

LETTER

Predissociation of the $b^3\Pi_g$ ($v=9$) State of He₂ ExcimerChuan-liang Li^a, Lun-hua Deng^a, Jun-li Zhang^a, Xiao-hua Yang^{a,b}, Yang-qin Chen^{a*}

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The predissociation of the $v=9$ level in the $b^3\Pi_g$ state by the $c^3\Sigma_g^+$ state of helium excimer (He₂) was studied based on the newly observed (9, 3) band in the $b^3\Pi_g$ - $a^3\Sigma_u^+$ system in the region of 12065–12445 cm⁻¹ employing optical heterodyne-concentration modulation absorption spectroscopy. With the help of the previous potential energy curves and molecular constants of He₂, the corresponding predissociation mechanism for the $b^3\Pi_g$ ($v=9$) state was analyzed. An RKR potential energy curve of $b^3\Pi_g$ and an *ab initio* potential curve of $c^3\Sigma_g^+$ were used to calculate the predissociation linewidths that show basic agreement with observations, which can quantitatively explain the experiments.

Key words: Helium excimer, Predissociation, Concentration modulation absorption spectroscopy

Helium excimer (He₂) is the simplest Rydberg molecule. It plays an important role in many aspects, such as the chemical bond formation, the mechanism of low-temperature discharge plasma, and the spectroscopic study of superfluid helium nano-droplets [1–7]. Its electronic structures have been the focus of the spectroscopy and more than 60 electronic states have been identified, of which the low-lying triplet states ($a^3\Sigma_u^+$, $b^3\Pi_g$, and $c^3\Sigma_g^+$) are the most extensive studied ones [8–12].

The previous studies of predissociation for He₂ mainly focused on the $c^3\Sigma_g^+$ state, because it is a quasi-bound state separated by a potential barrier which was first discovered by Jordan *et al.* using the crossed beam scattering experiments [13]. Subsequently, Bjerre *et al.* studied the predissociation of the $c^3\Sigma_g^+$ state owing to the tunneling effect based on the fast beam photodissociation absorption spectroscopy and predicted the predissociation of $b^3\Pi_g$ due to the coupling interaction between the $b^3\Pi_g$ and $c^3\Sigma_g^+$ states [14, 15]. Meanwhile, Yarkony made a nonadiabatic coupling calculation between these two states, which indicates the strong coupling near the barrier of the $c^3\Sigma_g^+$ state [16]. Yet, the predissociation of the $b^3\Pi_g$ state hasn't been studied in detail. The possible reason is that most of the investigations are based on the emission spectroscopy, and the spectra are too weak to be observed since the lifetimes of these predissociating levels are typically as short as a couple of pico-seconds.

However, the predissociation of $b^3\Pi_g$ state can be

studied via absorption spectroscopy since the radiative lifetime of the lower $a^3\Sigma_u^+$ metastable state is as long as up to 15 s [17]. In the present work, we study a new observation of the predissociating band of the $b^3\Pi_g$ - $a^3\Sigma_u^+$ system employing the optical heterodyne-concentration modulation absorption spectroscopy (OH-CMS). The linewidths varying with rotational quantum number N due to the predissociation of the $b^3\Pi_g$ state by the $c^3\Sigma_g^+$ state was analyzed. A computation was carried out to quantitatively explain the N -dependent linewidth.

The detailed experimental setup for OH-CMS is similar to the optical heterodyne-velocity modulation spectroscopy which has been described previously [18]. Briefly, a tunable Ti:sapphire laser (Coherent Ring 899-29) was used as the excitation source. The laser beam was first phase-modulated by an electro-optical modulator at a radio frequency of 500 MHz, then passed through an audio frequency (23 kHz) glow discharge absorption cell and was detected by a PIN detector (ET-2030A). The output of the detector was first demodulated by a double balance mixer at 500 MHz, then further demodulated by a lock-in amplifier at 2×23 kHz (concentration demodulation) with a time constant of 100 ms and finally processed by a computer. He₂ was produced in the discharge absorption cell by glow discharging the flowing helium gas (99.995% purity, 400 Pa) at a discharge current of 400 mA (peak-to-peak). The wavelength of the laser beam was determined by an attached wavemeter with a resolution of 0.001 cm⁻¹ and simultaneously calibrated to the iodine spectrum [19] with an accuracy of 0.006 cm⁻¹.

