Ultrashort-Lived Non-Rydberg Doubly Excited Resonances Observed in Molecular Photoionization

P. Erman, A. Karawajczyk, U. Köble, E. Rachlew, and K. Yoshiki Franzén
Department of Physics I, Royal Institute of Technology, S-10044 Stockholm, Sweden

L. Veseth
Department of Physics, University of Oslo, N-0316 Oslo, Norway
(Received 20 November 1995)

The $N_2^+(B - X)$ dispersed fluorescence from photon excited N_2 molecules has been measured in the 19–34 eV excitation range, where our theory predicts the existence of non-Rydberg doubly excited resonances which autoionize in the sub-fs regime into the $N_2^+ B^2\Sigma_u^+$ ionic state. The experimentally deduced vibrational branching ratios $(v' = 1)/(v' = 0)$ revealed five prominent features, four of which could be identified as such doubly excited resonances based on the lowest order of the many-body perturbation theory. [S0031-9007(96)00230-X]

PACS numbers: 33.80.Eh, 33.70.Jg

Although the photoionization dynamics of small molecules such as N_2 has been studied for many decades [1], the exploration of non-Rydberg-like, doubly excited resonances remains an unrevealed and most challenging problem. Their study deals with a particular interesting aspect of many-electron effects, i.e., the excitation of two electrons under the influence of a weak external perturbation such as an electromagnetic field, which appear as prominent satellites to the main transition line in photoelectron spectroscopy. The description of this kind of process therefore goes beyond the simple picture of a single electron excitation and multiple correlations among the final electron-hole states have to be taken into account.

Wendin [2] first proposed for N_2 the existence of such a non-Rydberg-like doubly excited resonance (NRDER) $(3\sigma_g)^{-1}(1\pi_u)^{-1}(1\pi_g)^2$, autoionizing rapidly into the $3\sigma_g \epsilon\sigma_u$ continuum in order to explain the observed prominent and broad feature at 23 eV photon energy [3,4], where no symmetry allowed single electron bound to bound transitions exist. Very recently the first experimental investigation was undertaken by Ukai *et al.* [5] in order to determine the energetic localizations of repulsive doubly excited resonances in N_2. Predissociation appears here as an alternative decay channel to autoionization and leads to fluorescence from the neutral photodissociated fragments, which was measured in the 20–38 eV excitation region. Although the fluorescence spectrum showed two broad and prominent features, a conclusive interpretation of these observations was not provided.

Stimulated by the recent attempts to give evidence for NRDER's in N_2, we utilized the Hartree-Fock theory in order to calculate the energetic positions of seven NRDER's which are optically accessible from the ground state in the 19–34 eV excitation range. We furthermore computed their potentials and lifetimes due to decay via autoionization. A theoretical lifetime in the order of only a few femtoseconds was obtained, short enough to make them appear as broad resonances with a natural width of about 1 eV. The short lifetime of the NRDER's may be immediately understood by considering their compact nature; i.e., the orbitals of the two excited electrons occupy the same space, where the outer valence electron shape resonance also tends to be localized [6] causing their motions to be highly correlated. Furthermore, since two electrons are involved in the excitation process, the transition strength is extremely small, which explains why these very short-lived NRDER's have not been observed before [3,4].

However, the vibrational distribution within a constant ionic state (CIS) photoionization yield can be significantly affected through the interaction with autoionizing NRDER's. For nonresonant photoionization the final state vibrational distribution is largely governed by the Franck-Condon factors between the initial and final state. The intensity for a given vibrational line is then proportional to the square of the overlap matrix element between the vibrational wave functions of the neutral ground state and the final ionic state. When the photoionization cross section is influenced by a discrete autoionizing resonance, the electron matrix element can strongly depend on the intermediate state and the vibrational distribution does not correspond to the intensity calculated using the Franck-Condon factors for the direct process alone. Although our calculations show that the autoionization width of the NRDER's tends to be too large in order to resolve their vibrational structure, their effect on photoionization should be evident by studying CIS vibrational branching ratios.

For this reason we have measured the final state vibrational distribution of the $N_2 X \rightarrow N_2^+ B$ photoionization. We have utilized the dispersed fluorescence (DF) technique, which recently has been applied successfully as a very sensitive tool for studying decay processes in photon-excited molecules [7]. The $N_2^+ B$ $(v' = 1)/(v' = 0)$ branching ratios were deduced from the record vibrationally resolved $N_2^+(B - X)$ fluorescence measurements in order to reveal the NRDER's.

