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Phys. Rev. A **86**, 041401 — Published 2 October 2012

DOI: 10.1103/PhysRevA.86.041401

Orientation of Doubly-Excited States in N_2

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(Dated: September 10, 2012)

Abstract

We have measured the total fluorescent intensity and circular polarization of light emitted in $3p\ ^4P^o \rightarrow 3s\ ^4P$ transitions of excited neutral nitrogen atoms created by the photofragmentation of the N_2 molecule with circularly-polarized light having energies between 21 eV and 26 eV. The intensity measurements show the effect of predissociation of the N_2 R(C) $^1\Sigma_u^+$ states by Non-Rydberg Doubly Excited Resonances (NRDERs), while non-zero values of circular polarization allow us, for the first time, to unambiguously identify the presence of a directly-excited NRDER with $^1\Pi_u$ symmetry in this energy range.

PACS numbers: 33.,33.50.Dq,33.70.-w,33.80.-b,33.80.Gj

The interaction of light with diatomic molecules causing dissociation is perhaps the simplest chemical reaction. However the dynamics of dissociation processes involving super-excited [1] or doubly-excited states are not well understood. Such states are interesting because they provide good examples of energetic but highly correlated systems. While these doubly-excited states have been studied often in H_2 [2–5], their study in, e.g., N_2 is simpler because in such a molecule they are more separated in energy and the atomic asymptotic states are not highly degenerate. For the photodissociation of N_2 in the energy range within 10 eV above the first ionization energy, there is a complex series of processes which has yet to be fully unraveled (See Fig. 1). It is possible to have direct dissociation, autoionization and dissociation, or predissociation of bound states by repulsive states. Previous experiments involving the dissociation of doubly-excited states in N_2 have involved either the measurement of the fluorescence intensity from excited fragments [6, 7] as a function of incident photon energy or the detection of neutral or ionic fragments [8]. These measurements have been able to identify the presence of predissociating states though they are less successful at identifying the mediating repulsive states associated with this predissociation or the presence of any direct dissociation. In this paper we show how the measurement of fluorescence polarization can provide information about dissociation dynamics. The development of a complete quantum mechanical treatment of diatomic dissociation [14, 15] provides us with the basis for using the measurement of photofragment polarization to probe the angular momentum state of the excited molecule and the dissociation dynamics. While previous work on other molecules has used polarization analysis to examine the dissociation process, all such studies have involved the polarization of non-fluorescing ground states [16–20]. We report here the first measurement of the circular polarization, P_3, of light emitted directly from neutral atoms created in the photo-fragmentation of diatomic molecules.

When a molecule is excited by a photon, the number of possible final excited states is limited by dipole selection rules ($\Delta\Lambda = 0, \pm 1$ and $\Delta S = 0$) so that only states of $^1\Sigma_u^+$and$^1\Pi_u$ symmetry can be populated directly from a $^1\Sigma_g^+$ ground state, though spin conservation rules are not strict for heavy molecules. If circularly-polarized photolysis radiation is used then orientation (differences in the +M and -M populations yielding a magnetic dipole) of the excited molecular state is possible. Orientation of the photofragments along the incident beam direction can only be produced with circularly-polarized photolysis radiation when a perpendicular transition ($\Delta\Lambda = \pm 1$) occurs [14, 15]. Thus, the orientation of N_2 excited

