It is also interesting to measure the fluctuations around equilibrium, which are typical of a Brownian motion. A detailed study of the pulse-to-pulse random variations of ΔN around $\langle \Delta N \rangle$ should allow us to probe the large fluctuations of the photon number in the cavity mode and to reconstruct their Bose-Einstein probability distribution. Of course the phenomenon described here is general, not *a priori* restricted to Rydberg atoms. For ordinary atoms with $d \sim 1$ a.u. however, $\Delta t/T_R$ is very small unless N is of the order of $\sim 10^9$. The relative excitation $\langle \Delta N \rangle / N = \bar{n}/N$ is then undetectable ($\sim 10^{-7}$): Only Rydberg atoms can produce Bloch vectors "light" enough to exhibit Brownian motion. There is a link between this work and Rydberg maser studies[7] where the atoms are prepared in the upper level of the transition resonant with the cavity. The Bloch vector at $t = 0$ is then in the up position; its superradiant decay towards the down direction is triggered by the blackbody field and it obeys an equation similar to Eq. (1). It is striking that the atomic indiscernability, responsible for "superradiance" when the system is initially excited, leads to a kind of "subabsorption" when it starts from its lower state.

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Bond-Breakage Mechanism in the Predissociation of the $\tilde{A}$ State of N_2O^+: New Information from High Resolution Spectroscopy

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A recent study of high-resolution laser spectroscopy in a fast N_2O^+ beam indicates that the hyperfine structure of the $\tilde{A}(100)$ state is mainly due to Fermi contact interaction on the outer nitrogen nucleus. This new spectroscopic result is crucial for the interpretation of the laser predissociation of isotopically substituted N_2O^+ with a tandem mass spectrometer. Under such circumstances the fast-ion-beam laser-spectroscopy method yields new information on the bond-breakage mechanism during predissociation.

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In this communication, we report the analysis of a very-high-resolution photodissociation spectrum of the $\tilde{A}(100)$-$\tilde{X}(000)$ system of N_2O^+ in the near ultraviolet. Obtained by fast-ion-beam laser spectroscopy (FIBLAS), with a setup (see Carré *et al.*[1]) which reproduces, in a high energy range, the familiar tandem mass spectrometer geometry, this spectrum represents the first example of a fully resolved hyperfine structure in the electronic excited state of an asymmetrically triatomic molecular ion. Two main conclusions arise from our study of isotopically substituted $^{15}N_2O^+$, $^{14}N^{15}NO^+$, and $^{15}N^{14}NO^+$: First, we demonstrate that the hyperfine struc- of the molecule is essentially due to the external nucleus; second, we present evidence that in the predissociation of the $\tilde{A}(100)$ state the molecule dissociates by ejection of this external nucleus, thus without "scrambling." This last mechanism was invoked by Berkowitz and Eland[2] in their analysis of the photoionization of $^{14}N^{15}NO$, experiments which were carried out without selective excitation of the various vibrational modes. Our results indicate that scrambling does not affect the first stretching vibrational mode of the $\tilde{A}$ state.

The FIBLAS method, a novel combination of mass spectrometry and laser techniques,[1] offers unprecedented experimental opportunities in molecular ion spectroscopy. Following several applications to diatomic molecules, this technique was recently illustrated for triatomic ions in the infrared by Shy *et al.*[3] in D_3^+. Extension to electronic spectra presents no major difficulties, except for the fact that few laser lines are presently available in the spectroscopically interesting ultraviolet range.

