Magnetic Field Control of the NO_2 Photodissociation Threshold

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This is the first experimental observation of the control of the dissociation energy of a polyatomic molecule with an external magnetic field. We have observed by laser-induced fluorescence that the NO_2 photodissociation threshold is linearly lowered by a magnetic field. This effect reaches 13.2 cm^{-1} under 14 T, i.e., $2\mu_B B$. This result demonstrates that all the rovibronic levels of NO_2 energetically above the lowest dissociation channel are significantly coupled, without any barrier, to the lowest exit channel: NO ($^2\prod_{1/2}$, $v = 0$, $J = \frac{1}{2}$) and O ($^3P_2$, $M_J = -2$). This simple behavior is explained by the existence of quantum chaos within the NO_2 rovibronic levels. [S0031-9007(97)02957-8]

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The dream to selectively break chemical bonds in polyatomic molecules with lasers is driving a lot of efforts. When (at least) two dissociation channels (giving two different types of chemical products) are energetically open, the understanding of the competition between these two channels is a central question. A similar problem occurs when only one chemical dissociation channel is open, but when there are different ways (product state channels) of dividing up the energy excess. Few polyatomic molecules have been studied just above their lowest dissociation threshold and, up to now, their dissociation energy has been considered as a constant. In this Letter we demonstrate that it is possible to act on the dissociation energy threshold with an external magnetic field. This new phenomenon may open new ways of exploring photodissociation processes. This new magnetic field effect on molecular dissociation is analogous to the ionization of Rydberg states induced by an external electric field. However this magnetic field effect exists only if one of the products of dissociation is formed in a paramagnetic state. Here, both NO and O are paramagnetic like the NO_2 parent molecule. Before discussing the magnetic field effect itself, it is necessary to describe the properties of the NO_2 photodissociation process at zero field.

The zero field visible spectrum of NO_2 is famous for its complexity and its high density of lines. However, its photodissociation is well documented, especially near the threshold: owing to the supersonic jet technique which allows us to cool rotationally the molecule and the high resolution of the laser-induced fluorescence (LIF) technique, it has been possible to resolve the last bound levels just below the dissociation threshold [1–7]. It has also been possible to observe the first resonant levels just above the dissociation either by detection of the products (NO and/or O) [2–4] or by V-type double resonance [6]. The corresponding average dissociation rates, of the order of 10^{+10} sec^{-1}, is in rough agreement [4–6] with various statistical theories like Rice-Ramsberger-Kassel-Marcus (RRKM), Statistical Adiabatic Channel Model (SACM), Phase-Space Theory (PST). These theories require the density of states near the threshold, but this quantity is difficult to calculate [8] and to measure. Similarly, the average of the dissociation rates is difficult to measure [4–6]. Just above the threshold, the photodissociation products (the NO molecule and the O atom) are formed only in their lowest energy levels: NO is formed in the $^2\prod_{1/2}$, $v = 0$, $J = \frac{1}{2}$ state and the O atom is formed in its $^3P_2$ state. This is true as long as the excess of energy ($h\nu - D_0$, where $h\nu$ is the photon energy and D_0 the dissociation energy) is lower than the energy necessary to reach an excited state in one of the two products. The first excited state of the oxygen atom is the $^3P_1$ state which is 158.29 cm^{-1} above the $^3P_2$ state and the first excited state of NO is the $J = \frac{3}{2}$ rotational level, which is about 5 cm^{-1} above the $J = \frac{1}{2}$ level. This means that only one "exit" channel is energetically open in the $D_0, D_0 + 5$ cm^{-1} energy window. This fact has unambiguously been demonstrated experimentally by Miyawaki *et al.* [4]. One straightforward and important conclusion of these zero field experimental observations is the absence of barrier of photodissociation, at least for the lowest J values of NO_2. We have improved recently the resolution and the sensitivity of the LIF detection of the last bound states of NO_2, just below the dissociation limit, and we have determined very precisely $D_0 = 25\,128.57 \pm 0.05$ cm^{-1}.