Nine broadened spectral lines degrading to red were observed in the region of 12065–12445 cm⁻¹, in addition to the $c^3\Sigma_g^+$ - $a^3\Sigma_u^+$ transitions in our previous work

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TABLE I Assignment for the (9, 3) band in the $b^3\Pi_g-a^3\Sigma_u^+$ system.

N	Branch	Wavenumber ^a /cm ⁻¹
2	P(3)	12366.29 (0.29)
4	P(5)	12317.29 (-0.39)
6	P(7)	12258.16 (0.07)
8	P(9)	12185.94 (0.11)
10	P(11)	12096.51 (-0.04)
8	R(7)	12395.89 (-0.14)
12	R(11)	12301.11 (-0.09)
16	R(15)	12161.74 (0.04)
18	R(17)	12076.85 (-0.73)

^a Values in parentheses are ($v_{\text{obs}}-v_{\text{cal}}$).

[20]. The linewidths (FWHM) are in the range from 0.1 cm⁻¹ to 1.5 cm⁻¹, whereas the Doppler linewidth is merely about 0.07 cm⁻¹ derived from the normal spectrum in the $c^3\Sigma_g^+-a^3\Sigma_u^+$ system [20]. The signal-to-noise ratio of the spectrum is lower because of the predissociation broadening, the accuracy of the line position determination of the predissociating spectra is about 0.05 cm⁻¹.

The measured lines, listed in Table I, were assigned to the (9, 3) band in the $b^3\Pi_g-a^3\Sigma_u^+$ system of He₂. The nucleus spin of ⁴He atom is zero, thus the even N levels of the $a^3\Sigma_u^+$ state, the odd N levels of the $c^3\Sigma_g^+$ state and the negative components of the rotational levels of the $b^3\Pi_g$ state disappear and Hund's case (b) is a good approximation. Because the spin-triplet splittings of the three involved states are too small to be resolved, these states can be simplified as the singlet in analysis.

Normally, the higher vibrational transitions in the $b^3\Pi_g-a^3\Sigma_u^+$ system are difficult to be observed due to very low Franck-Condon factor which is about four orders lower than that of the $c^3\Sigma_g^+-a^3\Sigma_u^+$ transitions, calculated by Level 8.0 program [21]. The observation of the (9, 3) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system was responsible for the $b^3\Pi_g$ state borrowing the fractional transition intensity from the $c^3\Sigma_g^+$ ($v=6$) state through the coupling interaction between the b and c states. Based on the extrapolated calculation, the $v=9$ level in the $b^3\Pi_g$ state lies near the intersection of the $b^3\Pi_g$ and $c^3\Sigma_g^+$ states, which causes the spectral broadening to reduce with the increase of N .

Herzberg pointed that the Q branch will not be predissociated when the bound Π electronic state is overlapped by the dissociating Σ state [22]. According to the predissociation selection rule: $\Delta N=0$, $+\leftrightarrow+$, $-\leftrightarrow-$, $a\leftrightarrow a$, $s\leftrightarrow s$, the odd rotational levels in the $b^3\Pi_g$ state are totally immune to the predissociation by the $c^3\Sigma_g^+$ state. It results in the complete missing of the Q branch in our observation because of no coupling interaction between the odd rotational levels in the $b^3\Pi_g$ state with the $c^3\Sigma_g^+$ state. This is consistent with our

