electric field adds an additional term to the long-range potential, namely  $-Fz$ , where  $F$  is the field strength and  $z$  is chosen as the direction of the applied field.

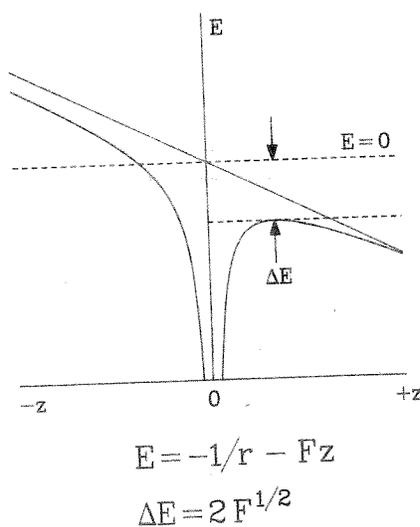


Fig. 3. Stark plus Coulomb potential showing the classical prediction for the shift in the ionization threshold; the figure and equations apply strictly only for the case of atomic hydrogen.

[21,22]. This is reflected as non-Franck-Condon vibrational branching ratios and  $\nu$ -dependent photoelectron angular distributions. One could further explore the dynamics of shape-resonant behavior by gently perturbing the molecular potential with an electric field and measuring the vibrational branching ratios by means of vibrationally resolved fluorescence spectroscopy. This is one illustration of how dispersed fluorescence might prove to be a useful extension of the method discussed here. Furthermore, polarization measurements on the fluorescence may be carried out<sup>‡</sup>, accessing information on degenerate ionization channels as has been done in the field-free case [18,19]. This type of study would be particularly useful considering that other techniques used in field-free conditions (e.g. angular-resolved photoelectron spectroscopy) are not applicable in the presence of an electric field.

## 5. Conclusions

Fluorescence excitation spectroscopy was performed to monitor production of  $N_2^+$  ions created in the  $B^2\Sigma_u^+$  state by photoionization of  $N_2$  in a uniform electric field. The main result of this study is an experimental one — fluorescence excitation spectroscopy may be utilized to selectively probe ionization channels leading to excited photoions in the presence of an applied electric field. In the present work, this permitted the observation of a very clear threshold versus field strength behavior which was compared to similar effects seen in other systems. Refinements and extensions of the technique are feasible given the large signal levels observed for the present measurements. Two examples are monochromatized fluorescence studies and fluorescence polarization studies. In any case, the ability to selectively probe ionization channels in the presence of external fields broadens the scope of future experimental and theoretical studies.

<sup>‡</sup> Some preliminary polarization measurements have been performed on  $CO_2$ , similar to those described in ref. [19], except that an electric field was introduced. Changes in polarization with the introduction of the electric field were observed and are being analyzed currently.

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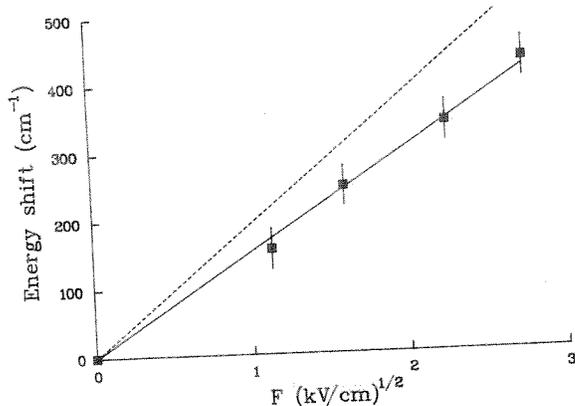


Fig. 4. Shift in the ionization threshold of the  $B^2\Sigma_u^+$  state of  $N_2$  as a function of  $F^{1/2}$ .

Hence, the long-range potential for the photoelectron is  $E = -1/r - Fz$  (atomic units), as sketched in fig. 3. Straightforward manipulation shows that the classical shift of the ionization threshold due to the electric field is  $\Delta E = 2F^{1/2}$  (atomic units), i.e. the threshold is expected to shift linearly with the square root of the applied electric field. The energy shift of the  $N_2^+$  B state threshold is plotted as a function of the square root of the electric field in fig. 4, and a linear relationship is seen. Also plotted in fig. 4 is the dependence predicted for photoionization of atomic hydrogen based on classical electrostatic considerations. It is seen that the nitrogen result is not as steep as that predicted for a pure Coulomb plus Stark potential. This is most probably a consequence of the deviation of the anisotropic molecular core potential from the pure Coulomb potential and may, in principle, yield information on the molecular potential.

Clearly, further interpretation of the present results is needed, and it is hoped that the present results will provide an impetus for theoretical efforts in

this vein. For the present, however, it is instructive to compare these results with those for other systems that also have clearly discernible shifts in ionization threshold [9,10]. Results have been obtained on benzene and the benzene-Ar complex for their respective ground-state ionization thresholds [10]. For these systems, the hydrogenic behavior was followed, including the slope of the line. Duncan, Dietz and Smalley [9] investigated the threshold shift for naphthalene and found linear behavior, but the slope has a smaller value than that for  $N_2$ . The experimental values for these systems are given in table 1. These comparisons demonstrate that the threshold behavior is dependent on the molecular environment, and that the differences in behavior can be resolved experimentally. Hence, additional experimental evidence together with detailed theoretical analyses should lead to new physical insight into the effects of different short-range potentials on photoionization dynamics in external fields.

It is clear that this method can be applied easily to many atomic and molecular excited-state thresholds to analyze the relative partial photoionization cross section for a particular electronic state as a function of wavelength. A useful extension of the method would incorporate a monochromator in the fluorescence channel in order to separate vibrational structure in molecular-ion fluorescence spectra. The resolution requirements for such studies would be modest, and the observed signal levels for the nitrogen case, which has a fairly small cross section, indicate that dispersed fluorescence experiments would be viable in many cases. Such vibrationally resolved measurements could, for example, elucidate shape-resonant behavior in an electric field. Molecular shape resonances depend sensitively on the effective molecular potential and, hence, on the internuclear separation

Table 1  
Compilation of observed threshold behavior. In the present work and two previous experimental studies, the ionization threshold has been observed to shift linearly with the square root of the electric field, i.e.  $\Delta E = mF^{1/2}$ . The values of the slopes given are conservatively estimated to be accurate to 5%

Molecule	State	Slope [ $\text{cm}^{-1}/(\text{kV}/\text{cm})^{1/2}$ ]	Ref.
$N_2$	$B^2\Sigma_u^+$	152	present work
naphthalene	ground state	124	[9]
benzene	ground state	189	[10]
benzene-Ar	ground state	189	[10]
H	ground state	193	classical prediction