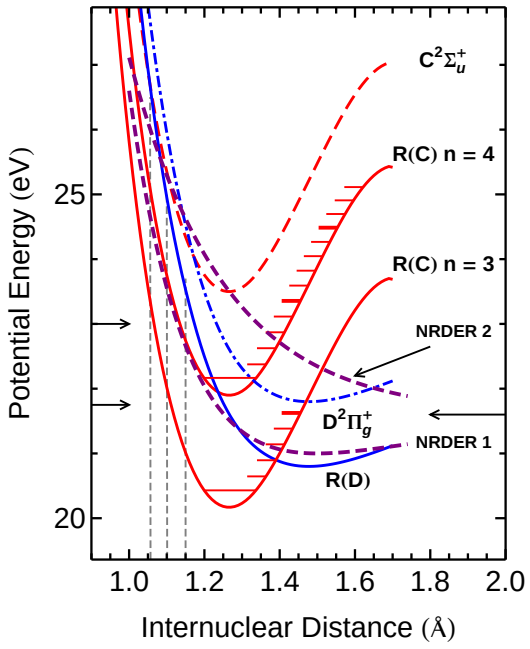

FIG. 1. Potential energy diagram for N_2 and N_2^+ showing from top down at the right: C $^2\Sigma_u^+$ [9]; R(C) n = 4 [10]; R(C) n = 3; NRDER 2 that predissociates the R(C) n=4 and n=5 states to produce N* 4P states; D $^2\Pi_g^+$ [11]; NRDER 1 which is directly excited and promptly dissociates to produce N* 4P states; the R(D) n = 4 state [6]. Arrow at right indicates the production threshold for N* 4P states, and the two arrows at the left indicate the energies of the intensity feature maxima at 21.75 eV and 23 eV (see text). The NRDER curves are based on the analyses of Refs. [6] and [12] and on quantititative considerations discussed below. The dashed grey vertical lines show the center and bounds of the Franck-Condon region [13].

from the $^1\Sigma_g^+$ state, as inferred from non-zero values of fluoresence P_3 from a photofragment, must involve the initial excitation of a $^1\Pi_u$ molecular state. This can be either a directly-dissociating doubly-excited state or one which is pre-dissociated by a state of either Σ or Π symmetry. Our measurements have yielded new insight into the nature of both predissociating and promptly dissociating states, allowing us to unambiguously identify one channel for dissociation of N_2 with an excited $N\,(3p\,(^4P^0))$ state: direct excitation of a Non-Rydberg Doubly Excited Resonance (NRDER) leading promptly to the excited-state photofragments. The NRDER states are essentially resonances in the photoionization continuum and can either autoionize or dissociate into neutral fragments with at least one of

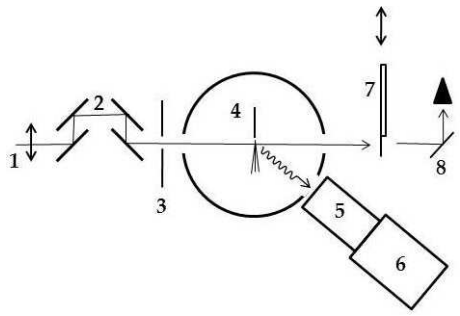

FIG. 2. Apparatus schematic showing 1) incident photon beam from ALS synchrotron, linearly-polarized in the plane of the diagram; 2) insertable four-reflection quarter-wave retarder; 3) beam-defining aperture; 4) effusive N_2 target; 5) optical polarimeter at the magic angle; 6) photon-counting photomultiplier tube; 7) photodiode for incident photon flux normalization; 8) linear photon polarimeter.

the neutral fragments in an excited state [6, 12].

In our experiment, we observe combined 818.5 nm and 818.8 nm fluoresence from NI $2p^2 3p(^4P^0)$ states produced in the reaction

$$\gamma + N_2 \rightarrow N_2^{**} \rightarrow N\left(3p\left(^4P^0\right)\right) + N\left(2p^3\left(^4S\right)\right). \quad (1)$$

In the range of incident photon energies we studied, 21-26 eV, these states are produced by (a) the predissociation by repulsive NRDERs of the doubly-excited Rydberg series R(C) $(^1\Sigma_u^+)$ that converge to the $C^2\Sigma_u^+$ states of N_2^+ [6], and (b) the direct excitation and dissociation of NRDER's. Our measurements were performed on the high-resolution Atomic, Molecular and Optical Physics undulator beam line 10.0.1.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. A schematic diagram of the apparatus is shown in Fig. 2. A grazing-incidence spherical-grating monochromator was used to scan the incident photon energy for both intensity and polarization measurements. Previous measurements [3] indicate that in this energy range there is contamination of our beam due to third-order on-axis harmonics of about 10%. The light from the monochromator had a linear polarization in the horizontal plane greater than 99%. A quadruple-reflector quarter-wave retarder was inserted to create circularly-polarized VUV radiation [21]. The linear polarization, P_1^i of the incoming light was measured using a Au reflector polarization analyzer

which could be rotated azimuthally [22]. Circular polarization of the beam, P_3^i,was inferred by measuring its linear polarization and using the following relationship:

$$P_3^i = \left(1 - P_1^{i2}\right)^{1/2}. \tag{2}$$

The circular polarization of the beam varied between 99% and at least 99.99% over the energy range of interest.