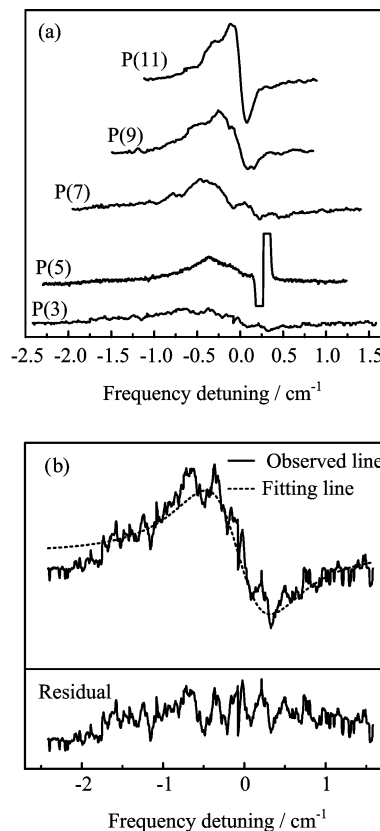


FIG. 1 (a) Observed spectrum of the P branch of the (9, 3) band in the $b^3\Pi_g-a^3\Sigma_u^+$ system. The line of P(5) is overlapped by P(3) of (1, 0) band in the $c^3\Sigma_g^+-a^3\Sigma_u^+$ system, in which the predissociation linewidth broadening is clearly shown. (b) The observed and fitting lines of P(3) and its fitting residual.

experimental results.

As a matter of fact, predissociation is one type of perturbations that induce level shifts [23–25]. Because the information of dissociating $v=6$ ($c^3\Sigma_g^+$) is unavailable, the deperturbation analysis is hard to be carried out. Herein, a nonlinear least-squares fitting without consideration of perturbation is performed to roughly deduce the molecular parameters, which gives band origin $T=12416(2)$ cm⁻¹, rotational constants and their high order correction terms for $b^3\Pi_g$ ($v=9$) and $a^3\Sigma_u^+$ ($v=3$) states: $B'=5.163(67)$ cm⁻¹, $D'=0.0067(7)$ cm⁻¹, $H'=0.000019(2)$ cm⁻¹, $B''=6.845(80)$ cm⁻¹, $D''=0.0072(8)$ cm⁻¹, and $H''=0.000024(3)$ cm⁻¹. Although the overall fitting error (0.4 cm⁻¹) is bigger than the uncertainty of spectral position (0.05 cm⁻¹) and the reliability of high order correction parameters are low, the main molecular constants which are not appreciably affected by the predissociation level shifts are in good agreement with the extrapolated.

Figure 1 shows the dependence of linewidths on the N in the observed P branch of the (9, 3) band of the $b^3\Pi_g-a^3\Sigma_u^+$ system. The predissociation lineshape is charac-

terized as the first derivative of the convolution of the Fano and the Gaussian profiles, due to the optical phase modulation [26, 27]. The asymmetry of the profile arises from the direct excitation of these levels to the continuum state [28]. The predissociation linewidths were obtained by fitting the observed lines to the first derivative of the convolution with the Gaussian component fixed at 0.07 cm^{-1} .

The predissociation linewidth (proportional to the predissociation rate) depends on the magnitude of the coupling matrix between the discrete and the dissociation states. The magnitude of the overlapping integral of the coupling eigenfunctions becomes large for the levels near the intersection of potential energy curves, and decreases away from the intersection [22, 29–31]. Since the $v=9$ level in the $b^3\Pi_g$ state locates above the intersection of the $b^3\Pi_g$ and $c^3\Sigma_g^+$ states, the predissociation rates of rotational levels for $v=9$ decrease with the increasing N and that can be seen in Fig.2. Furthermore, the predissociation linewidths of the P and the R branches from the same upper levels of the $b^3\Pi_g$ state are identical.

