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# Resonant two-photon ionization and laser induced fluorescence spectroscopy of jet-cooled adenine

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Electronic spectra of the jet-cooled DNA base adenine were obtained by the resonant two-photon ionization (R2PI) and the laser induced fluorescence (LIF) techniques. The 0–0 band to the lowest electronically excited state was found to be located at  $35\,503\text{ cm}^{-1}$ . Well-resolved vibronic structures were observed up to  $1100\text{ cm}^{-1}$  above the 0–0 level, followed by a slow rise of broad structureless absorption. The lowest electronic state was proposed to be of  $n\pi^*$  character, which lies  $\sim 600\text{ cm}^{-1}$  below the onset of the  $\pi\pi^*$  state. The broad absorption was attributed to the extensive vibronic mixing between the  $n\pi^*$  state and the high-lying  $\pi\pi^*$  state. © 2000 American Institute of Physics. [S0021-9606(00)00246-4]

## I. INTRODUCTION

The four bases of DNA are known to strongly absorb ultraviolet (UV) light and act as chromophores of DNA. Despite their very short lifetimes at electronically excited singlet states (of the order of picoseconds in condensed phase), these bases undergo various types of photoinduced reactions that lead to mutagenic and carcinogenic consequences.<sup>1–6</sup> Therefore, information on the electronic structure of DNA bases is of crucial importance in understanding the photo-physics and photochemistry of these bases as well as the DNA as a whole.

Extensive efforts have been made so far to elucidate the electronic structure of DNA bases. UV absorption spectra were obtained in the gas phase,<sup>7</sup> in solution,<sup>8,9</sup> and in a single crystal.<sup>10</sup> Fluorescence was observed in aqueous solution, and its quantum yield was measured.<sup>11</sup> The locations and transition moments of the  $n\pi^*$  and  $\pi\pi^*$  excited states were estimated by theoretical calculations.<sup>12–18</sup> Although most conventional studies in the condensed phase have found broad, structureless spectra, some recent investigations revealed better-resolved spectral features. For example, infrared spectra were obtained in a low-temperature inert gas matrix,<sup>19</sup> in a static gas cell,<sup>20</sup> and in a supersonic jet.<sup>21</sup> Microwave spectra of DNA bases were also obtained in the gas phase.<sup>22</sup> Electronic spectra of thymine and uracil in a supersonic jet were first reported by Fujii *et al.*,<sup>23</sup> and more thoroughly investigated and clarified by Brady *et al.*<sup>24</sup> Recently, Nir *et al.* carried out resonant two-photon ionization (R2PI) spectroscopy on jet-cooled guanine, which revealed a well-resolved vibronic spectrum.<sup>25</sup>

In this study, we report the R2PI and laser induced fluorescence (LIF) spectroscopy of the DNA base adenine in a supersonic jet. In contrast to the broad, structureless spectra

of thymine and uracil even in a jet-cooled condition,<sup>24</sup> a well-resolved vibronic structure was observed in the electronic spectrum of adenine, as in the case of guanine.<sup>25</sup> It has been suggested by theory that the  $n\pi^*$  and  $\pi\pi^*$  states lie close to each other in adenine,<sup>13–17</sup> while the identity of the lowest electronically excited state has been the subject of a long-standing debate.<sup>13,17</sup> Our findings strongly suggest that this state is of  $n\pi^*$  character, and that there exists extensive vibronic mixing between the  $n\pi^*$  and  $\pi\pi^*$  states.

## II. EXPERIMENT

The details of our experimental setup have been published elsewhere.<sup>26</sup> Briefly, the apparatus used in the R2PI study consists of a set of differentially pumped molecular beam chambers and a reflectron time-of-flight mass spectrometer (TOF-MS). The adenine powder sample was heated to 220–240 °C in a metal oven, and the beam was expanded through a 0.5 mm hole of a high-temperature pulsed nozzle with a helium carrier gas at a backing pressure of 1–2 atm. No indication of thermal decomposition was observed at these temperatures. The expanding gas was sampled by a skimmer and then ionized by the frequency-doubled output of a Nd:YAG-pumped dye laser using one- or two-color R2PI. The laser fluence was typically  $3 \times 10^6\text{ W/cm}^2$  in one-color R2PI. The ionized molecules were accelerated to 3.0 keV in a double electrostatic field and directed toward a reflectron through a 1.1 m field-free drift tube. The reflected ions travel another 50 cm in the second field-free region and become detected by a microchannel plate detector. The typical mass resolution  $M/\Delta M$  of the reflectron TOF-MS was 900. The adenine sample was purchased from Aldrich Chemical Company and used without further purification.

