One- and Two-Photon Dissociation of Na_2: Angular, Velocity, and Internal-State Distributions of Atomic Fragments Studied by Doppler Spectroscopy

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We report on the photodissociation of neutral diatomic molecules in a molecular-beam experiment where all the relevant quantities are well defined. The velocity and angular distributions and the internal states of the fragments were determined by Doppler spectroscopy. The quasibound level $v' = 31$, $J' = 42$ of the $B\,^1\Pi_u$ state of Na_2 dissociates into $Na^*\ 3^2P_{3/2}$ and $Na\ 3^2S_{1/2}$ atoms with an angular distribution characterized by $\beta = -1$. Direct dissociation of the $B\,^1\Pi_u$ state yields only $Na^*\ 3^2P_{3/2}$ fragments, which does not support reported $^2P_{3/2}$ and $^2P_{1/2}$ fragment emission. From two-photon dissociation we obtain $Na^*\ 3^2P_{1/2}$ fragments with much larger kinetic energy and a different angular distribution.

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The photodissociation of alkali-metal dimers, particularly of Na_2, has recently attracted considerable interest and has been studied by several groups experimentally[1] as well as theoretically.[2] So far the photodissociation has only been studied by measurement of the fluorescence of excited fragments. Rothe, Krause, and Düren[3] have reported a polarization of $-(5 \pm 1)\%$ of the Na $3^2P_{3/2}$-$3^2S_{1/2}$ line emitted from the photodissociation products of $Na_2(B\,^1\Pi_u)$ molecules. Vigué *et al.*[4] have observed an unexpectedly high degree of polarization (64%) of the fluorescence of excited Ca atoms resulting from photodissociation of Ca_2 molecules, which they explained by a coherence effect between the sublevels of the excited state. But the most detailed and important information on photofragmentation dynamics is provided by the analysis of the angular, velocity, and internal-state distributions of the fragments. The most advanced photofragment experiments have been carried out in recent years with small ion molecules by several groups.[5]

Photofragment experiments with small neutral molecules were first done by Wilson,[6] Bersohn,[7] and their co-workers, and more recently by several other groups.[8] We report the first measurements of angular, energy, and internal state distributions of atomic fragments resulting from photodissociation of a state-selected quasibound level of a neutral diatomic molecule ($Na_2\ B\,^1\Pi_u$). This has been done by application of the technique of Doppler spectroscopy[9] to the study of photodissociation processes occurring in neutral diatomic molecules. Despite the long lifetime of the dissociating quasibound level (1.6 ns) the anisotropy of the molecular excitation, which is a perpendicular Q transition, is completely preserved ($\beta = -1$). This situation has not been found before.

In the course of our experiments three different photodissociation processes were observed and identified: direct photodissociation by excitation from the $X\,^1\Sigma_g^+$ ground state to the dissociation continuum of the $B\,^1\Pi_u$ state, dissociation of quasibound levels of the B state, and induced two-photon dissociation of Na_2 leading to $Na^*(nl)$ fragments.

The basic experimental setup, partially described elsewhere,[10] consists of a sodium molecular beam crossed by two laser beams, all three being perpendicular to each other as shown in Fig. 1. The sodium beam was generated by an oven operated at 800 K. The beam was collimated by a heated skimmer and by apertures resulting in a residual Doppler width of about 40 MHz. Na_2 molecules were dissociated by the Ar^+ laser, while the dye laser served to analyze the fragmentation. With several Ar^+ laser lines, both multimode and single mode, Na_2 was photodissociated into an excited $Na^*\ 3^2P_{3/2}$ atom and a $Na\ 3^2S_{1/2}$ ground-state atom, recoiling in opposite directions. In our experiment dissociation was analyzed perpendicular to the molecular beam, as indicated in Fig. 1, by measurement of the velocity component in direction of the analyzing laser so that the measured fragment velocity distribution coincides with the center-of-mass distribution. The velocity component v_z of the atomic frag-

