

Photodissociation Spectrum of Naphthalene Dimer Cation

Yoshiya Inokuchi, Kazuhiko Ohashi, Masaki Matsumoto, and Nobuyuki Nishi*

Department of Chemistry, Faculty of Science, Kyushu University,

Hakozaki, Fukuoka 812, Japan

Abstract

The electronic spectrum of $(C_{10}H_8)_2^+$ is obtained in the 455–1400 nm region by applying photodissociation spectroscopy to the ion produced by laser-induced plasma technique. The spectrum shows a local excitation band at 580 nm and a charge resonance band at 1180 nm. The locations of these bands coincide with those reported for intramolecular dimer cations of dinaphthyl propanes with a partially overlapped conformation, suggesting that $(C_{10}H_8)_2^+$ has a similar conformation in the gas phase.

Introduction

One of the fundamental issues in molecular cluster works is to determine the geometric structure of weakly bound complexes. The direct absorption spectra of monomer and dimer cations of naphthalene were measured in glassy solutions by γ -ray irradiation.¹⁻⁵ However, there remains some ambiguity in identifying the size of the species responsible for the photoabsorption. Study of intramolecular dimeric compounds, where the two molecules are linked by a methylene chain, makes it possible to selectively observe the spectra of the dimer cations. Yamamoto and co-workers measured transient absorption spectra of intramolecular dimer cations of naphthalene in solution by using nanosecond laser photolysis.⁶⁻⁸ They discussed the position of the absorption band in relation to the particular conformations of the two naphthalene parts: partially and fully overlapped conformations. Here the question arises whether the free dimer cation of naphthalene in the gas phase has a partially overlapped conformation or a fully overlapped one. Photodissociation spectroscopy is the most common approach to obtain electronic spectra of cluster ions in the gas phase. Recently Saigusa and Lim measured the photodepletion spectra of naphthalene cluster cations, $(C_{10}H_8)_n^+$ with $n=2-7$, created through resonant two photon ionization (R2PI).⁹ Since the main purpose of their work was to present evidence for a dimer core structure of $(C_{10}H_8)_n^+$, the photodepletion yield was measured at a limited number of wavelengths.

In this letter, we report the photodissociation spectrum of $(C_{10}H_8)_2^+$. The parent ion is formed at the nozzle exit by laser-induced plasma technique. With this ion source we expect to prepare the parent ion colder than that by the R2PI method. The photodissociation spectrum is recorded by using a triple-pole configuration: parent separation quadrupole - octopole ion trap - fragment separation quadrupole. We vary the wavelength of the photodissociation laser with so fine step that we can compare the observed spectrum with the absorption spectra in the condensed phase. Possible conformation of $(C_{10}H_8)_2^+$ is discussed on the basis of the position of a local excitation band corresponding to the $D_2 \leftarrow D_0$ transition of $C_{10}H_8^+$.

Experimental

The experiment was carried out by using an octopole ion trap with two quadrupole mass filters. A mixture of naphthalene and argon was expanded through a pulsed nozzle. Naphthalene was placed in the head of the nozzle, which was heated to 80°C for vaporization. The total stagnation pressure was ≈ 3 atm ($1 \text{ atm} \approx 1.01 \times 10^5 \text{ Pa}$). The parent ion was prepared by laser-induced plasma technique.¹⁰ A rotatory disk (stainless steel) was situated parallel to the expansion axis beyond the nozzle exit. The fundamental output (1064 nm, 45 mJ/pulse) of a Nd:YAG laser (Spectra-Physics GCR-14S) was focused onto the disk to induce a plasma. The dimer cation was formed by accretion of a neutral molecule to the ionized one and was successively cooled in the expansion. After passing through a skimmer, the dimer cation was selected by a quadrupole mass filter. Then, the cation was deflected through 90° by a quadrupole ion bender¹¹⁻¹³ and introduced into an octopole ion trap.^{14,15} The photodissociation laser beam propagated coaxially along the octopole and irradiated the trapped ions. The photoexcitation induced the fragmentation of $(\text{C}_{10}\text{H}_8)_2^+$ into $\text{C}_{10}\text{H}_8^+$ and C_{10}H_8 . The photofragment cation was mass-analyzed by another quadrupole filter and detected by a secondary electron multiplier.

The output of a dye laser (Spectra-Physics PDL-3) pumped with a Nd:YAG laser (Spectra-Physics GCR-18S) was used for the photodissociation in the visible region (560–780 nm). The output of an optical parametric oscillator (Spectra-Physics MOPO-730) pumped with a Nd:YAG laser (Spectra-Physics GCR-250) was utilized in the regions of 455–560 nm and 780–1400 nm. The fragment ion intensity was normalized by the laser power monitored with a PIN photodiode (Hamamatsu S1722-02) or an InGaAs photodiode (Hamamatsu G3476-05). The photodissociation spectrum was obtained by plotting the normalized intensities of the fragment ion against the laser wavelengths.