The fluorescence excitation spectrum was obtained in a different molecular beam apparatus. The frequency-doubled output of a dye laser was slightly focused onto the expanding

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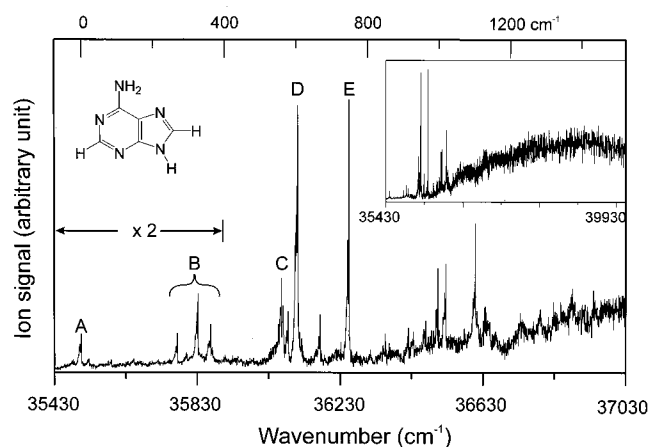


FIG. 1. Composite one-color R2PI spectrum of adenine. The intensity was not normalized against the laser fluence. The scale factor for the relative ion intensities was determined by a spectrum that contains both segments. Peak A is the origin band of the  $n\pi^*$  transition, while peak D was assigned to be that of the  $\pi\pi^*$  transition. The wave number scale on the top is relative to the 0–0 band of the  $n\pi^*$  state. Starting from  $\sim 800$   $\text{cm}^{-1}$  above the 0–0 band, there appears a broad background underneath the sharp vibronic features. The inset shows the spectrum over a much wider spectral range, with a near full view of the broad absorption band.

gas at about 7 mm downstream from the nozzle. Total fluorescence was collected and then detected by a photomultiplier tube (PMT) as the wavelength of the excitation laser was scanned. Glass filters were inserted in front of the PMT to eliminate the scattered light at and near the excitation frequency.

### III. RESULTS AND DISCUSSION

Figure 1 shows a one-color R2PI spectrum of the jet-cooled adenine under 1 atm helium. A thorough scan over a wide wavelength range of 290–240 nm (34 130–41 667  $\text{cm}^{-1}$ , 4.23–5.17 eV) using either one- or two-color R2PI failed to reveal sharp spectral bands in any other regions. The wavelength region of Fig. 1 corresponds to the red edge of the first absorption band of adenine known in the gas phase with a maximum at 249 nm (40 161  $\text{cm}^{-1}$ , 4.98 eV).<sup>7</sup> Since the vertical and adiabatic ionization energies of adenine are 8.48 eV (Ref. 27) and 7.8 eV (Ref. 28), respectively, the two-photon energy of virtually any wavelength in this region is sufficient to ionize the molecule by one-color R2PI.

Figure 1 is a composite spectrum of the two R2PI spectra separately obtained in adjacent wavelength ranges. By varying the backing pressure, and also by employing other carrier gases, we made sure that the vibronic features in Fig. 1 genuinely come from the adenine molecule, but not from the complexes of adenine with themselves or with the carrier gas molecules. We often found, however, that broad background absorption could develop underneath the sharp vibronic peaks as the backing pressure was increased. Such background appears to be due to the absorption of adenine complexes, followed by dissociative ionization. The inset of Fig. 1 represents the spectral profile over a wider region,

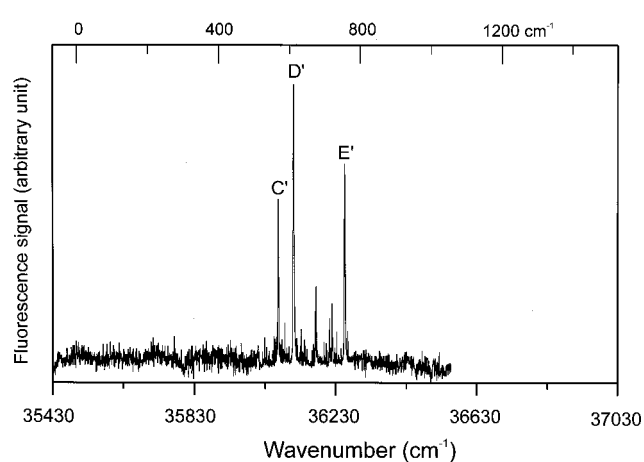


FIG. 2. Fluorescence excitation spectrum of adenine. The peaks denoted as C', D', and E', respectively, correspond to the R2PI peaks C, D, and E of Fig. 1.

showing sharp spectral bands at lower energies and a broad, continuous absorption band at higher energies. The origin of this broad absorption band has nothing to do with dissociative ionization since the experimental conditions were employed to avoid complex formation, as stated above.