 0031-9007/96/76(22)/4136(4)$10.00

A very similar experiment on N_2 has been performed earlier by Poliakoff *et al.* [8,9] in the same excitation energy region. Their experimental results were compared with theoretical branching ratios calculated by Basden and Lucchese [10] utilizing a two state coupled channel calculation. The theory predicted that the $3\sigma_g \rightarrow \epsilon\sigma_u$ shape resonance should have a profound effect on the $(2\sigma_u)^{-1}$ excitation channel which results in deviations from the Franck-Condon behavior for the resulting $N_2^+ B\,^2\Sigma_u^+$ ion. Although the experimental data by Poliakoff *et al.* [8,9] revealed an enhancement of vibrational excitation near the excitation energy of 29 eV, which they attributed to the interchannnel coupled shape resonance, the agreement between experimental and theoretical data is rather poor. In an effort to elucidate the discrepancy between experiment and theory, we remeasured the vibrational branching ratios for the $(2\sigma_u)^{-1}$ photoionization of N_2. Although our data confirm the general trend measured by Poliakoff *et al.* [8], the results are far from identical.

The experiment was performed using synchrotron radiation (SR) emitted by the Swedish 500 MeV storage ring MAX in Lund. A 1 m normal incidence monochromator equipped with a 1200 g/mm diffraction grating was used to produce monochromatic radiation in a wavelength range down to 34 nm. The photon flux at 50 nm was approximately $10^{10}-10^{11}$ photons/s using a ring current of typically 130 mA and 100 μm slits, for which a resolution of 0.4 nm was obtained. With a background pressure of 10^{-6} Torr the base pressure was kept below 3×10^{-2} Torr for which the dependence of the fluorescence intensity is perfectly linear with the gas pressure indicating that collisional quenching is negligible. This was verified experimentally by focusing the nitrogen fluorescence via a MgF_2 lens onto the photocathode of a photomultiplier (PM), where the intensity was recorded as a function of the gas pressure. In order to disperse the fluorescence, the emitted light was imaged into a secondary monochromator (with 19 cm focal length) equipped with a 360 g/mm grating and a position sensitive, liquid nitrogen cooled charge coupled device multichannel array detector. A spectral coverage from 190 to 450 nm with a resolution of 1.5 nm was achieved. A shutter mounted behind the entrance slit of the secondary monochromator determined the exposure time (typically 15×100 s) during which, for a given SR energy, the entire $N_2^+(B - X)$ emission spectrum was acquired. This kind of detection technique differs from the one used in previous DF experiments by [8,9], where a PM as a single channel detector was used.

In Fig. 1 a magnified section of the $N_2^+(B - X)$ at 191 eV excitation energy spectrum is shown. This section involves the (1, 2) and (0, 1) bands whose line profiles were fitted with an instrumental function in order to compare their relative intensities with an approximate uncertainty of $(6 \pm 1)\%$. As described in detail by Poliakoff *et al.* [8,9], the ratio of the fluorescence intensities are

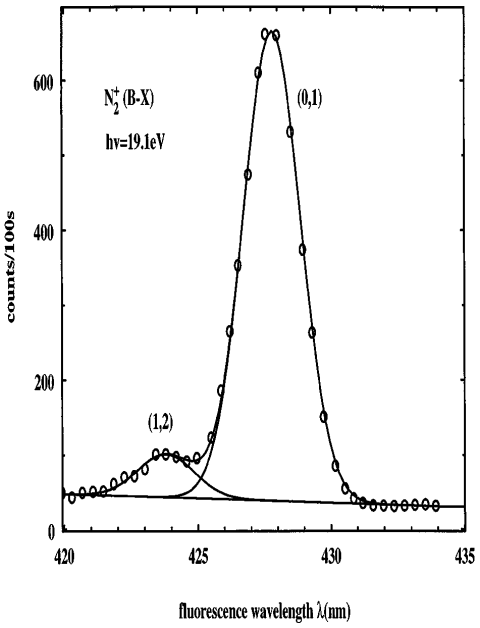

FIG. 1. The $N_2^+(B - X)$ (1, 2) and (0, 1) bands at the excitation energy 19.1 eV. In order to compare their relative intensities, the transition lines were fitted with an instrumental function superimposed on a linear background.

convertible into vibrational branching ratios σ_1/σ_0 using of the Franck-Condon factors and frequencies (taken from Ref. [11]) of the appropriate transitions. Figure 2 shows the derived σ_1/σ_0's for the $N_2\,X\,^1\Sigma_g^+ \rightarrow N_2^+\,B\,^2\Sigma_u^+$

