Electric Field Induced Dissociation of Molecules in Rydberg-like Highly Vibrationally Excited Ion-Pair States

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The energetic thresholds for ion-pair photodissociation of diatomic oxygen [$O_2 + h\nu \rightarrow O^+ + O^-(^2P_{3/2}, {}^2P_{1/2})$] were measured using a novel technique. The technique depends on the production and selective detection of highly vibrationally excited ion-pair states which last for at least 5 μs following single photon excitation from the ground electronic state of O_2. These ion-pair states are analogous to Rydberg states, and they may be dissociated by an electric field in a similar manner to the field ionization of high principal quantum number Rydberg states, allowing for their selective detection. [S0031-9007(97)04265-8]

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There has been a variety of techniques applied to the fundamental problem of determining molecular dissociation energies [1]. One method is to monitor photofragment yield of the molecule while scanning incident photon energy—determining the energetic threshold for dissociation from the minimum photon energy at which the fragments appear. Unfortunately, thermal excitation of the sample, resonances above threshold, and poor Franck-Condon factors conspire to confuse identification of thresholds in this manner. An alternative approach is to use the spectroscopically determined bound state energy levels of a molecule near its dissociation thresholds (the different thresholds corresponding to varying internal energy in the fragments). For diatomic molecules, this involves the Birge-Sponer extrapolation [2], or suggested extensions [3]. However, these rely on the existence of extensive, unperturbed spectroscopic data near the dissociation limit, and their application is not always straightforward [4], nor easily extendable to triatomic and larger molecules.

Since the different dissociation thresholds are related by conservation of energy (given the fragment energies), it is natural to ask if any of the different thresholds lend themselves more readily to dissociation energy determination. Consider the long range potentials describing the attraction of the two atoms of a diatomic molecule. These are typically characterized as having a $-1/R^k$ behavior, where k is some positive integer, and R is the distance between the atoms. Typical values are $k = 6$ for van der Waals attraction, $k = 4$ for ion-neutral attraction, etc. [2]. The value of k is known to determine the spacing of the bound vibrational energy levels near the threshold [3]. For states which dissociate into two oppositely charged fragments—the ion-pair states—the long range potential varies as $1/R$. In contrast with the weaker potentials, this long range Coulombic potential supports an infinite number of vibrational energy levels below its dissociation threshold [5]. These states are similar to the Rydberg states of atoms, have a spacing given by the familiar Rydberg formula: $E = -\mathcal{R}/(n - \delta)^2$, where the Rydberg constant $\mathcal{R}$ is replaced by a constant suitable for the reduced mass of the two relevant fragments, the principal quantum number n is interpreted as a vibrational quantum number, and the quantum defect δ is related to the phase shift of the vibrational wave function [5]. Since ion-pair states have an infinite number of vibrational levels below the dissociation threshold, they appear to have the ideal asymptote for dissociation energy determination. With the ionization potential of the positive ion fragment and electron affinity of the negative ion fragment, neutral dissociation energies may be inferred. However, the high spectral densities of these ion-pair states and the difficulty in selectively detecting their excitation by conventional means requires a novel detection scheme—one analogous to pulsed-field ionization zero-kinetic-energy electron spectroscopy (PFI-ZEKE) [6,7].

A turning point in molecular photoionization threshold determination was the discovery of the PFI-ZEKE technique [6]. Selectively detecting a range of high-n Rydberg states while scanning the excitation wavelength maps out each of the various ionization thresholds since Rydberg series converge on each ionization threshold. Pulsed electric field ionization is used to free the weakly bound electrons. To discriminate against the electrons which may already be present from lower ionization thresholds, a time delay is inserted between excitation and field ionization in which the "hot" prompt electrons from the lower thresholds leave the ionization region. Once this discrimination is complete, the field ionization pulse can be applied with a magnitude suitable for ionizing down to a certain n, and the corresponding electrons detected. Spectra taken with different sized dc fields applied during the waiting period modify the blue edges of the PFI-ZEKE peaks and allow the field-free ionization thresholds to be accurately determined [6].

In contrast with the atomic case, molecular Rydberg state extrapolation is rarely straightforward, because of extensive perturbations. In addition, autoionizing resonances obscure the step structure in the photoion yield spectra, hampering threshold determination in this manner. Thus the PFI-ZEKE technique has been highly successful in obtaining new spectroscopic information on cations and molecular ionization potentials. When coupled with the concept of "continuity of oscillator strength," information on the dynamics of the photoionization process may also be obtained [7].