A maximum flux of $\sim 3{\times}10^{13}$ photons/s was available at 25 eV with an unmodified linearly-polarized beam as used in the total intensity measurements. However, the flux is reduced by at least a factor of 100 by the quarter-wave retarder. The incident photon flux was monitored using a NIST calibrated photodiode (IRD AXUV100). The polarized light was collimated to a beam spot size of $\sim$ 0.5 mm and then intersected an effusive target of N_2 gas at room temperature. Target gas purity was 99.9995% as specified by the supplier. The chamber pressure was kept between $9{\times}10^{-6}$ Torr and $2{\times}10^{-5}$ Torr corresponding to a pressure in the interaction region between 20 μTorr and 5 mTorr.

The collision region was observed by photon detectors in two different configurations. The photon detector axis for the intensity measurements made a polar angle of 35.3° relative to the incident photon axis. This detector was in the plane defined by the electric field of the incident photons and their propagation axis when linearly polarized light was used. The photon detector comprised a f/1.9 fused-silica collection lens, a polarization analyzer, an interference filter to select the observed atomic transitions, and a lens to refocus the collimated light onto the photocathode of a photomultiplier tube (Hamamatsu R943-02). The P_3 measurements used a detector with its axis at 30° to the incident beam direction. The optical polarimeter used a rotating quarter-wave retarder followed by a fixed polarizer. An interference filter which had a center wavelength of 818.7 nm selected two N I lines, the $3p\ ^4P^o_{3/2} \rightarrow 3s\ ^4P_{1/2}$ transition at 818.8 nm and the $3p\ ^4P^o_{5/2} \rightarrow 3s\ ^4P_{3/2}$ transition at 818.5 nm. The detection of these of lines is free from any molecular contamination [6].

The photon emission axis used in the intensity measurements was at the "magic"angle of 54.7° with respect to the incident beam polarization axis. Thus the measured intensity was proportional to the excitation cross section and independent of the polarization of the fluorescent emission; no polarization analyzer was used in these experiments. The incident beam energy had an energy resolution of 40 meV and was scanned in 10 meV steps. Measurements of P_3 were obtained by rotating the retarder fast-axis in the polarimeter and

measuring the variation in the detected light intensity [23]. For these experiments, which used circularly-polarized incident light, the energy was scanned in 0.1 eV steps and the photons had an energy resolution less than 50 meV. In all cases the full detector photon counting rate was corrected for dark counts and beam-related background and normalized to the incident beam flux and gas target pressure. Our results have also been corrected for deviations from ideal quarter-wave retardance and the extinction coefficient of the polarizers. The reported P_3 values have been calculated as a moving weighted average of P_3 for three consecutive energies.

Since predissociation occurs over a period that is shorter than 25 fs [24], little hyperfine or rotational depolarization occurs in the excited molecular state. However, the polarization of the light emitted from the neutral fragments is decreased due to hyperfine effects [25–27]. The hyperfine splitting of the $^4P^o_{5/2}$ state is approximately 25 MHz and that of the $^4P^o_{3/2}$ state is approximately 110 MHz [28] with lifetimes of 116 ns and 79 ns respectively, so the polarization of the detected fluoresence is reduced between 15% and 30%. The P_3 data include the effects of hyperfine depolarization.

The fluorescent intensity spectrum is shown in FIG. 3(a). It has several features, including a small peak at 21.7 eV which is about 0.4 eV wide and a much more intense, broad peak at 23 eV. Superimposed on the broader underlying peak between 22.5 eV and 25 eV is vibrational structure associated with the R(C) state. The circular polarization P_3 shown in FIG. 3(b) has definite non-zero values above 22.5 eV and is consistent with zero elsewhere.

In terms of the broad feature between 22.5 eV and 25 eV, we observe a much better defined vibrational structure with different relative intensities when compared with Erman et al. [6] due to the improved resolution of the present measurement and possibly the selection of only two (J =1/2 and J=3/2) of the four possible lines emitted from the ^4P fine-structure states. This vibrational structure is consistent with the excitation of the $2\pi_u^3 2\sigma_g 2\pi_g ns\sigma\ (^1\Sigma_u^+)$ R(C) n= 4 and n = 5 states (See FIG. 4) [10]. The vibrational assignments shown in FIG. 3 for the n=4 and n=5 R(C) states are taken from Codling; our data was shifted by 10 meV to match these energies. We note that with our present energy resolution of 40 meV are able to distinguish features in both the R(C) n= 4 and n= 5 states, e.g. the n=4, $\nu = 8$ and the n = 5, $\nu = 5$ states, which are separated by 50 meV [10]. The existence of these vibrational state features indicates that one dissociation channel involves direct production of the n=4 and n=5 R(C) states which are then predissociated by NRDERS [6–8, 29]. The NRDERS

