PHYSICAL REVIEW A VOLUME 29, NUMBER 5 MAY 1984

Direct measurement of the potential-barrier height in the $B^1\Pi_u$ state of the sodium dimer

John Keller and John Weiner
Department of Chemistry, University of Maryland, College Park, Maryland 20742
(Received 28 December 1983)

We report a direct measurement of the barrier height of the Na_2 B-state potential curve. The technique is a two-step spectroscopy—optical pumping followed by photodissociation—on a beam of rotationally cold Na_2. Our measured value is $366 \pm 8\ cm^{-1}$ above the energy of the separated atoms (Na $3s\,^2S_{1/2}$ + Na $3p\,^2P_{3/2}$). Based on observed structure due to tunneling, we propose a form of the potential valid near the top of the barrier.

I. INTRODUCTION

Since the work of King and Van Vleck,[1] it has been well known that the potential curve of the $B^1\Pi_u$ state of Na_2 exhibits a maximum at intermediate internuclear separation. However, up to now the height of this energy barrier has not been directly measured but has been estimated by extrapolation of the potential curve determined at lower energy.[2] This extrapolated value and that determined from the more recent theoretical calculations are not in accord.[3] Because the Na_2 B state may be useful in testing theories recently developed to describe nonadiabatic photodissociation of molecules to fragments with nonzero angular momentum,[4] we undertook to accurately describe the potential curve near the top of the barrier.

Two major difficulties have prevented accurate measurement of the B-state potential barrier in the past. First, direct $B \leftarrow X$ transitions from low vibrational levels in the X-state to vibrational levels near the B-state dissociation limit lie outside the Franck-Condon region and are effectively forbidden. Secondly, attempts to measure the height of the barrier by measuring a cutoff in continuum absorption are hampered by the broad distribution of thermally populated initial-state rotation-vibration levels.[5]

In this Rapid Communication we report the measurement of the B-state potential maximum in which we use an experimental method designed to circumvent both of these problems. First, we produce a beam of sodium dimers cooled to the lower rotation-vibration states through free-jet expansion of the metal vapor. Then, as illustrated in Fig. 1, we populate high vibrational levels of the ground electronic state through optical pumping.

$$X\,^1\Sigma_g^+(v=0,J)+\hbar\omega_1 \rightarrow B^1\Pi_u(v',J') \ , \tag{1}$$

$$B\,^1\Pi_u(v',J') \rightarrow X\,^1\Sigma_g^+(v'',J'')+\hbar\omega \ . \tag{2}$$

After sufficient time is allowed to complete the fluorescence, a second, scanning laser dissociates the B state from the optically pumped $X\,^1\Sigma_g^+(v'',J'')$. As the second laser is tuned to higher energy, molecules in successively lower vibrational states photodissociate:

$$X\,^1\Sigma_g(v'',J'')+\hbar\omega_2 \rightarrow \mathrm{Na}(3s\,^2S_{1/2})+\mathrm{Na}^*(3p\,^2P_{3/2}) \ . \tag{3}$$

We monitor dissociation by observing emission from the excited atom product. If we ignore tunneling and variations of photodissociation cross sections we expect a step function in the observed atomic fluorescence intensity as a function of the second laser wavelength. The positions of the steps give the energy required to photodissociate the molecule from a given vibrational level and hence the B-state barrier height.

Optical pumping of the dimer jet permits us to obtain a narrow distribution in the rotational manifold of the final X-state vibrational levels which, through judicious choice of initial-pump transition, have large Franck-Condon factors for transitions near the B-state dissociation continuum. Thus the two major experimental problems, thermal