In agreement with the observation of Thomas, Dale, and Paulson,[4] we found that krypton-ion uv laser light photodissociates the N_2O^+ beam produced from the radiofrequency discharge ion source of a 150-keV accelerator fed with N_2O gas or a mixture of N_2O and N_2.[5] With proper intracavity optical elements (mirrors, prism, and temperature-stabilized Fabry-Perot) it is possible to obtain several milliwatts of single-longitudinal-mode uv light at 337.4 nm from our krypton-ion laser. By Doppler tuning the beam energy over the range 20 to 120 keV a spectral window approximately 50 cm^{-1} wide is opened when the collinear laser-ion-beam setup is used in a copropagating beam configuration. This spectral range (29 550–29 600 cm^{-1}) is adequate for excitation of the $\tilde{A}^2\Sigma^+(100)$-$\tilde{X}^2\Pi_{3/2}(000)$ system of all isotopic variants.[6]

As expected from previous diatomic work, postinteraction mass analysis of the NO^+ fragments (which result from a well-documented predissociation of the excited state[2,7]) provides an indirect detection scheme of high efficiency. The resulting combination of laser and mass spectroscopies is particularly powerful in the case of the two isotopic molecules $^{15}N^{14}N^{16}O^+$ and $^{14}N^{15}N^{16}O^+$, since even the best mass spectrometry techniques, when applied without high-resolution optical information, are unable to identify the parent molecule leading to a given photofragment $^{14}N^{16}O^+$ or $^{15}N^{16}O^+$.

In the FIBLAS method, optical resonance is detected as a modulation of the photofragment current, in phase with an applied intensity modulation of the laser beam. On the basis of previous excited-state lifetime measurements in N_2O^+,[7] the natural linewidth of the $\tilde{A}(100)$ level is expected to be less than 1 MHz. With our experimental setup, the accelerator stability is sufficient to reduce the Doppler linewidth along the beam direction, via kinematic compression of the velocity spread, to 80 MHz at 70 keV beam energy.

In $^{14}N_2O^+$, we recorded more than 100 rovibronic transitions within the accessible spectral range. A typical example of the signals observed is shown in Fig. 1 for a single rotational line. Clearly displayed are two groups of peaks of widely different intensities. The analysis of such a line pattern is not trivial. Indeed it was not clear *a priori* that the entire structure could be explained as a pure hyperfine structure. Quite to the contrary, the theoretical work of Hopper[8] showed conclusively that the bonding orbitals involved mainly $2p$ electrons, a situation which would predict small hyperfine splittings. On the other hand, we knew from the previous fine-structure analysis by Callomon and Creutzberg[6] that the spin rotation constant of the $\tilde{A}$ state was small because of the fact that $\tilde{A}$ lies about midway between the $\tilde{X}$ and $\tilde{B}$ states which make opposite contributions to the $\tilde{A}$-state γ value. It was only by careful inspection of the entire observed spectral range that contamination by hot bands

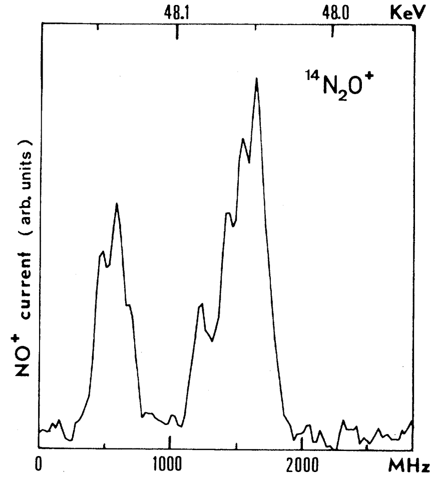

FIG. 1. NO^+ photofragment current signal obtained for the $Q(21.5)$ rotational line. The accelerator energy was varied in discrete steps and a Doppler scan was recorded by a Doppler switching technique in an insulated drift tube with a voltage step size of 1.25 V. Integration time was 3 sec. Full width at half maximum was 90 MHz. The group of two lines at the left corresponds to $G=\frac{1}{2}$ $(F'=N\pm\frac{1}{2})$, and the group of four lines on the right corresponds to $G=\frac{3}{2}$ $(F'=N\pm\frac{1}{2}$ and $F'=N\pm\frac{3}{2})$.

could be ruled out as a possible explanation for the weaker set of lines. For example, the predissociated (110)-(010) band could conceivably be excited via the same laser line.