Figure 2 shows the LIF spectrum of the jet-cooled adenine taken over a narrower wavelength range than the R2PI spectrum of Fig. 1 because of the low fluorescence quantum yield and the interference by scattered light, but shown over the same range for comparison. This fluorescence excitation spectrum was obtained in virtually the same experimental conditions as in Fig. 1. The two spectra show a good agreement (for example, between peaks denoted as C, D, and E vs C', D', and E') in the limited wavelength range where the fluorescence was successfully obtained. The fluorescence lifetimes for the vibronic peaks D' and E' were too short to be measured with a 6 ns laser light. Their fluorescence signal decayed as fast as the scattered light of the excitation laser.

It is well-known that vibronic interaction between closely lying  $n\pi^*$  and  $\pi\pi^*$  states in *N*-heterocyclic and aromatic carbonyl compounds gives them the characteristic photophysical properties, which are distinct from those of other types of hydrocarbon compounds.<sup>29</sup> Hochstrasser and Marzocco proposed that a sudden increase in bandwidth or a diffuse transition in electronic spectra of *N*-heterocyclic and aromatic carbonyl compounds is a manifestation of the perturbation between the  $n\pi^*$  and  $\pi\pi^*$  states.<sup>30</sup> Fischer and Naaman explained the tangled electronic spectrum of isoquinoline with irregular sequence structure by employing a simple coupling model between the  $n\pi^*$  and  $\pi\pi^*$  states.<sup>31</sup>

The first electronic absorption band of adenine comprises two adjacent  $\pi-\pi^*$  transitions<sup>12</sup> and a third, rather weak  $n-\pi^*$  transition.<sup>9,10</sup> Only a few experimental observations of the  $n-\pi^*$  transition have been reported so far, however, because of their weak oscillator strength which is estimated to be an order-of-magnitude or two smaller than that

of the  $\pi-\pi^*$  transition.<sup>9,10</sup> As for the relative locations of these states, Lipiński<sup>13</sup> and Hug and Tinoco<sup>14</sup> suggested that the  $n\pi^*$  state is located between the two lowest  $\pi\pi^*$  states, whereas Stewart and Davidson,<sup>10</sup> Danilov *et al.*,<sup>16</sup> and Takahata<sup>17</sup> proposed that the  $n\pi^*$  state is the lowest singlet excited state of adenine. Broo also concluded that the geometrically relaxed lowest excited state of adenine has an  $n\pi^*$  character, while a related compound, 2-aminopurine, has a strong  $\pi\pi^*$  character that gives the molecule totally different photophysical properties.<sup>15</sup> Most of these studies agree, however, that the energy difference between the  $n\pi^*$  and  $\pi\pi^*$  states is too small (and perhaps within the accuracy of the calculations) to allow unequivocal determination of the relative locations of the two states.<sup>16</sup> In contrast to the case of adenine, the electronic structure of guanine is quite well known. The lowest electronic state of guanine is unambiguously characterized to be a  $\pi\pi^*$  state, and the lowest  $n\pi^*$  state appears to be much higher in energy by about 0.5 eV to 0.9 eV.<sup>13,14,16</sup> Therefore, it is expected that the vibronic mixing between the  $n\pi^*$  and  $\pi\pi^*$  states occurs in a much higher frequency region, perhaps well outside the range of the spectrum experimentally observed (Fig. 1 of Ref. 25). This leads to totally different features in the electronic spectra of adenine and guanine.

It is also quite possible that the spectrum in Fig. 1 comes from the two adjacent  $\pi\pi^*$  states, not from the  $n\pi^*$  and  $\pi\pi^*$  states of adenine. However, from the large variations in the peak intensities of different vibronic bands and also from the diffuse absorption band apparently caused by state mixing, we believe that the electronic states involved are not a set of  $\pi\pi^*$  states but an  $n\pi^*$  and a  $\pi\pi^*$  state, with a considerable coupling between them. We note that the magnitude of vibronic coupling between an  $n\pi^*$  and a  $\pi\pi^*$  state is generally much larger than that between two  $\pi\pi^*$  or two  $n\pi^*$  states.<sup>30</sup> The broadening of the higher state is also generally larger if the coupling is between an  $n\pi^*$  and a  $\pi\pi^*$  state than when the two states have the same orbital origin.<sup>30</sup>