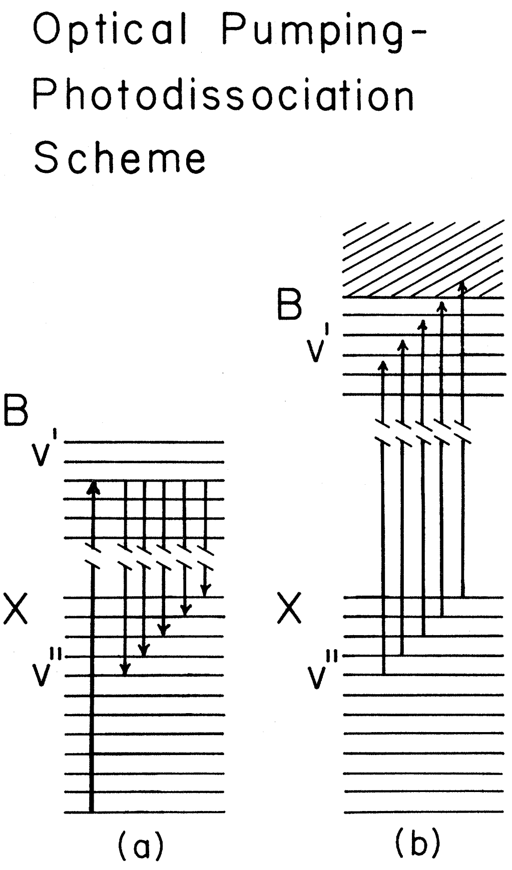

FIG. 1. (a) High vibrational levels of the X state are optically pumped through a low-lying level of the B state. (b) Then a second laser scans near the B-state photodissociation continuum.

broadening of continuum-absorption cutoff frequencies and small Franck-Condon factors, are overcome.

II. EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere.[6] Briefly, an intense beam of sodium dimers cooled to the lower rotation-vibration states is formed through free jet expansion of the metal vapor. We determined, through laser-induced fluorescence, that the dimer rotational temperature is less than 60 K while the vibrational temperature is less than 150 K. The beam is located in a high vacuum chamber and surrounded by water– and liquid-nitrogen–cooled heat shields to condense excess sodium vapor. The two laser beams are aligned colinearly, counter propagating to each other, and perpendicular to the molecular beam. Imaging optics, a 0.25-m monochromator tuned to either sodium D line, and a sensitive photomultiplier tube detect the atomic fluorescence signal. The optical system resolves the D_1,D_2 Na resonance lines. Many laser shots are accumulated with a boxcar integrator gated on the second laser pulse ($\hbar\omega_2$).

We use a flashlamp pumped dye laser with a 3-cm^{-1} bandwidth as the initial pump and a Nd^{3+}:YAG (Nd-doped yttrium aluminum garnet) pumped dye laser with a 0.1-cm^{-1} bandwidth as the dissociating laser. In order to obtain greater rotational selectivity it would be preferable to use a narrow bandwidth laser as an initial pump but we are prevented from interchanging the roles of the lasers by the restricted spectral range of the flashlamp pumped dye laser. In the experiment we tune the pump laser so that it is centered on the band origin. From the rotational constants we can estimate the maximum number of rotational fine-structure lines that the laser bandwidth overlaps, and therefore the maximum number of rotational levels populated. These levels range from $J=0$ to $J=10$ which represents, in terms of energy, a 15-cm^{-1} width.

III. RESULTS AND DISCUSSION

Three spectra corresponding to different initial pump $B \leftarrow X$ transitions are displayed in Fig. 2. We observe thresholds for onset of D_2 atomic fluorescence spectra corresponding to photon absorption from vibrational levels in the X state to continuum states above the potential barrier. In addition, we observe that the fluorescence onsets are preceeded by structure which we attribute to tunneling through the potential barrier. Only tunneling from the last quasibound level supported by the B-state potential is observed. We observe no fluorescence from the $^2P_{1/2}$ level.

The height of the B-state potential barrier x is given by

$$x = \hbar\omega + G(v'') - D_e - T_D \ , \tag{4}$$

where $G(v'')$ is the energy of the ground-state vibrational level,[2] D_e is the X-state dissociation energy,[7,8] T_D is the energy of the $(3p)^2P_{3/2}$ atomic level, and $\hbar\omega$ is the energy corresponding to the onset of photodissociation from a level v''. Compared with the terms in (4) the rotational contribution to the barrier height is negligible.