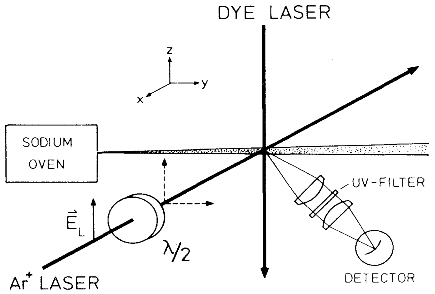

FIG. 1. Experimental arrangement for Doppler photofragment spectroscopy. The Na_2 molecules are dissociated by an Ar^+ laser while a dye laser serves to analyze the dissociation products.

ments was derived from the Doppler shift $\Delta\nu = \nu v_z/c$ by tuning of a single frequency rhodamine-6G dye laser over the Na $3^2P_{3/2}$-$4^2D_{3/2,5/2}$ transitions at 568.82 nm. The fragments were monitored by the emission of the $4^2P_{1/2,3/2}$-$3^2S_{1/2}$ lines at 330 nm, part of the $4D$-$4P$-$3S$ cascade. This detection scheme is shown on the right-hand side of Fig. 2, together with the schematic representation of the dissociation of a quasibound level by tunneling through the potential barrier of the $B\ ^1\Pi_u$ state. The kinetic energy of the resulting fragments is given by the energy W of the quasibound level referred to the dissociation limit. The quantum numbers of the quasibound state $v' = 31$, $J' = 42$, excited by a single-mode Ar$^+$ laser at 457.9 nm, were determined by double-resonance spectroscopy. The linewidth of this state was found to be ≈ 100 MHz corresponding to a lifetime of 1.6 ns.

Doppler spectra due to photodissociation with the 457.9-nm single-mode laser are shown in Fig. 3(a). Traces B and C are Doppler spectra obtained for parallel and perpendicular laser polarizations relative to the direction of observation. As has been shown previously,[11] the angular distribution in the center-of-mass system can always be represented by $f(\theta) = (\frac{1}{4}\pi)[1 + \beta P_2(\cos\theta)]$, where θ is the angle between the electric vector $\mathbf{E}_L$ of the polarized light and the fragment-recoil direction. The anisotropy parameter β depends on the type of the transition (Σ-Σ or Σ-Π) and varies between $+2$ and -1 corresponding to the limiting cases of recoil parallel and perpendicular to the direction of the transition moment of the parent molecule resulting in distributions $f(\theta) \sim \cos^2\theta$ and $f(\theta) \sim \sin^2\theta$, respectively. Trace A in Fig. 3(a) shows the unshifted excitation spectrum of the monitored transitions $3^2P_{3/2}$-$4^2D_{3/2,5/2}$. Since the two fine-structure components are only 1.02 GHz apart, spectra B and C are the sum of two overlapping Doppler spectra. They represent the distribution of the z component of the fragment velocity given by

$$g(v_z) = 1 - \tfrac{1}{2}\beta + \tfrac{3}{2}\beta(v_z/v)^2$$

for $\mathbf{E}_L \parallel z$, and

$$g(v_z) = 1 + \tfrac{1}{4}\beta - \tfrac{3}{4}\beta(v_z/v)^2$$

for $\mathbf{E}_L \perp z$, where v is the fragment velocity. In order to describe the spectra B and C of Fig. 3(a) by these distributions, we have to subtract the contribution of the direct dissociation of Na$_2$ via the B-state continuum also induced by the 457.9-nm single-mode Ar$^+$ laser. This contribution was determined in separate measurements with slightly changed excitation frequencies. For the case of perpendicular polarization $\mathbf{E}_L \perp z$ the result is shown in Fig. 4. The spectrum represents the velocity distribution $g(v_z)$ of atomic fragments arising from the quasibound level $v' = 31$, $J' = 42$, which was excited by a Q transition from $v'' = 8$, $J'' = 42$. It can be described by a distribution calculated with the parameters $v = 465$ m/s (corresponding to $W = 400$ cm^{-1} kinetic energy) and