In the final analysis, the only interpretation which reconciles all currently available spectroscopic evidence assumes that the $^2\Sigma^+$ state is described by the $b_{\beta S}$ angular momentum coupling[9] and that a single nitrogen nucleus is responsible for the observed hyperfine splittings. In this coupling scheme, the nuclear spin I is first coupled to the spin angular momentum S to produce a resultant G which, in turn, couples to the rotational angular momentum N to yield F. Pictorially, the two observed groups of lines correspond to the $I \cdot S$ interaction ($G=\frac{1}{2}$ and $\frac{3}{2}$ for N_2O^+ with $I=1$) while the splittings within a given subgroup represent the coupling of G with N.

This interpretation is confirmed by the $^{15}N_2{}^{16}O^+$ spectrum (Fig. 2). Again we observe two sets of lines (but with reversed relative positions and intensities) with a total of four lines for each rotational transition. This is in complete agreement with the known value, $I=\frac{1}{2}$, of the nuclear spin of ^{15}N as well as with the opposite sign of the nuclear magnetic moment.[10] It thus seems experimentally justified to conclude that the large hyperfine splittings observed for the $\tilde{A}$-$\tilde{X}$ transition arise from an upper-state Fermi contact interaction on a single nitrogen nucleus. The corresponding hyperfine interaction constant, b_F, is measured to be 630 ± 30 MHz in $^{14}N_2{}^{16}O^+$ and −950 ± 30 MHz in $^{15}N_2{}^{16}O^+$ while identical values of the spin rotation constant, $\gamma = 21 \pm 3$ MHz, are found in both isotopes. With our current spectral resolution, the small size of the spin rotation constant frustrates further efforts to extract the dipolar constant for the two nitrogen atoms in both upper and lower electronic states.

In order to explain the large value of the measured b_F, we must assume that, in the electronic configuration of the $\tilde{A}$ state [which, expressed in terms of molecular orbitals is $(1\sigma)^2(2\sigma)^2 \cdots (6\sigma)^2 \times (1\pi)^4(7\sigma)^1(2\pi)^4$], the unpaired σ electron has a large probability of being in a 2s atomic nitrogen orbital. The 2s orbital participation in a p_σ bond can be explained by a strong interaction between $2s_\sigma$ and $2p_\sigma$ giving rise to an sp hybridization. The atomic ^{14}N value of $\psi^2(0)$ in a 2s orbital, calculated by Hurd and Goodin,[11] yields

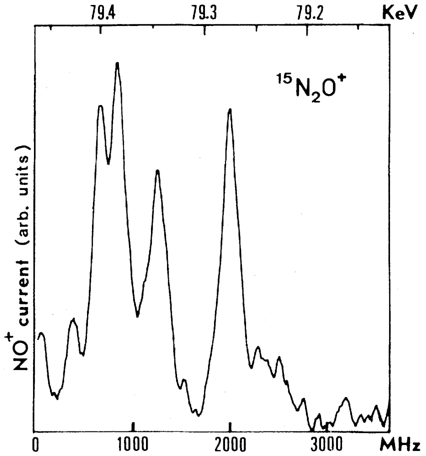

FIG. 2. $^{15}NO^+$ photofragment current signal obtained from the R (25.5) rotational transition. The group of three lines on the left corresponds to $G=1$ ($F'=N+1$, $F'=N$, $F'=N-1$) and the line on the right corresponds to $G=0$ ($F'=N$).