While the Franck-Condon factors restrict the optically pumped vibrational levels to a narrow distribution, the precision of measured vibrational spacings is not sufficient to permit an absolute labeling of the vibrational level from which photodissociation takes place. However, Chawla, Vedder, and Field,[9] have also observed the last quasibound level through modulated gain spectroscopy. Their results fix precisely the assignment of v''. We take the dissociation limit as the dropoff of the plateau formed by the cutoff of continuum absorption. This assures that we include the $J''=0$ level in dissociation. In Fig. 3 the dropoff, marked by arrow d, is 8 cm^{-1} to the blue of the onset. This is the value that we take as the estimate to our experimental error, although the position of the dropoff is reproducible to within a 5-cm^{-1} standard deviation. Our measured value for the barrier maximum is 366 ± 8 cm^{-1}. The value extrapolated from spectroscopic data given by Kusch and Hessel[2] is 437 cm^{-1} where we have corrected for a more accurate X-state dissociation energy.[7,8] The *ab initio* calculation by Konowalow and Rosenkrantz[10] predicts a barrier height of 520 cm^{-1}. A composite long-range potential curve constructed by Zemke and Stwalley,[11] which incorporates the exchange energy calculations of Konowalow and Rosenkrantz and a C_3 coefficient based on the atomic resonance line strength,[12] gives a barrier height of 401 cm^{-1}.

A preliminary estimate of the shape near the top of the potential barrier can be obtained from the tunneling struc-

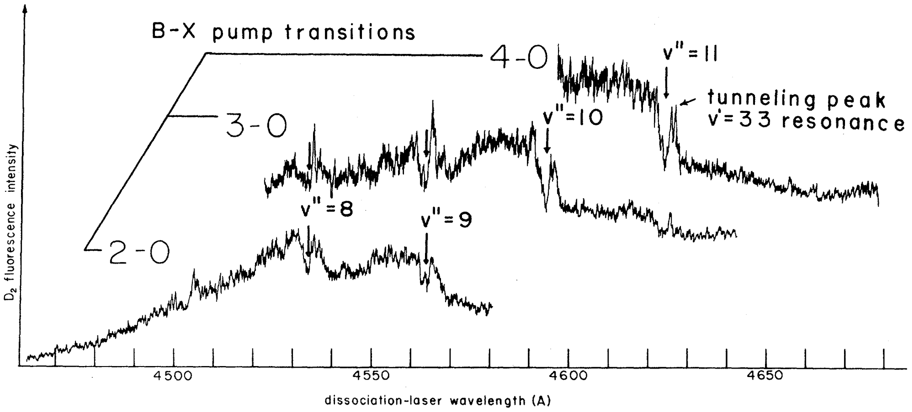

FIG. 2. Sodium atom fluorescence intensity spectra for three initial-laser B-X pump transitions. Arrows point to onset of photodissociation from X-state vibrational levels starting from $v''=11$ at the far right.

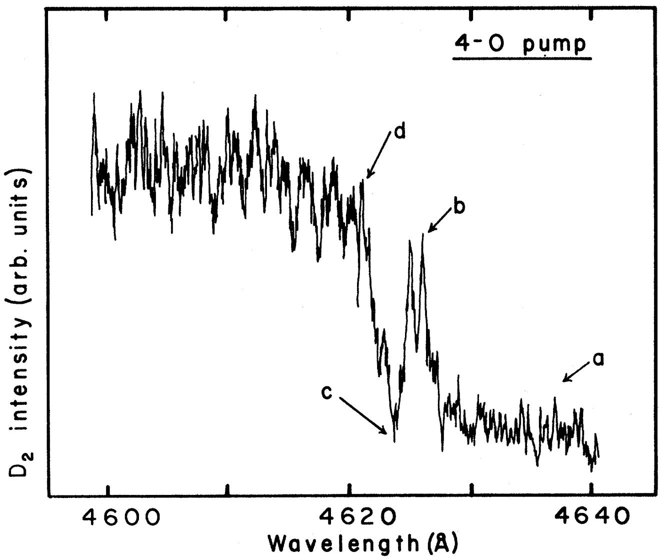

FIG. 3. Dissociation spectra arising from the B-X (4,0) pump transition. Regions of intense D_2 fluorescence are due to dissociation from the $v''=11$ level. The base line at a consists of photodissociation from higher, lightly populated vibrational levels. The peak at b is due to tunneling from the $v'=33$ quasibound level. The apparent structure superimposed on this peak is spurious and is due to shot-to-shot laser intensity fluctuation. Direct photodissociation above the barrier begins in the region between c, where the highest populated rotational levels dissociate, and d, where the lowest populated ($J=0$) level dissociates.