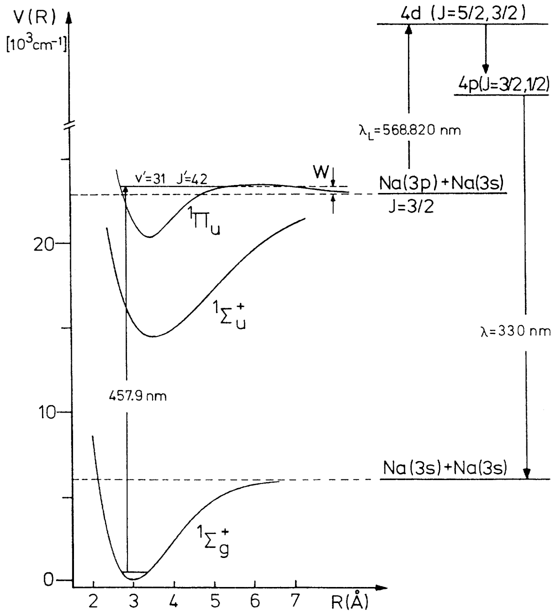

FIG. 2. Schematic representation of the excitation process and the dissociation of a quasibound level of the Na$_2$ $^1\Pi_u$ state. The applied scheme for the detection of the atomic fragments (including observation of the 330-nm line) is shown on the right-hand side.

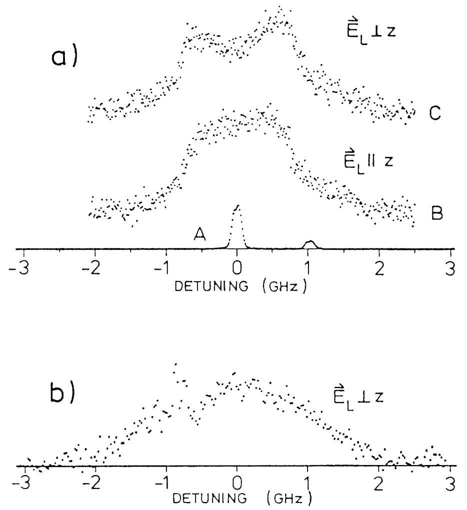

FIG. 3. (a) Doppler spectra of Na* $3^2P_{3/2}$ fragments due to one-photon dissociation of Na$_2$. Trace A shows the fine-structure components of the monitored $3P \rightarrow 4D$ transition. (b) Doppler spectrum of Na* $3^2P_{1/2}$ fragments due to two-photon dissociation of Na$_2$.

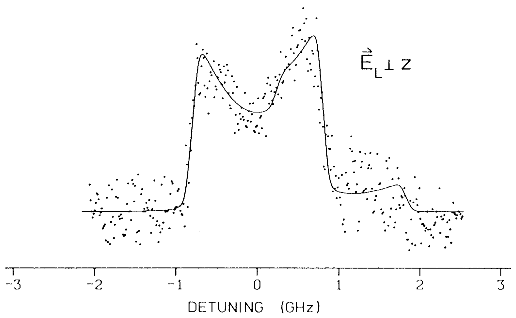

FIG. 4. Doppler spectrum of Na* $3^2P_{3/2}$ fragments resulting from dissociation of the quasibound level $v'=31$, $J'=42$ of the $B\ ^1\Pi_u$ state of Na_2. The solid curve represents a fragment distribution with $W=400\ cm^{-1}$ kinetic energy and $\beta=-1$ anisotropy parameter.