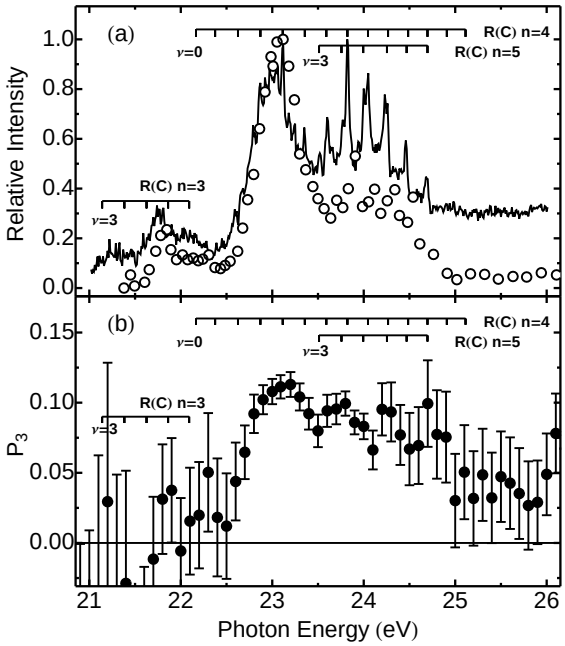

FIG. 3. (a) 818 nm intensity data : solid black line is present intensity data, open circles are the experimental results of Erman et al [6]. The position of the vibrational structure is based on the assignments of Codling [10]. (b) Filled circles are the present circular polarization P_3 data

proposed by Wendin [29] and Erman et al.[6] (the latter specifically for predissociation of the R(C) states) and shown in FIG. 4 seem to be the most likely candidates to play this role, given the similarity of their configurations and that of the R(C) state.

This predissociative mechanism, however, must be associated with $P_3 = 0$ because the R(C) states have Σ symmetry. Thus our circular polarization data require a second dissociative mechanism: the direct production and dissociation of NRDERs with $^1\Pi_u$ symmetry. The polarization, P_3, is reduced from its maximum because of increasingly important contributions from the predissociative R(C) channels to NI production as the incident photon energy increases above 23 eV. Both Ukai et al. [7] and Erman et al.[12] have suggested that the prominent peak at 23.5 eV in the visible fluorescence observed by Ukai et al., and which corresponds to our feature at this energy, is due to direct $^1\Pi_u$ NRDER production followed by dissociation. Hikoska et al.[8] attributes a similar broad feature in N atom neutral production to the same process. The broad featureless nature of these peaks at 23.5 eV certainly implies that rapid dissociation of a short-lived doubly-excited state is responsible for them.

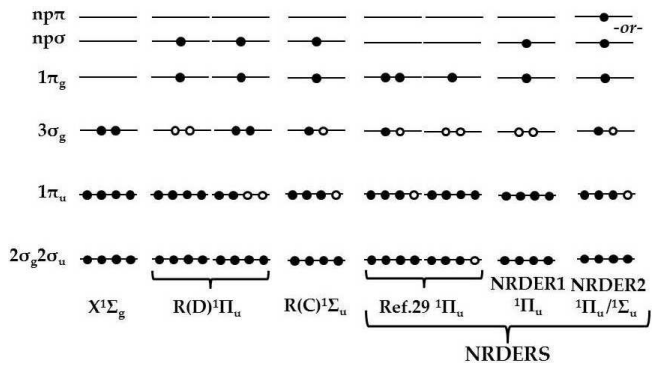

FIG. 4. Configurations of various neutral N_2 molecular states including the ground state (X), Rydberg states converging to the ions N_2^+ C (R(C)) and D(R(D)), and NRDER states discussed in various refrences (see text). The "G"' $1\sigma_g 1\sigma_u$ orbitals are filled for all of these states and are not shown. In the cases where two configurations have been suggested for a given state (R(D) [30] and the NRDER proposed by Wendin [7, 29]) both are shown, with the primary configuration at the left.

However, Ukai et al. [7],and Hikosaka et al. [8] suggest that the $^1\Pi_u$ doubly-excited state of Wendin [29] (indicated as "Ref. 29" in FIG. 4) is responsible for this feature, whereas Erman et al.[12] propose a higher-lying NRDER (NRDER1; FIG. 4).