In 1992 Pratt and co-workers [8] demonstrated that they could lower the threshold for photoion-pair formation of H_2 in a systematic manner by the application of a dc electric field. This was the impetus for our work, in which it was hypothesized that it may be possible to use a pulsed field to dissociate highly vibrationally excited ion-pair states after a delay to allow discrimination against the prompt ion-pair fragments—in analogy with PFI-ZEKE. However, unlike PFI-ZEKE, prompt ions would have to be discriminated against, instead of prompt electrons. Discrimination against ions is much more difficult than with electrons because of the mass difference. However, Zhu and Johnson [9] were able to demonstrate a scheme similar to PFI-ZEKE, in which the ions originating from field ionization are selectively detected rather than the electrons. Discrimination against prompt ions is achieved by using a small dc field in the waiting period. This technique has the advantage that the ions can be mass analyzed—prompting the description mass analyzed threshold ionization spectroscopy (MATI). The small electric field used for discrimination does deplete the highest-n Rydberg states, but the field ionization pulse is still able to ionize a range of lower-n states. Thus it appeared as though an experimental spectrometer designed for MATI experiments might be able to record threshold ion-pair production spectra corresponding to the electric field induced dissociation of highly vibrationally excited ion-pair states.

To test these ideas, we studied the O_2 ion-pair formation thresholds. Attempts to determine the energetic threshold for ion-pair formation by scanning the photon energy and monitoring ion-pair production encountered the problems typical of appearance spectroscopy (see Berkowitz [10] for a review of photoion-pair formation). A steplike structure in the ion-pair yield spectrum of O_2 was observed [11], the steps corresponding to the individual thresholds depending on the initial amount of quantized rotational energy in each molecule. However, predissociating resonances above threshold create strong wavelength dependencies in the ion-pair yield spectrum which obscure the identification of the steps and limit the precision to which the energetic threshold for dissociation may be determined.

The first energetic threshold for ion-pair formation from ground state O_2 is at roughly 17 eV [11], and thus requires vacuum ultraviolet radiation (VUV). The VUV was generated by resonantly enhanced four-wave sum-frequency mixing in krypton [12,13] in a modified version of an apparatus described previously [14]. The light source operated at 10 Hz, producing 10 ns pulses of roughly 10^7 photons in a 1 cm^{-1} bandwidth. This VUV beam crossed a pulsed free jet of O_2 at right angles (see Fig. 1). The vacuum chamber pressure was typically 10^{-7} torr, and rose to an average pressure of 10^{-5} torr with the beam on. The O_2 number density at the VUV interaction point is estimated to be on the order of 5×10^{13} cm^{-3}. Above and below the intersection point are nickel mesh electrodes (P2 and P3 in Fig. 1) which were used to apply electric fields in the region. Approximately 300 ns following the VUV excitation, an electric field of 2.1 V/cm was applied between P2 and P3, pushing prompt photoions towards P2. Ions which passed through this grid were further accelerated, and traveled down to the solid electrode P1 where they were not detected. Prompt but initially stationary O^+ fragments are pushed into the region between P2 and P1 approximately 3 μs after application of the 2.1 V/cm field. To ensure complete rejection of the prompt O^+ fragments, the 2.1 V/cm "discrimination field" was maintained for 4.9 μs. After this time period, if they exist, the O_2 molecules in highly vibrationally excited ion-pair states will have continued to travel with the unexcited O_2 molecules downstream in the beam. The weak discrimination field is expected to dissociate a small range of excited ion-pair states below threshold, and thus these will also be rejected. After the 4.9 μs delay, a field larger in magnitude (60 V/cm) and opposite in polarity from the discrimination field was then applied in the region between P2 and P3. This field dissociates highly vibrationally excited ion-pair states and draws the fragments up to a detector (towards P4 in Fig. 1). The region between plates P2 and P3 then acts as the first acceleration stage of a Wiley-McLaren time-of-flight