$\beta=-1$ (solid line in Fig. 4). The obtained value $W=400\pm20\ cm^{-1}$ agrees well with the energy of the quasibound level $v'=31$, $J'=42$ above the B-state dissociation limit, $E=397.7\ cm^{-1}$, which was determined by use of the ground-state molecular constants of Kusch and Hessel[12] and the dissociation energy $D_e(X)=6022.6\ cm^{-1}$ of Barrow *et al.*[13]

The value $\beta=-1$ of the anisotropy parameter is surprisingly large in view of the quasibound-state lifetime $\tau=1.6$ ns. Under these conditions of "slow predissociation" the anisotropy is in general strongly reduced since the initial orientation is substantially altered by the rotation.[14] However, for the particular case of a perpendicular $Q(\Delta J=0)$ transition, where the transition moment $\boldsymbol{\mu}$ is parallel to the angular momentum $\mathbf{J}$[15] and perpendicular to the internuclear axis, the electric vector $\mathbf{E}_L$ of the polarized light is parallel to $\mathbf{J}$. The rotation, therefore, cannot change an angular distribution having rotational symmetry around the $\mathbf{E}_L$ axis, thus preserving the initial anisotropy $\beta=-1$ of our excitation process.

The influence of aligned parent molecules in the Na_2 beam[16] on the determined β parameter is negligible under our experimental conditions (800-K oven temperature and 0.2-mm nozzle diameter).

Direct dissociation by excitation from a manifold of $X\ ^1\Sigma_g^+$ ground state levels to the continuum of the $B\ ^1\Pi_u$ state was also observed. With all applied Ar^+ laser lines only Na* $3^2P_{3/2}$ fragments with continuous energy distributions could be observed. The energy and angular distributions were found to depend on the wavelength (457.9, 454.5, 488.0, or 476.5 nm) of the exciting laser line. Calculated Franck-Condon factors for bound-continuum transitions,[17] including the correct B-state potential barrier region,[18] indicate that excitation of the B-state continuum can only be performed from levels $v''\geqslant10$ of the ground state. The energy of the 457.9-nm line is just sufficient to reach the continuum out of $v''=10$ for low J. For the less energetic Ar^+ laser lines much higher v'' levels are involved. Direct dissociation with these lines, even in a molecular beam, is still possible because of the large number of weakly populated v'', J'' levels. The vibrational and rotational temperatures in our experiment are $T_{vib}=400$ K and $T_{rot}=200$ K, respectively.

Another interesting result of our molecular-beam experiments is that we observe Na* $3^2P_{1/2}$ fragments neither by direct dissociation via the $B\ ^1\Pi_u$ continuum nor by tunneling through the B-state potential barrier with any of the Ar^+ laser lines 454.5, 457.9, 476.5, or 488.0 nm. This is in contrast to the findings of Rothe, Krause, and Düren[3] and Janson and Papernov[19] who have reported Na_2 photodissociation via the B state with the 488.0- and 476.5-nm lines leading to the emission of both the Na D_2 ($^2P_{3/2}$-$^2S_{1/2}$) and D_1 ($^2P_{1/2}$-$^2S_{1/2}$) lines. However, in an additional experiment with higher oven temperature ($pd\approx0.7$ Torr cm), we did observe Na* $3^2P_{1/2}$ fragments after excitation with the 488.0- and the 476.5-nm lines. The $^2P_{1/2}$ fragments were detected by inducing the $3^2P_{1/2}$-$4^2D_{3/2}$ transition at 568.26 nm and subsequently recording the $4P$-$3S$ fluorescence at 330 nm. The Doppler spectrum of Na* $3^2P_{1/2}$ fragments obtained with the 488.0-nm line and perpendicular laser polarization, shown in Fig. 3(b), clearly demonstrates the different angular distribution and higher energy of the $^2P_{1/2}$ fragments. Moreover, the much weaker $^2P_{1/2}$ signal increases with higher pd values relative to the decreasing $^2P_{3/2}$ signal. If a wavelength of 457.9 nm is used for the photodissociation under the same experimental conditions only Na $3P$ $J=\frac{3}{2}$ atoms, but no Na $3P$ $J=\frac{1}{2}$ atoms, are observed. This excludes an effect by fine-structure changing collisions. The analysis of the 488.0-nm fragmentation process leads to the conclusion that the Na* $3^2P_{1/2}$ fragments result from a two-photon excitation of a high-lying Na_2^* state dissociating into two Na* $3P$ atoms.