The lowest energy peak A at 35 503  $\text{cm}^{-1}$  in the R2PI spectrum of Fig. 1 was tentatively assigned as the 0–0 band. It is located 2625  $\text{cm}^{-1}$  higher than the 0–0 band of guanine,<sup>25</sup> which agrees well with the general theoretical predictions.<sup>13,14,16–18</sup> The spectrum reveals no apparent vibrational progressions. This could signify no major change in the geometry of the molecule upon electronic transition, in agreement with the findings of Stepanek and Baumruk in their UV absorption study in single crystal at 10 K.<sup>32</sup>

A puzzling feature of this spectrum is the anomalously small peak intensity of the 0–0 band. It is only about one-twentieth the intensity of the strong peaks, if the scale factor is taken into account. In the case of guanine, the peak intensity of the 0–0 band is quite comparable to those of the other strong vibronic peaks (within a factor of 2 or so).

Another intriguing peculiarity of the spectrum in Fig. 1 is that the sharp vibronic peaks are observed in a rather narrow wavelength range, only up to 1100  $\text{cm}^{-1}$  from the origin, while the slow-rising broad absorption starts to appear under the sharp vibronic features at around 800  $\text{cm}^{-1}$  even at backing pressures low enough to avoid complex formation.

The source of this broad feature is obviously quite different from what we mentioned earlier in terms of complex formation. We searched for more vibronic peaks above 1100  $\text{cm}^{-1}$ , but could not find anything other than this broad, structureless absorption spectrum with a maximum at around 3700  $\text{cm}^{-1}$  above the 0–0 level. For comparison, numerous vibronic peaks were observed over a much wider wavelength range of  $\sim 2500 \text{ cm}^{-1}$  in the case of guanine, with no such broad absorption.<sup>25</sup>

These two anomalous spectral features of Fig. 1 cannot be easily explained by an electronic transition to a single excited state. We note that a more plausible explanation could be given if there existed two different kinds of electronic states closely lying together, with an extensive vibronic mixing between them because of their near degeneracy. The low-lying state appears to have a much smaller oscillator strength than the higher-lying state, considering the small peak intensity of the 0–0 band. It has been suggested that the  $n\pi^*$  state of *N*-heterocyclic and aromatic carbonyl compounds has a much lower fluorescence quantum yield than the  $\pi\pi^*$  state.<sup>33,34</sup> It seems to be thus reasonable to assume that the low-lying excited state is of  $n\pi^*$  character, while the higher-lying state is a  $\pi\pi^*$  state.

It may be also quite tempting to assume that all vibronic peaks detected by LIF in Fig. 2 (labeled by C', D', and E') belong to the higher-lying  $\pi\pi^*$  state, in view of its much higher fluorescence quantum yield than that of the  $n\pi^*$  state. In this case, the lowest energy peak in this series denoted as C' at 36 066  $\text{cm}^{-1}$  would be the origin band of this  $\pi\pi^*$  state, while the other two peaks D' and E' in Fig. 2 would represent fundamental vibrations in the excited state. But this cannot be the case since the lowest energy vibration would then be  $\sim 42 \text{ cm}^{-1}$  (the energy difference between the peak D' at 36 108  $\text{cm}^{-1}$  and the peak C' at 36 066  $\text{cm}^{-1}$ ), which is probably too small for a molecule the size of adenine. In fact, the lowest energy vibration of adenine is theoretically estimated to be in the range of 150–300  $\text{cm}^{-1}$  in the ground state, while the vibrational frequencies are expected not to be very different between the ground and the excited states.<sup>32</sup>

The above argument suggests that the lowest energy fluorescence peak C' at 36 066  $\text{cm}^{-1}$  cannot be the origin band of the  $\pi\pi^*$  state. We therefore surmise the following:

- (1) the 0–0 band of the  $\pi\pi^*$  state is the fluorescence peak D' at 36 108  $\text{cm}^{-1}$ , which also happens to be one of the two strongest R2PI peak;
- (2) the lowest energy fluorescence peak C' at 36 066  $\text{cm}^{-1}$  belongs to the  $n\pi^*$  state;
- (3) the anomalously strong fluorescence intensity of the C' peak despite its electronic character of an  $n-\pi^*$  transition is due to a strong vibronic mixing between the  $n\pi^*$  and  $\pi\pi^*$  states that allows the  $n\pi^*$  state to “borrow” the transition moment from the  $\pi\pi^*$  state.