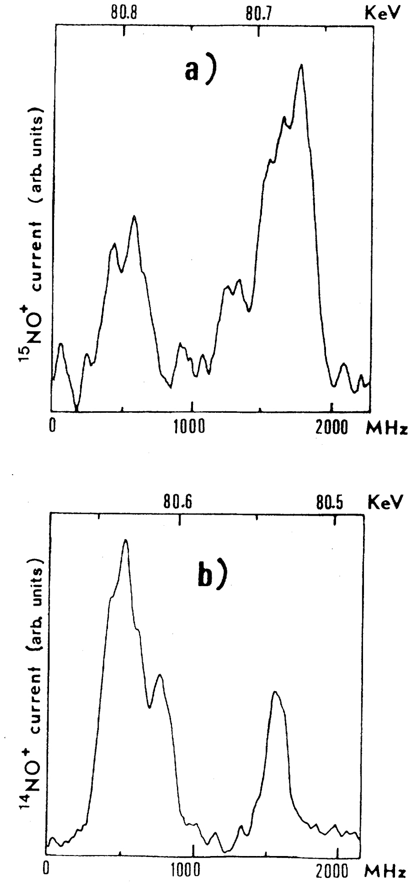

FIG. 3. Individual rotational components obtained for (a) $^{14}N^{15}N^{16}O^+$ observed on the $^{15}NO^+$ photofragment current, and (b) $^{15}N^{14}N^{16}O^+$ observed on the $^{14}NO^+$ photofragment current.

an isotropic constant of 1700 MHz, while in a $2p$ orbital, the same calculation gives an anisotropic constant of 55.5 MHz. Thus we conclude that the unpaired electron is in an $\tilde{A}$-state molecular orbital with 40% N-$2s$ atomic orbital character.

The large isotope shift of the optical transitions and the isolation of the hyperfine interaction to a single nitrogen nucleus open exciting new diagnostic possibilities when a beam of mass-unresolved $^{15}N^{14}N^{16}O^+$ and $^{14}N^{15}N^{16}O^+$ is used. Isotope shifts can be calculated with great accuracy so that each photopredissociation line can be attributed to a given parent. With this piece of information, we are able to label the nucleus which is responsible for the hyperfine structure and to distinguish whether the N-N-O$^+$ molecule dissociates by ejection of the terminal N atom or by a more complex rearrangement process.

Figures 3(a) and 3(b) are examples of the signals observed respectively in the $^{15}N^{16}O^+$ and $^{14}N^{16}O^+$ photofragment detection channel. In the first case, the parent molecule is $^{14}N^{15}N^{16}O^+$ and the observed hyperfine structure corresponds to an $I=1$, ^{14}N nucleus. In the second case, the parent molecule is $^{15}N^{14}N^{16}O^+$ and the hyperfine structure arises from an $I=\frac{1}{2}$, ^{15}N nucleus. We have thus established experimentally that the single nucleus which is responsible for the hyperfine interaction is the outer N nucleus.

Information on the bond-breakage mechanism can now be obtained by comparison of the photofragment signals in the two detection channels $^{15}NO^+$ and $^{14}NO^+$ for the same tuning of the laser and ion beam energy, assuming that the parent ion beam contains the same proportion of the two molecules $^{14}N^{15}NO^+$ and $^{15}N^{14}NO^+$. Figure 4 provides a typical example. Lines corresponding to $^{14}N^{15}NO^+$ appear only in the $^{15}NO^+$ channel whereas the $^{15}N^{14}NO^+$ lines are observed only in the $^{14}NO^+$ channel. Lack of correlation between the two spectra of Fig. 4 (at our current level of sensitivity) clearly indicates that predissociation of the $\tilde{A}$-state (100) level proceeds via the ejection of the terminal atom.

This result is somewhat surprising since Berkowitz and Eland[2] definitely established in their photoionization experiment of N_2O that "scrambling," i.e., complex rearrangement leading to the ejection of the central atom, played an important role in the predissociation of the $\tilde{A}$ state of N_2O^+. Our experimental technique is, however, a much finer probe of the excited-state dissociation mechanism. With our setup, it becomes possible to study the influence of the vibrational and eventually rotational excitation energy where-