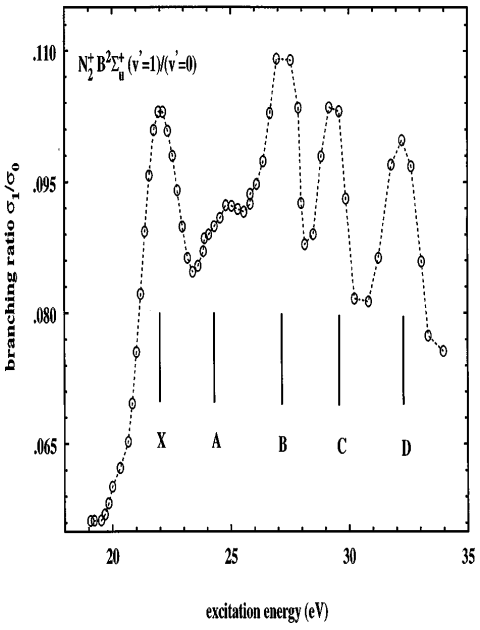

FIG. 2. Branching ratio σ_1/σ_0 for the $N_2^+\,B\,^2\Sigma_u^+$ $(v' = 1)/(v' = 0)$ emission following autoionization from upper doubly excited resonance in N_2. The feature X is suggested to originate from interchannel interaction with the $(3\sigma)^{-1}$ shape resonance, while the features $A \rightarrow D$ coincide with some of the calculated NRDER configurations shown in Table I. The theoretical energy values in Table I have been reduced by 0.8 eV in the figure to get a best fit to the experiment.

photoionization obtained from our dispersed $N_2^+(B - X)$ fluorescence measurements in the 19–34 eV excitation energy region. A rich structure is revealed in Fig. 2 exhibiting several broad features centered at about 22.1, 24.5, 27.2, 29.3, and 32.2 eV (named X, A, B, C, and D, respectively). This structure represents a fingerprint of NRDER's in N_2, and serves as an ideal test case for our computations. The results are summarized in Table I.

The calculations were carried out utilizing the relaxed Hartree-Fock (RHF) technique. Relaxation has been included in the computation of separate initial and final state orbitals. The RHF potential curves of the NRDER's are shown in Fig. 3, which provide information about their repulsive nature. NRDER states tend to be repulsive, if the two electron excitation takes place from bonding σ_g, π_u orbitals to antibonding σ_u, π_g orbitals, whereas bound NRDER states may be characterized through their electron configuration having two holes in the antibonding orbitals and the bounding nature of the excited orbitals. The energy uncertainty due to excitation probabilities from an extended Franck-Condon region is derived to be in the order of 0.4 eV and adds up to the computed autoionization width. The autoionization lifetimes of the NRDER's have been estimated in the lowest order many-body perturbation expansion, taking into account strong interactions between the continuum channels as described elsewhere [12]. The continuum states included in the calculations have been identified in accordance with Ref. [13]. First we calculated the NRDER proposed by Wendin [2] and investigated its influence on the $N_2 X \rightarrow N_2^+ B$ photoionization process. The $(3\sigma_g)^{-1}(1\pi_u)^{-1}(1\pi_g)^2$ electron configuration couples to three repulsive $^1\Pi_u$ states which can be photon excited from the ground state. The RHF theory as a first order approximation, predicts the energy of lowest state $^1\Pi_u$ to be 20.9 eV in the center of the Franck-Condon region. In order to study higher order effects, many-body perturbation expansions up to the third order have been applied to this state. As a result, the new excitation energy of the $^1\Pi_u$ state is shifted only 1.0 eV below the RHF value, which gives us confidence that the RHF method is accurate enough for an unambiguous assignment of the observed structure. An autoionization width of 0.24 eV was obtained for the $^1\Pi_u$ state which may decay into $X\,^2\Sigma_g^+$ or to an even larger extent into the $A\,^2\Pi_u$ state of N_2^+. Since the $2\sigma_u$ shell is closed, the decay of $^1\Pi_u$ into $B\,^2\Sigma_u^+$ is possible only via a substantial mixing with other $2\sigma_u$ open shell states, and they should play only a very minor role for the explanation of the 22 eV feature X. We therefore suggest that a different excitation mechanism is present here [14]. Here we have shown that the large $(2\sigma_u)^{-1}$ photoionization around 22 eV is profoundly affected by strong interchannel interactions with the $(3\sigma_g)^{-1}$ shape resonance. It is well known, however, that shape resonances in molecular photoionization may cause large deviations from the Franck-Condon intensity distributions [6] as exemplified by feature X.