ture. Tunneling will not be observed if the rate of molecular fluorescence greatly exceeds the tunneling rate. We have fitted, through a nonlinear, least-squares algorithm, a potential of the form

$$V=C_3/R^3+C_6/R^6+A\exp(-aR) \tag{5}$$

to the last two points of the RKR curve published by Kusch and Hessel,[2] the barrier maximum reported here, and the same C_3 coefficient used by Zemke and Stwalley. By varying the potential curvature of the maximum and solving numerically the Schrödinger equation for the radial motion of the nuclei, we find a potential for which the position of the last quasibound level reproduces the experimental data. The parameters are

$$C_3=2.0058\times10^5\ \text{cm}^{-1}\,\text{Å}^3\ ,$$

$$C_6=-7.5207\times10^6\ \text{cm}^{-1}\,\text{Å}^6\ ,$$

$$A=-5.5883\times10^5\ \text{cm}^{-1}\ ,$$

$$a=1.169\,48\ \text{Å}^{-1}\ .$$

To solve the Schrödinger equation we used a computer code written by Julienne[13] which incorporates the fully quantum-mechanical method due to Gordon.[14] The code presents as output the phase η_l of the wave function. The phase shift near resonance can be related to the resonance width (and hence the lifetime of the quasibound level) by the celebrated Breit-Wigner formula[15,16]

$$\eta_l(E)=\eta_l^0(E)-\tan^{-1}\left[\frac{\Gamma_l}{2(E-E_l)}\right]\ , \tag{6}$$

where $\eta_l^0(E)$ is a slowly varying background, E is the total energy of the nuclei, and Γ_l is the width associated with the resonance at E_l. We calculate a resonance width of 0.15 cm^{-1}, which, in accord with our results, implies a tunneling rate greater than the fluorescence rate.

The choice for the potential expression in Eq. (5) is based on the expected long-range form derived from perturbation theory. However, the parameter values are not compatible with the values for the long-range potential calculated by Konowalow and Rosenkrantz.[10] Thus our potential is applicable only near the barrier maximum and must be modified at longer range to approach the long-range perturbative potential.

---

[1] G. W. King and J. H. Van Vleck, Phys. Rev. 55, 1165 (1939).
[2] P. Kusch and M. M. Hessel, J. Chem. Phys. 68, 2591 (1978).
[3] D. D. Konowalow, M. E. Rosenkrantz, and Mark L. Olsen, J. Chem. Phys. 72, 2612 (1980).
[4] S. J. Singer, K. F. Freed, and Y. B. Band, J. Chem. Phys. 79, 6060 (1983), and references cited therein.
[5] R. H. Callender, J. I. Gersten, R. W. Leigh, and J. L. Yang, Phys. Rev. A 14, 1672 (1976).
[6] J. Boulmer and J. Weiner, Phys. Rev. A 27, 2817 (1983); J. Keller and J. Weiner, Phys. Rev. A (in press).
[7] H. Kato, T. Matsui, and C. Noda, J. Chem. Phys. 76, 5678 (1982).
[8] K. K. Verma, J. T. Bahns, A. R. Rajaei-Rizi, W. C. Stwalley, and W. T. Zemke, J. Chem. Phys. 78, 3599 (1983).
[9] D. Chawla, J. Vedder, and R. W. Field (unpublished).
[10] D. D. Konowalow and M. E. Rosenkrantz, J. Phys. Chem. 86, 1099 (1982).
[11] W. T. Zemke and W. C. Stwalley (unpublished).
[12] W. L. Wiese, M. W. Smith, and M. M. Miles, *Atomic Transition Probabilities*, U.S. National Bureau of Standards, National Standards Reference Data Series—22 (U.S. GPO, Washington, D.C., 1969), Vol. 2.
[13] P. Julienne (private communication).
[14] R. G. Gordon, J. Chem. Phys. 51, 14 (1969).
[15] F. H. Mies and P. S. Julienne, J. Chem. Phys. 77, 6162 (1982).
[16] S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1969).