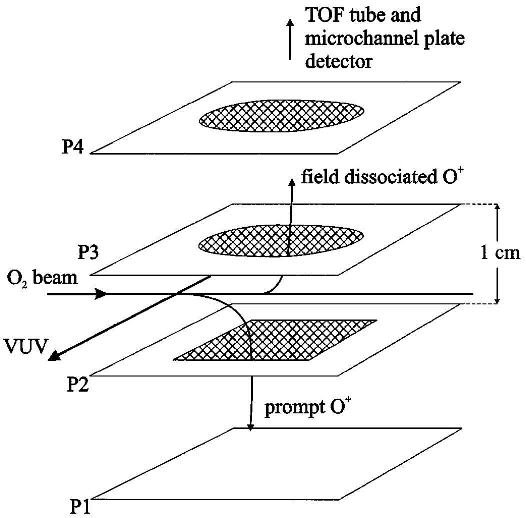

FIG. 1. Experimental apparatus. P1 is a solid electrode, P2, P3, and P4 are nickel mesh covered electrodes. The pulsed fields are generated by applying voltages to P2 and P3.

spectrometer [15], enabling the electric field dissociated O$^+$ fragments to be discriminated from the other ions (O$_2$$^+$, etc.) on the basis of their time of flight to a microchannel plate detector.

Figure 2 shows a spectrum obtained by varying the excitation energy and recording the gated O$^+$ pulsed field dissociation signal. Each of the peaks in the energy range from 139 160 to 139 320 cm^{-1} correspond to a range of unresolved ion-pair vibrational levels converging on the first ion-pair dissociation asymptote, and the individual lines arise from the different initial thermally populated rotational levels of O$_2$ ($X^3\Sigma_g^-$, $v = 0$, $N = 1, 3, 5$, etc.). The splitting of the rotational levels due to electron spin is unresolved [2,16]. Since the dissociation asymptote is independent of rotation, the spacing of the peaks is given by the well known rotational constants of O$_2$ [16]—molecules with more initial rotational excitation require less energy for excitation to the same ion-pair dissociation threshold. It is noted that since the long range Coulomb potential is stronger than the "effective" centrifugal contribution ($1/R^2$), no centrifugal barrier to dissociation forms, in contrast with weaker long range potentials [2].

In the spectrum in Fig. 2 energetics dictate that the O$^+$ ions are produced in their ground electronic state ($^4S_{3/2}$). However, the O$^-$ ion has two spin-orbit states, $^2P_{3/2}$ (ground) and $^2P_{1/2}$ (excited), separated by 177 cm^{-1} [17]. Dehmer and Chupka hypothesized that structure in their ion-pair yield spectrum could be rationalized by the "opening" of a second dissociation channel corresponding to the production of excited O$^-$ [11]. This is a second ion-pair dissociation asymptote, and produces the set of peaks at the energies from 139 320 to 139 500 cm^{-1} in Fig. 2, corresponding to the field dissociation of highly vibrationally excited ion-pair states in which the O$^-$ ion is electronically excited. The second set of rotational lines is shifted from the first by exactly the spin-orbit splitting in O$^-$, demonstrating that this technique can be used to determine the spectroscopy of negative ions, some of which may be difficult to do otherwise. Moreover, the observation establishes that photoion-pair formation in O$_2$ produces O$^-$ ions in both spin-orbit states—a dynamical aspect of ion-pair formation which would otherwise have to be gleaned from a kinetic energy analysis of the ion-pair photofragments (see, for example, Ref. [18]).

The computed field-free thresholds have been marked with lines on Fig. 2. These were computed using the literature values of the ionization energy of O, 109 837.02 ± 0.06 cm^{-1} [19], the electron affinity of O, 11 784.645 ± 0.006 cm^{-1} [17], the first dissociation energy of O$_2$, 41 268.6 ± 1.1 cm^{-1} (measured from the $N = 1$, $J = 0$ ground state level of O$_2$) [20], and the rotational term energy values for ground electronic state O$_2$ [16]. As expected, the pulsed field ion-pair signal peaks are located at slightly lower energies than the field-free thresholds, as they correspond to the signal from states which are almost, but not quite, free ion pairs. Recall that the weak discrimination field will deplete the highest energy ion-pair states, so that the blue sides of the peaks do not reach the field-free thresholds. Figure 3 shows two pulsed field ion-pair spectra over the limited range 139 200 to 139 250 cm^{-1}, taken with different sized discrimination fields. As expected, increasing the size of the discrimination field shifts the blue edge of the line to lower energies. By extrapolating these systematic shifts of the blue edge to zero field, the field-free ion-pair dissociation threshold for the $N = 1$, $J = 2$ state