The $(3\sigma_g)^{-2}(1\pi_g)(3\sigma_u)\,^1\Pi_u$ NRDER calculated to be at 23.6 eV is also a repulsive, autoionizing state, which decays very slowly into the X state but not into the B state of N_2^+. A long autoionization lifetime of 1.2×10^{-13} s leaves the state time to dissociate and is therefore clearly visible in the fluorescence data of Ukai *et al.* [5] at 23.5 eV.

The $(2\sigma_u)^{-1}(3\sigma_g)^{-1}(1\pi_g)^2$ electron configuration couples to a $^1\Sigma_u^+$ state, which can be photon excited from the ground state and autoionizes into the $N_2^+ X\,^2\Sigma_g^+$, $B\,^2\Sigma_u^+$, and $C\,^2\Sigma_u^+$ continua. The resonance calculated

TABLE I. Optically allowed, non-Rydberg doubly excited resonances (NRDER's) of N_2 calculated in the $(2\sigma_u)^{-1}$ excitation range. The energies E (eV) relative to the N_2 ground state are calculated within the relaxed Hartree-Fock theory. The total autoionization FWHM Γ_t (eV) and the partial width Γ_B (eV) of the NRDER decaying into the $B\,^2\Sigma_u^+$ continuum are calculated within the lowest order of the many-body perturbation theory. The computed energies are compared with the experimental values.

Electron configuration	States	E (eV)	Γ_t (eV)	Γ_B (eV)	E^{expt} (eV)	Feature
$(3\sigma_g)^{-1}(1\pi_u)^{-1}(1\pi_g)^2$	$^1\Pi_u$	20.9	0.24	⋯	⋯	
	$^1\Pi_u$	⋯				
	$^1\Pi_u$	⋯				
$(3\sigma_g)^{-2}(1\pi_g)^1(3\sigma_u)^1$	$^1\Pi_u$	23.6	0.006	⋯	23.5[a]	
$(2\sigma_u)^{-1}(3\sigma_g)^{-1}(1\pi_g)^2$	$^1\Sigma_u^+$	25.1	0.64	0.006	24.5[b]	A
$(1\pi_u)^{-2}(1\pi_g)^1(3\sigma_u)^1$	$^1\Pi_u$	26.5	0.11	⋯	26.5[a]	
	$^1\Pi_u$	⋯				
	$^1\Pi_u$	⋯				
$(2\sigma_u)^{-1}(1\pi_u)^{-1}\ldots$	$^1\Sigma_u^+$	27.9	1.04	0.12	27.2[b]	B
$\ldots(1\pi_g)^1(3\sigma_u)^1$	$^1\Sigma_u^+$	30.4			29.3[b]	C
$(2\sigma_u)^{-2}(1\pi_g)^1(3\sigma_u)^1$	$^1\Pi_u$	33.1	0.92	0.05	32.2[b]	D

[a]From Ref. [5].
[b]This work.

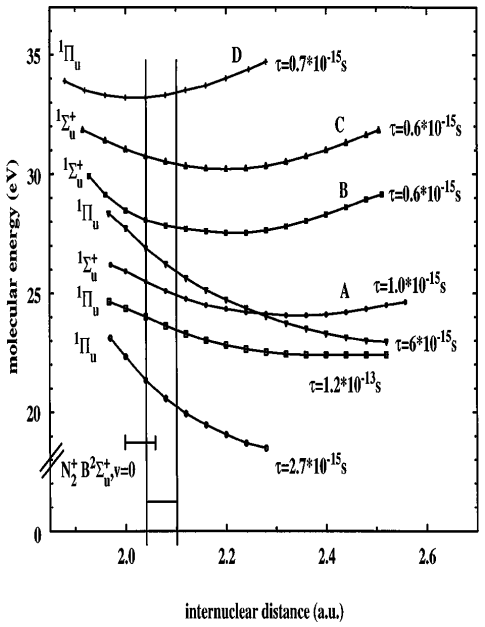

FIG. 3. Theoretical potential curves of $^1\Pi_u$ and $^1\Sigma_u^+$ NRDER's in N_2 and their lifetimes τ. The Franck-Condon region for transitions from neutral ground state $X\,^1\Sigma_g^+$ is also shown. The states denoted $A \rightarrow D$ are observed in our measurements displayed in Fig. 2, while the three lowest $^1\Pi_u$ states do not autoionize into $N_2^+\,B$.

at 25.1 eV photon energy has a considerable total width Γ_t of 0.64 eV, but a partial width Γ_B of only 0.006 eV determines a weak decay rate into $B\,^2\Sigma_u^+$. The theory therefore predicts a broad but very weak feature in the σ_1/σ_0 branching ratio, which is visible in our experimental observations at around 24.5 eV excitation energy (feature A in Fig. 2).