Fermi-Golden rule indicates that the predissociation linewidth is determined by a radical matrix element containing a coupling function between the coupled electronic states and the radial vibrational wavefunctions of the isoenergetic bound initial and continuum final states [27]. The predissociation of the $b^3\Pi_g$ state is caused by the L-coupling between the $b^3\Pi_g$ and the $c^3\Sigma_g^+$ state. Near the barrier region, the $c^3\Sigma_g^+$ state is unstable and will dissociate to two atoms of He (1^1S) and He (2^3S). The calculation of the predissociation linewidth follows after the recent investigation of the $2^3\Sigma$ state of Li₂ [32]. The L-coupling matrix element is

$$\begin{aligned} H_{v,J;E,J} &= \langle \psi_{v,J} | -\frac{1}{2\mu R^2} J^\pm L^\mp | \psi_{E,J} \rangle \\ &\cong -\langle v | \frac{1}{2\mu R^2} | E \rangle \langle {}^3\Pi | \sum_i l_i^\mp | {}^3\Sigma \rangle \cdot \\ &\quad \sqrt{J(J+1)} \end{aligned} \quad (1)$$

here, $\langle \psi_{v,J} |$, $\langle v |$, and $\langle {}^3\Pi |$ are the total wavefunction, vibrational wavefunction, and electronic wavefunction of the stable state. And the $| \psi_{E,J} \rangle$, $| E \rangle$, and $| {}^3\Sigma \rangle$ are the total wavefunction, vibrational wavefunction, and electronic wavefunction of the unstable state, respectively. The term, $\langle v | 1/2\mu R^2 | E \rangle$, can be calculated using LeRoy's BCONT program [33]. The other term is expressed as

$$\langle {}^3\Pi | \sum_i l_i^\mp | {}^3\Sigma \rangle \cong \sqrt{l(l+1)} = \sqrt{2} \quad (2)$$

Linewidth Γ is

$$\Gamma = \frac{1}{\hbar c} |H_{v,J;E,J}|^2 \quad (3)$$

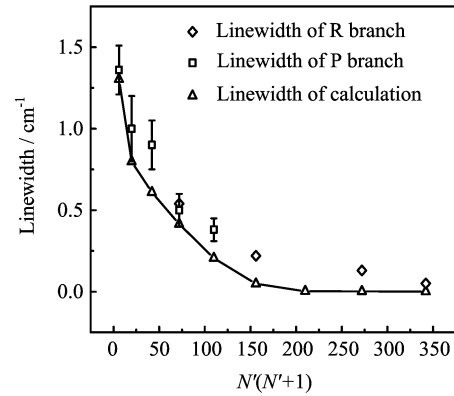


FIG. 2 Variation of linewidths versus $N'(N'+1)$ for the (9, 3) band of the $b^3\Pi_g$ - $a^3\Sigma_u^+$ system. N' is the rotational quantum of the $b^3\Pi_g$ state.

The $c^3\Sigma_g^+$ state potential curve is not a complete repulsive state and is represented as the piecewise functions [13]. Since the predissociation interaction between the $b^3\Pi_g$ ($v=9$) state and the $c^3\Sigma_g^+$ state occurs at the top of potential barrier of the $c^3\Sigma_g^+$ state, the main contribution of the $c^3\Sigma_g^+$ state to the predissociation comes from its right-sided repulsive part of *ab initio* potential curve, which is set as the input of the BCONT program.

As plotted in Fig.2, the calculated linewidths agree with the experimental ones, especially at low rotational levels. With the increase of rotational quantum number, the calculated linewidths become smaller than the observed one. The possible reason may be the inaccuracy of potential energy curves. The RKR potential curve of $b^3\Pi_g$ is extrapolated based on its available constants of $v=0$ and 1, and the precision of *ab initio* potential curve would be lowered in dissociation region, so the discrepancy between the calculated and the experimental ones could be caused at high rotational levels.

In summary, we report the first observation of the predissociation (9, 3) band in the $b^3\Pi_g$ - $a^3\Sigma_u^+$ system of He₂ in the region of 12065–12445 cm^{-1} employing OH-CMS. The predissociation linewidth is calculated using LeRoy's BCONT program based on the predissociation arising from the L-coupling between the $b^3\Pi_g$ and the $c^3\Sigma_g^+$ states, and the calculation agrees basically with the experiment.

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