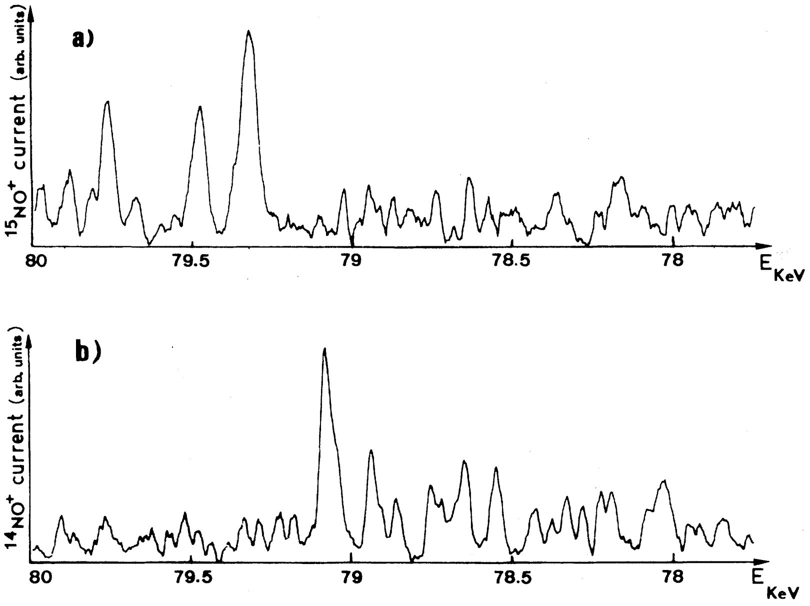

FIG. 4. In (a) and (b) we show respectively the $^{15}NO^+$ and $^{14}NO^+$ photofragment current, for the same Doppler tunings of the same laser line (337.4 nm). The lack of correlation between the two spectra indicates that predissociation proceeds via a single mechanism: ejection of the outer nucleus. Scrambling (see Ref. 2) is not detected with our current level of sensitivity.

as photoionization measurements are usually carried out under conditions which lead to severe averaging over upper-state excitation energy.

One way to reconcile both types of measurement would be to assume that the predissociation mechanism depends strongly on the excited-state vibrational-mode symmetry. Our results suggest that levels with vibrational energy in a stretching mode dissociate preferentially via ejection of the terminal atom. Study of bending vibrational levels at high optical resolution is definitely necessary in order to establish whether or not they suffer from predissociation with central-atom ejection, a likely interpretation of the photoionization data.

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Resonance in Singlet-Triplet Mixing in Two-Electron Systems Caused by Perturbing Configurations

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The hyperfine structure of the $6snd\,^1D_2$ $(10 \leq n \leq 50)$ Rydberg states of barium has been measured and analyzed in terms of singlet-triplet mixing. A dispersionlike resonant behavior of the mixing coefficient Ω was observed for barium and strontium in the vicinity of doubly excited configurations. In barium strong disagreement with multichannel-quantum-defect-theory wave functions was found. The present results are compared with the spin polarization and anisotropy of photoelectrons.

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Multichannel quantum defect theory[1] (MQDT) is a powerful tool to describe the electronic structure of atomic states simultaneously in the discrete and the continuous parts of the spectrum. Specifically, the wave functions of continuum states of an electron-ion system are closely related to those of the bound states. In order to obtain information about the atomic wave functions the total photoionization cross section and the spin polarization of emitted photoelectrons[2] are equally suited for the determination of lifetimes of Rydberg states,[3] their electronic g factors,[4] Stark shifts,[5] and even isotope shifts.[6] However, such properties of Rydberg states are insensitive to the relative phases of the mixing coefficients in the wave function and only allow the amount of admixture of different configurations to be determined. Similar to the spin polarization of photoelectrons,[7] the hyperfine structure of Rydberg states contains both the magnitude and the relative sign of the admixture coefficient. In this Letter we report the hyperfine splitting of $6snd\,^1D_2$ Rydberg states of barium. Singlet-triplet mixing coefficients Ω are derived and compared with existing MQDT wave functions.[8] Sharp disagreement between experimental and theoretical amplitudes is observed. On the other hand, for strontium we found that MQDT wave functions[9] are consistent with published hyperfine splitting data.[10] To our knowledge, this is the first time that the hyperfine structure of Rydberg states has been exploited to check the relative phases of existing