The anisotropy of the two-photon process is reflected in the angular distribution $f(\theta)$ of the photofragments[20]

$$f(\theta)=(\tfrac{1}{4}\pi)[1+\beta_DP_2(\cos\theta)+\gamma_DP_4(\cos\theta)].$$

Since the Franck-Condon factors for the $Na_2X\ ^1\Sigma_g^+$-$A\ ^1\Sigma_u^+$ transitions with 488.0 nm are vanishingly small ($<10^{-8}$), we need only consider $X\ ^1\Sigma_g^+$-$B\ ^1\Pi_u$ transitions. From symmetry considerations it follows that only $^1\Sigma_g^+$, $^1\Sigma_g^-$, $^1\Pi_g$, and $^1\Delta_g$ states can be reached by two-photon excitations out of a $^1\Sigma_g^+$ state. From the different possible transitions Σ-Π-Σ, Σ-Π-Π, and Σ-Π-Δ we can exclude the Σ-Π-Σ and Σ-Π-Δ processes, since in these cases the two perpendicular transitions result in an angular distribution $f(\theta)\sim\sin^4\theta$ (classical limit), which is definitely not observed. With the assumption of a Σ-Π-Π process it was found that the observed Doppler spectrum [Fig. 3(b)] can be described by a distribution with a kinetic energy of $W=1900 \pm 300$ cm^{-1} and parameters $\beta_D=2.37$ and $\gamma_D=0.49$ taken from Ref. 20. However, because of the low statistics of the measurement it was not possible to obtain these parameters from a fit to the observed distribution.

The two-photon excitation with the 488.0-nm line proceeds via the $B\,{}^1\Pi_u$ state, the dominant first transition being $(v''=3,\ J''=43)$-$(v'=6,\ J'=43)$. Since the excitation energy is just 1870 cm^{-1} above the Na* $3P$ + Na* $3P$ dissociation limit, the dissociation into two Na* $3P$ atoms is strongly suggested by the measured photofragment energy of $W=1900$ cm^{-1}. The symmetry of the upper state must be ${}^1\Pi_g$ as is inferred from the observed angular distribution [Fig. 3(b)]. It should be mentioned that Na_2^+ formation has been reported[21] for two-step excitation of Na_2 with the 488.0- and 476.5-nm lines, a process which might be in competition with the dissociation process observed by us.

In summary, our experiments demonstrate that the technique of Doppler spectroscopy is ideally suited for the study of the photofragmentation of neutral diatomic molecules. For Na_2 it has been found that single-photon dissociation with wavelengths between 450 and 490 nm proceeds via the $B\,{}^1\Pi_u$ state and yields Na* $3^2P_{3/2}$ as the only excited fragment state, indicating that there are no (or very weak) nonadiabatic interactions between molecular states converging to the Na* $3^2P_{3/2}$ and Na* $3^2P_{1/2}$ states. The completely different angular distribution, kinetic energy, and temperature dependence of the observed Na* $3^2P_{1/2}$ fragments lead us to the conclusion that they result from the dissociation of a high-lying Na_2^* state excited in a two-photon process. The best agreement with our experimental data is found for a ${}^1\Pi_g$ state dissociating into Na* $3P$ + Na* $3P$ atoms. The reported dissociation of the quasibound level $v'=31$, $J'=42$ of the $B\,{}^1\Pi_u$ state (Fig. 4) represents the first example where for a neutral diatomic molecule all the quantities governing the process are well determined. The quantum numbers v' and J' and the lifetime τ were obtained, and the energy and angular distributions as well as the internal states of the atomic fragments were analyzed.

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