A single mode tunable ring dye laser, parallel to the field, crosses the jet expansion and excites the NO_2 molecules which are rotationally cooled ($T_{\mathrm{rot}} \cong 2$ K) in the seeded supersonic jet (Ar or He + 1% of NO_2). We monitor the fluorescence intensity emitted perpendicularly to the jet and to the laser as a function of the laser frequency (excitation spectrum) for a fixed magnetic field. At zero field the LIF excitation spectrum [7] consists of resolved lines (residual Doppler width of 120 MHz) up to the limit of dissociation, while no fluorescence can be observed above this energy [1–7]. By using a homogeneous Bitter coil (130 mm bore) in which the jet is located, we have been able to study the 0 to 14 T magnetic field range owing to the 10 MW power supply. An example of a jet cooled NO_2 excitation spectrum under a magnetic field of 3 T is shown in Fig. 1 for σ^+, σ^-, and linear polarizations. Because of the limited fluorescence collection in the coil, the experiment under magnetic field suffers from a less efficient and less selective fluorescence detection; as a result the linewidth is 300 MHz and the signal to noise ratio, about 50, is 10 times lower than for the zero field experiment. It is important to note that the radiative lifetime of the eigenstates of NO_2 just below the dissociation threshold is of the order of a few microseconds, i.e., more than 4 orders of magnitude longer than the inverse of the average photodissociation rate above D_0 (see below). Consequently, the photodissociation threshold is defined experimentally as the highest photon energy at which fluorescence can be observed [7]. The two main differences between the LIF spectra under magnetic field and the zero field spectrum are the increase of the line density and the lowering of the photodissociation threshold. This second point is the main result presented in this Letter. The increase of the line density is due to the looseness of selection rules (or symmetry breaking): Under magnetic field only $M = M_N + M_S$ remains a good quantum number for the eigenstates around D_0, whereas J is a good quantum number at zero field (N and K are no longer good quantum numbers around D_0 and below [9]). The nuclear spin $I = 1$ is a good quantum number at all energies and can be omitted. The LIF excitation spectrum under magnetic field can be split into two independent subspectra corresponding to σ^+ and σ^- circular polarization. A schematic representation of the allowed transitions is given in Fig. 1 of Ref. [10]. Three points should be noted: (i) the photodissociation threshold is the same for the two polarizations, (ii) the density of lines is the same for the two polarizations, and (iii) the two subspectra are uncorrelated in position and intensity.

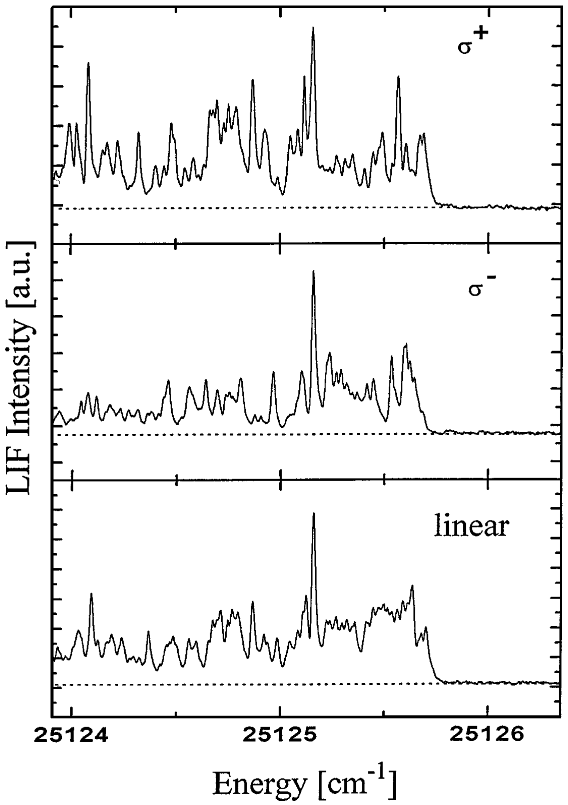

FIG. 1. Jet cooled NO_2 laser induced fluorescence spectrum under 3 T near the photodissociation threshold for σ^+, σ^-, and linear laser polarizations. The dashed line indicates the background of the light scattered on the clusters formed in the jet expansion. This background exists above and below D_0, without and with an external magnetic field. Each of the two subspectra are made of a dense set of bound-bound rovibronic transitions below $(D_0 - 2\mu_B B)$ while the resonant states above this energy do not fluoresce. The photodissociation threshold is the same for the two polarizations. There is no correlation between the line positions (and intensities) of these two spectra because they correspond to two independent subsets of upper levels: $M = -\frac{3}{2}$ for σ^- polarization and $M = +\frac{1}{2}$ for σ^+ (see Ref. [14] and Fig. 1 of Ref. [10]).