Given its appropriate calculated energy in the N_2 Franck-Condon region (23.6 eV), we suggest that the second lowest $^1\Pi_u$ state of Erman et al. [12] is the best candidate for this NRDER (NRDER1 in FIG.4). As mentioned above, Erman et al.[6] only discuss this feature in terms of predissociative processes involving NRDER2 (FIG. 4). Our data provide unambiguous evidence for direct population, through an optically-allowed two-electron NRDER with $^1\Pi_u$ symmetry leading to prompt dissociation.

With regard to the feature at 21.6 eV we can say two things. Firstly P_3 in this energy range is consistent with zero. This implies that either a directly-excited NRDER or a predissociated initial state responsible for this feature must be of Σ symmetry. Secondly we observe no discernible vibrational structure in the intensity spectrum. Features in other spectra in the vicinity of 21.6 eV have been suggested to be caused by the predissociation of R(D) $^1\Pi_u$ states [6, 30, 31]. Our polarization data do not support this. Moreover, there is indirect evidence that the R(D) designation is wrong. Firstly, the NRDERs suggested by Erman et al. [6] as being responsible for coupling the R(D) state to the dissociative continuum (NRDER2; FIG. 1 and FIG.4) would almost certainly be more strongly coupled

to an R(C) configuration than one associated with R(D), as can be seen in FIG. 4. Secondly, the energy of the R(C) n= 3 $\nu = 0$ level, as inferred from the established quantum defect for the R(C) states [10, 30] occurs at 20.43 eV. Indeed, the threshold for R(C) Franck-Condon excitation as seen in FIG. 1 indicates an onset for this feature at 21.6 eV, in good agreement with our intensity spectrum. The R(C) assignation is supported by Ukai et al. [7] (although this is questioned by Erman et al. [31]). Referring again to FIG. 1 it is apparent that excitation of an R(D) state by a Franck-Condon transition is forbidden. While it has been pointed out that configuration mixing and ${\sigma_g}^{-1}$ shape resonances are responsible for significant deviations from Franck-Condon behavior [10, 12, 32], no calculations of which we are aware support such an extreme break-down of the Franck-Condon approximation in this situation.

Our failure to observe vibrational structure in the 21.6 eV feature is consistent with the data of Ukai et al. [7], Wu et al. [30], and Erman et al. [6]. Erman et al. [31], who studied VUV fluorescence spectra, do see hints of structure at this energy. A recent report by Lo et al. [33], who also study VUV fluorescence spectra (but with roughly a factor of 100 better resolution than that of Erman et al. [31]) see irregular structure superimposed on a broader feature between 21.5 and 21.9 eV, but with no consistent spacings to suggest vibrational structure associated with either an R(C) or an R(D) state. One can only say that the lack of obvious structure in most data sets suggests an alternate possibility: that this feature is due not to a predissociative channel but rather the direct production of an optically-allowed Σ-symmetry NRDER, possibly of the type identified by Sannes and Veseth[34].

In summary, we have measured the total fluorescent intensity and circular polarization of light emitted from the $3p\,^4P^o$ to 3s ^4P transitions of excited neutral nitrogen created in the photofragmentation of the N_2 molecule by circularly-polarized light between 21 eV and 26 eV. Vibrational structure in the total intensity measurements above 22.5 eV corresponding to the doubly-excited Rydberg series R(C) that converge to the C $^2\Sigma_u^+$ states of N_2^+, provide a clear indication of predissociation of the excited molecular R(C) states by NRDER's. These R(C) states have $^1\Sigma_u^+$ symmetry. However the observation of orientation via the measurement of non-zero P_3 values in the energy region where this predisocciation occurs indicates that direct excitation of a $^1\Pi_u$ NRDER state must also occur. Thus while the total intensity measurements involve the predissociating R(C) states, the P_3 measurements unambiguously reveal the primary influence of directly-excited NRDER's. The polarization

analysis also suggests the interpretation of the feature in the total intensity measurements near 21.6 eV as being due to excitation of a state with Σ symmetry since a zero P_3 in the vicinity of 21.6 eV rules out the possibility of R(D) $^1\Pi_u^+$ predissociation. This supports the assignment by Ukai et al [7] of this feature as an R(C) $^1\Sigma_u^-$ predissociated state. It could also result from direct excitation of a directly dissociating state with Σ symmetry.

ACKNOWLEDGMENTS

Discussions with Alberto Beswick are gratefully acknowledged. This work was funded by the DOE through the use of the ALS, the US NSF through grants PHY-0653379 and PHY-0821385, and travel for JEF was funded by the Access to Major Research Facilities program which is supported by the Commonwealth of Australia under the International Science Linkages program.

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