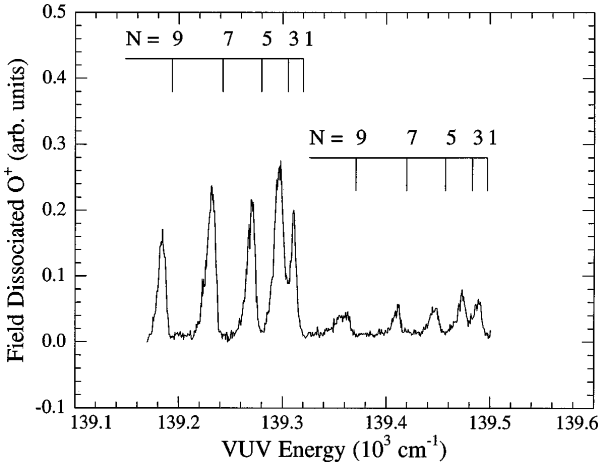

FIG. 2. Threshold ion-pair production spectrum. The O$^+$ signal arising from electric field induced dissociation of highly vibrationally excited ion-pair states is shown as a function of photon excitation energy. The field-free ion-pair formation thresholds (corresponding to different initial rotational states and the two final O$^-$ states) are displayed based on the previously known spectroscopic information (see text).

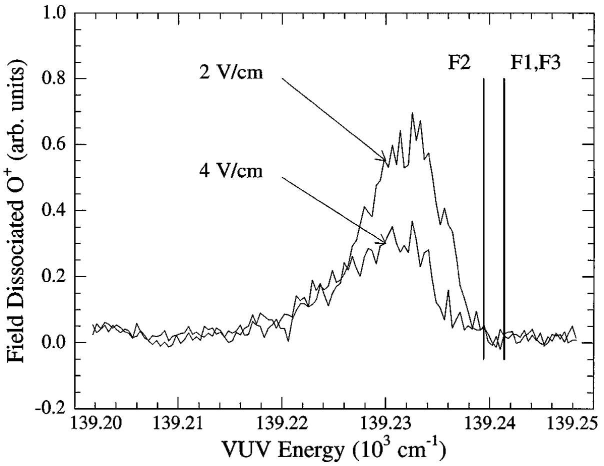

FIG. 3. Threshold ion-pair production spectra of the $N = 7$ line with two different discrimination fields. The three thresholds corresponding to the unresolved splittings due to electron spin in the O$_2$ ground electronic state (F1, F2, and F3, in the notation of Herzberg [2]) are indicated based on the accepted spectroscopic constants (see text).

is determined to be $139\,319.1 \pm 0.7\ \mathrm{cm}^{-1}$, compared to the value determined using the literature constants (discussed previously): $139\,318.9 \pm 1.1\ \mathrm{cm}^{-1}$. This is similar to the procedure used in PFI-ZEKE [6], and the details will be presented in the future. So although ultimately some form of extrapolation must applied to determine the field-free ion-pair formation threshold, it is clearly much less uncertain than the traditional Birge-Sponer extrapolation and its extensions.

The shift of the red sides of the peaks with extraction voltage has not been systematically studied yet. By using larger fields, eventually one would expect to reach down to energies where the individual vibrational levels of the ion-pair states could be spectrally resolved. These "vibrational Rydberg series" could then be extrapolated to determine the field-free dissociation thresholds. Unfortunately, the fields required would be much larger than in the Rydberg case (for the same excitation bandwidth), because of the denser spacing of the ion-pair levels. In addition, in parallel with Rydberg states, lower ion-pair vibrational levels would involve more frequent collisions of O^+ and O^-, which through nonadiabatic behavior could lead to autoionization or predissociation, depleting the signal in the discrimination waiting period. As far as we are aware, little is known about this type of loss mechanism in either O_2 specifically, or any other highly vibrationally excited ion-pair state. Unfortunately, since excitation to these highly vibrationally excited ion-pair states accounts for such a small fraction of the total photoabsorption cross section, a selective technique such as delayed pulsed electric field dissociation would probably be critical for detection. It is noted however that lower vibrational levels of ion-pair states have been observed by laser-induced fluorescence, and extrapolated to determine dissociation energies [21].

Although the dissociation energy measurement technique described in the present paper will not be applicable to every molecule, the number of promising targets is large (see Table I of Ref. [10]). There is no reason to believe that it will not be possible to determine accurate dissociation energies of many of these, including triatomic and higher systems, particularly with high flux third generation light sources such as the Advanced Light Source (ALS). Additionally, many interesting Rydberg state experiments could be applied to these "new kinds of Rydberg atom" [4]. For example, the size of these enormous diatomic molecules could be verified in a similar manner as for Rydberg atoms [22].

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