The lowering of the photodissociation threshold has been observed for magnetic fields ranging from 0 to 14 T. Figure 2 demonstrates that this lowering is linear with a slope of 0.946 ± 0.013 cm^{-1} per tesla, which corresponds to a g factor of 2.028 ± 0.028, i.e., an energy lowering of $2\mu_B B$. This effect, which is sketched in Fig. 3, is due to the difference between the sum of the Zeeman energies of the products (the NO molecule and the oxygen atom) and the Zeeman energy lowering of the ground state of NO_2 $(\tilde{X}^2A_1)$; $0,0,0$; $N = 0$, $K = 0$, $S = \frac{1}{2}$, $M_s = -\frac{1}{2}$. In order to analyze the magnetic field dependence of the photodissociation threshold, we have to consider the Zeeman effect in the following states: (i) the ground state of NO_2, (ii) the ground states of NO and O, i.e., the sum of the energies of the products under magnetic field, and (iii) the excited states of NO_2 near the photodissociation threshold.

The Zeeman effects of (i) and (ii) are well known: The g factor of the ground state NO_2 molecule is close to the free spin value, i.e., approximately 2. In NO_2, g is

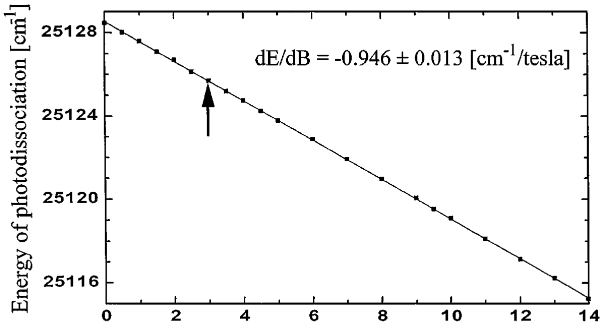

FIG. 2. Plot of the observed photodissociation threshold versus magnetic field. The arrow indicates the threshold for the spectrum displayed in Fig. 1. The slope of 0.946 ± 0.013 cm^{-1} per tesla is discussed in the text.

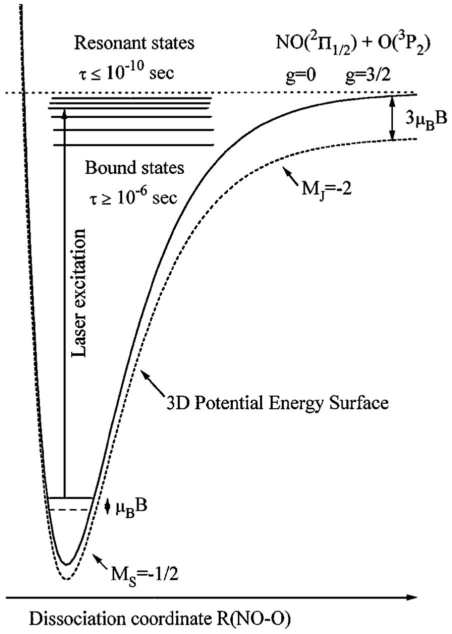

FIG. 3. 1D schematic representation of the potential energy surface along the dissociation coordinate at zero field (full line) and under magnetic field (dashed line). The lowering of the horizontal asymptote corresponds to the Zeeman energy lowering of the products (NO and O) in their lowest energy sublevels (see text). The zero point energy corresponds to the dissociation coordinate only. The zero point energies of the two other coordinates of NO_2 and the O-O coordinate are not represented.