Higher up in energy at about 26.5 eV, our calculations show the three repulsive $(1\pi_u)^{-2}(1\pi_g)^1(3\sigma_u)^1\,^1\Pi_u$ NRDER's, which do not decay into the $N_2^+\,B\,^2\Sigma_u^+$ state. However, their lifetime due to autoionization is 5.8×10^{-15} s, i.e., long enough to be detectable in the photodissociation measurements [5], where we suggest that they constitute the second most prominent peak at 26.5 eV.

Two shallow bound $(2\sigma_u)^{-1}(1\pi_u)^{-1}(1\pi_g)(3\sigma_u)\,^1\Sigma_u^+$ states are obtained theoretically at 27.9 and 30.4 eV, and they should autoionize into the $A\,^2\Pi_u$, $B\,^2\Sigma_u$, $C\,^2\Sigma_u^+$, and $D\,^2\Pi_g$ states in N_2^+. A large total width of 1.04 eV is calculated, and here a substantial amount decays into $B\,^2\Sigma_u^+$ ($\Gamma_B = 0.12$ eV), which should result in large variations in the branching ratios σ_1/σ_0. We therefore attribute the features B and C in Fig. 2 to autoionizations from these two $^1\Sigma_u^+$ NRDER states.

Feature D in Fig. 2 should originate from a bound state $(2\sigma_u)^{-2}(1\pi_g)(3\sigma_u)\,^1\Pi_u$, which can host several vibrational levels. The following ionic N_2^+ states have been included in the calculation of the decay rates: $B\,^2\Sigma_u^+$, $D\,^2\Pi_g$, $F\,^2\Sigma_g^+$, $^2\Pi_u$, and $3\,^2\Sigma_g^+$. Also in this case we obtain a large total width ($\Gamma_t = 0.92$ eV), which agrees well with the width of the observed feature. A considerable partial width Γ_B (0.05 eV) is responsible for the occurrence of this NRDER state in our σ_1/σ_0 data.

In summary, we have calculated seven NRDER's in N_2 which can be photon excited from the ground state. Four of them are found to be attractive, decaying into the $N_2^+\,B\,^2\Sigma_u^+$ state and they have been identified in our $N_2^+(B - X)$ DF measurements. Thus, we have shown, that the DF technique is a very sensitive tool, most suitable for studies of extremely short-lived (<1 fs) NRDER's. Furthermore we attribute the strong feature observed at 22 eV to the interchannel coupled $(2\sigma_u)^{-1}$ shape resonance. In addition the two most prominent features in the data of Ukai *et al.* [5] could be identified as repulsive NRDER's. However, the autoionizing state first proposed by Wendin [2] still remains experimentally unrevealed.

[1] J. L. Dehmer, D. Dill, and A. C. Parr, in *Photophysics and Photochemistry in Vacuum Ultraviolet*, edited by S. McGlynn, G. Findley, and R. Huebner (Reidel, Dordrecht, 1983) p. 341.
[2] G. Wendin, Int. J. Quantum Chem. **13**, 659 (1979).
[3] G. Gürtler, G. V. Saile, and E. E. Koch, Chem. Phys. Lett. **48**, 245 (1977).
[4] E. W. Plummer, T. Gustafsson, W. Gudat, and D. E. Eastman, Phys. Rev. A **15**, 2339 (1977).
[5] M. Ukai, K. Kameta, N. Kouchi, and Y. Hatano, Phys. Rev. A **46**, 7019 (1992).
[6] J. L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. **43**, 1005 (1979).
[7] M. Ukai, S. Machida, K. Kameta, M. Kitajima, N. Kouchi, Y. Hatano, and K. Ito, Phys. Rev. Lett. **74**, 239 (1995).
[8] E. D. Poliakoff, Ming-Hang Ho, G. E. Leroi, and M. G. White, J. Chem. Phys. **84**, 4779 (1986).
[9] E. D. Poliakoff, Sandeep Kakar, and R. A. Rosenberg, J. Chem. Phys. **96**, 2740 (1992).
[10] B. Basden, and R. R. Lucchese, Phys. Rev. A **37**, 89 (1988).
[11] F. R. Gilmore, R. R. Laher, and P. J. Espy, J. Phys. Chem. Data **21**, 1005 (1992).
[12] L. Veseth (to be published).
[13] P. Baltzer, M. Larsson, L. Karlsson, B. Wannberg, and M. Carlsson Göthe, Phys. Rev. A **46**, 5545 (1992).
[14] L. Veseth, J. Phys. B **27**, 481 (1994).