Based on these assumptions we note from Fig. 1 that the origin bands of the  $n\pi^*$  and  $\pi\pi^*$  states are only  $\sim 605 \text{ cm}^{-1}$  apart, which will certainly lead to a very severe vibronic mixing between the two electronic states. The peak C of Fig. 1 is much closer to the  $\pi\pi^*$  state (such as D) than the peaks A and B in the low energy side are. Therefore, the

strength of vibronic coupling will be much greater for the peak C, which will give it a much stronger  $\pi\pi^*$  character for the vibronic transition, with perhaps a much larger emission quantum yield as well. This could explain why the LIF spectrum of Fig. 2 reveals only the C' peak that corresponds to C, but not those that would have corresponded to the R2PI peaks A and B.

The identity of the peak E is rather puzzling. If it's a vibronic band of the  $\pi\pi^*$  state, it is expected that another member of the progression should be observed, given the intensity of the peak E. The absence of such peak in Fig. 1 might suggest that peak E be the origin of the second  $\pi\pi^*$  state predicted by theory.<sup>12</sup> On the other hand, calculations suggest<sup>13–15,18</sup> that the energy gap between these two  $\pi\pi^*$  states is  $\sim 1500\text{--}2000\text{ cm}^{-1}$ , with the higher-lying state having a transition dipole 2 or 3 times larger. Therefore, the assignment of this peak as the origin of the second  $\pi\pi^*$  state seems to be at odds with the theoretical predictions. Another possibility is that this peak belongs to the  $n\pi^*$  state and interacts strongly with the origin of the  $\pi\pi^*$  state, just like the peak C, but only more strongly because of the nature of its vibrational mode.

Stepanek and Baumruk measured the absorption spectrum of adeninium sulfate single crystal at 8 K, and found the 0–0 transition at  $\sim 35\,300\text{ cm}^{-1}$ .<sup>32</sup> Since the two protons attached to adenine in the adeninium cation would further suppress whatever little transition moment present in the  $n\pi^*$  state of adenine by depriving it of its nonbonding character, we believe that their absorption spectrum solely represents the  $\pi-\pi^*$  transition. Since our origin of the  $\pi\pi^*$  state is  $36\,108\text{ cm}^{-1}$ , this means that there is a  $\sim 800\text{ cm}^{-1}$  red shift in energy for the single crystal from the gas phase molecule, which is a quite reasonable and typical value. Furthermore, we can even make a comparison of vibrational frequencies measured in their spectrum and ours. They reported detecting vibrational frequencies at 216, 336, 414, 486, 515, 579, 679, and  $854\text{ cm}^{-1}$ . The corresponding positions of our R2PI spectral peaks in the  $\pi\pi^*$  segment are 205, 324, 412, 496, 526, 630, 683, and  $829\text{ cm}^{-1}$ . We note that the agreement is rather good, except for a peak or two, to be within  $\sim 10\text{ cm}^{-1}$ . Considering the broadness of the peaks in the Stepanek and Baumruk's single crystal absorption spectrum, our result may in fact be in a remarkable accord with theirs.

The conclusion about the relative locations of the  $n\pi^*$  and  $\pi\pi^*$  states also appears to be in support of the postulation made by us in our recent photoionization study of hydrated adenine clusters.<sup>26</sup> There, we proposed that the lowest electronic state of adenine is an  $n\pi^*$  state, which exhibits a general behavior of a spectral blue shift upon formation of hydrogen bonds with proton donors like water, thereby enhancing the vibronic coupling with the red-shifted  $\pi-\pi^*$  transition as a result of hydration.

Since the energy difference between the origin bands of the two electronic states is only about  $600\text{ cm}^{-1}$ , the level density of the  $n\pi^*$  state near the bottom of the  $\pi\pi^*$  state is expected to be rather small. Therefore, we were able to obtain well-resolved vibronic features at lower energies. On the other hand, as the excess energy becomes larger, the number of vibrational levels in resonance with those of the other

electronic state increases rapidly. Therefore, highly congested absorption would soon result through the extensive vibronic coupling between these levels, which appears to be the origin of the broad, featureless absorption band observed at high energies.

#### IV. SUMMARY

The electronic spectrum of adenine was obtained in a supersonic jet by the R2PI and LIF techniques. The spectrum consisted of two bands of the  $n\pi^*$  and  $\pi\pi^*$  character. The lowest electronically excited state was proposed to be an  $n\pi^*$  state. A  $\pi\pi^*$  state was found to be located only  $\sim 600\text{ cm}^{-1}$  above the  $n\pi^*$  state. The broad absorption whose onset is located  $1100\text{ cm}^{-1}$  above the  $n\pi^*$  origin was attributed to the extensive vibronic mixing between the two states.

#### ACKNOWLEDGMENTS

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