a tensor [11], but the anisotropy is negligible, and we will consider g as a scalar for all the levels. Consequently, the lowest Zeeman sublevel of the NO_2 ground state, $M_S = -\frac{1}{2}$, is lowered by $\frac{1}{2} g \mu_B B$, i.e., by $\mu_B B$. The Zeeman energies of the products (NO and O) are also well known: NO in the $^2\prod_{1/2}$, $v = 0$, $J = \frac{1}{2}$ state has a Landé factor close to zero and the oxygen atom in the $^3P_2$ state has a g factor of 1.5 [12]. As a result, the energy of its lowest Zeeman sublevel, $M_J = -2$, is lowered by $3\mu_B B$. We can consider the Zeeman effect in O ($^3P_2$) as linear because the Zeeman energy remains weak, even at 14 T, compared with the oxygen fine structure splitting. Globally the sum of the energies of the products is lowered by $3\mu_B B$ and the energy of the optical transition between the lowest state of NO_2 and the lowest state of the product is lowered by $2\mu_B B$ (see Fig. 3). Our experimental observations of the Zeeman effect in NO_2 around 17 000 cm^{-1} [10], 24 000 cm^{-1}, and up to 25128.57 cm^{-1} show that numerous rovibronic interactions (overlapping anticrossings) are present. At the photodissociation threshold, the rovibronic density at zero field [7] is 17 levels/cm^{-1} and the mean rovibronic matrix element V is expected to be about 0.25 cm^{-1} [9]. Then $\rho V > 1$ [13] and N and K are destroyed. As a result, only J remains a good quantum number. Our parameter-free random matrix model [14] shows that the dependence of the energy levels on magnetic field is in agreement with predictions of quantum chaos [15–17]. For this reason, it seems impossible to correlate the highly excited levels of NO_2 with the energy levels of the products [18].

A completely different (and much simpler) approach is to give up any assignment and correlation diagram and to use a heuristic argument, based on the existence of quantum chaos, i.e., to worry only about energy conservation. We will first draw the consequences of this approach and then present the evidences of vibronic and rovibronic chaos which justify it. The main feature of quantum chaos is to destroy the quantum numbers (i.e., the separability or the integrability of the corresponding degrees of freedom) within a given subset of degrees of freedom and, consequently, to relax the corresponding selection rules for various kinds of physical or chemical processes. Equivalently, the diagram of correlations between the excited states of NO_2 and the products becomes meaningless and only the energy conservation should be taken into account (note that the conservation of the total angular momentum can be satisfied without any constraint by taking into account the orbital angular momentum of the products). In other words, any eigenstate (resonance) of NO_2 energetically above the dissociation threshold belongs to the set of strongly coupled levels (in which quantum chaos exists) and can be efficiently coupled to the dissociative channel. The arguments using quantum chaos as a line of force to explain the simplicity of our experimental observation are valid at zero field and under magnetic field. However, there are two important differences: (i) the remaining good quantum numbers (J or M) and the corresponding selection rules are different and (ii) the magnetic field allows us to tune continuously the photodissociation threshold. This tunability (taking into account our 0 to 14 T range) allows us to study the dissociation of about 200 rovibronic levels of NO_2 which are bound at zero field. This opens the possibility to improve the statistical analysis of dissociation rates just above the threshold. Conversely, we point out that our experimental result presented in Fig. 2 reinforces previous evidence of chaos within the rovibronic levels of NO_2, significantly below [9,19] and just below [7] the photodissociation threshold.

We may wonder if there is a barrier of dissociation. The previous experiments show that there is no significant energy barrier at zero field [2–4,6] and our experiment under magnetic field leads to the same conclusion: As a matter of fact, the fluorescence lifetime does not decrease below the dissociation threshold, even in the last cm^{-1} below D_0.

To conclude, this new magnetic field effect (controlling molecular dissociation energies) allows us to study the photodissociation processes near threshold when at least one of the products is in a paramagnetic state. Up to now, there is, to our knowledge, a unique achievement of this idea on the NO_2 molecule, but there are numerous molecules for which this new approach can be used. The growing interest and the experimental progress on dissociation mechanisms may lead to new applications of the dissociation energy magnetic field control in order to increase experimental data. This new possibility is especially interesting to study the molecular properties like rovibronic level (or resonance) density and rates of dissociation, because their statistic is intrinsically poor when a narrow energy range corresponding to a single open product state channel is considered. This is important when we want to know if the statistical assumptions of standard theories such as RRKM, PST, and SACM are valid or if nonstatistical effects are dominant. A second idea is to break a weak molecular bond with a magnetic field. A third and related idea is to modify the spin of the ground state of a weakly bound molecule with an external magnetic field. Owing to strong magnetic field facilities, these new ideas can be used to improve our knowledge of chemical bonds.

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