Results and Discussion

Figure 1 shows the photodissociation spectrum of $(C_{10}H_8)_2^+$ in the 455–1400 nm region. The photodissociation cross sections (opened circles) are plotted at 2.5 or 5 nm intervals in the visible region and at 10 nm intervals in the near IR region. The error bars indicate one standard derivation of statistical uncertainties determined from repeated laser scans. The spectrum exhibits two distinct maxima at 580 and 1180 nm. The cross section at the 1180-nm band is approximately five times larger than that at the 580-nm band.

The direct absorption spectra of $(C_{10}H_8)_2^+$ in γ -ray irradiated solutions were reported by several groups.¹⁻⁵ In all cases, two absorption bands were observed at 580 and 1100 nm. The 1100 nm-band was attributed to the charge resonance (CR) band.¹ This band is characteristic of $(C_{10}H_8)_2^+$ which is due to the electronic transition between the two CR states correlated to $C_{10}H_8^+(D_0)$, the ground doublet state) + $C_{10}H_8(S_0)$, the ground singlet state). These states are described as

$$\Psi_{\pm} = 2^{-1/2} (\psi_1^+ \psi_2 \pm \psi_1 \psi_2^+)$$

where ψ^+ and ψ are the electronic wavefunctions of $C_{10}H_8^+(D_0)$ and $C_{10}H_8(S_0)$, respectively. The 580 nm-band was assigned to the $D_2 \leftarrow D_0$ local excitation (LE) band.² Here the electronic transition of a monomer cation unit is locally excited within $(C_{10}H_8)_2^+$. The $D_1 \leftarrow D_0$ transition of $C_{10}H_8^+$ is dipole-forbidden¹⁶ and the corresponding LE band has not been found in the dimer spectra.

Recently Saigusa and Lim have reported the photodepletion spectra of mass-selected $(C_{10}H_8)_n^+$ with $n=2-7$ in the 500–1100 nm region.⁹ The spectra showed two maxima at 580 and 1000 nm, both of which were found to be independent of cluster size. From the similarity of the spectra, they insisted on a dimer core structure for the larger clusters. The 500–800 nm region of the photodepletion spectrum of $(C_{10}H_8)_2^+$ reported by Saigusa and Lim is essentially the same as the present one. But it is inconsistent in longer wavelength region. The photodepletion yield measured by Saigusa and Lim shows a maximum at around 950 nm and decreases with increasing wavelength from 950 to 1100 nm. However, our data points continue to increase toward 1180 nm. In

addition, their spectrum showed a long tail of the CR band toward the high-energy side. There are two major differences in the experimental procedures. First, they produced $(C_{10}H_8)_2^+$ by R2PI of the neutral dimer. We feel that the temperature of $(C_{10}H_8)_2^+$ formed by the R2PI method is higher than that of the collisionally cooled $(C_{10}H_8)_2^+$ in our experiment. The long tail of the CR band can be reasonably attributed to this temperature effect. Second, they kept the power of the photodissociation laser at a constant value of 50 μ J/pulse. With this laser power they obtained the depletion yield as large as 80% at around 950 nm. The depletion yield at the 950-nm band was comparable with that at the 580-nm band. The result is inconsistent with the condensed-phase spectra, where the absorbance of the CR band is approximately 6 times larger than that of the LE band.³ On the other hand, we carefully control the laser power to avoid saturation around the absorption maxima. Our spectrum exhibits an intense band at 1180 nm, where the cross section is reasonably larger than that of the 580-nm band. We think therefore that the maximum detected at \approx 950 nm by Saigusa and Lim may be artificial because their laser power is too high to find the correct maximum. They could not observe the increasing cross section toward 1180 nm because approximately 80% of the parent ion was already destroyed at 950 nm. Thus we assign the accurate position of the CR band of $(C_{10}H_8)_2^+$ to 1180 nm.

An energy diagram of $(C_{10}H_8)_2^+$ is displayed in Figure 2. The energy levels for $(C_{10}H_8)_2^+$ are determined from the photodissociation spectrum in Figure 1. The energy of the $D_2 \leftarrow D_0$ transition of $C_{10}H_8^+$ (1.84 eV) is taken from the literature.¹⁶ For $(C_6H_6)_2^+$,¹⁷ half the energy of the CR transition was shown to be nearly equal to the binding energy of $(C_6H_6)_2^+$.¹⁸ The similar trend was found for dimer ions of toluene and *p*-difluorobenzene.¹⁷ Therefore we use half the CR transition energy determined here (0.53 eV) as a lower limit of the binding energy of $(C_{10}H_8)_2^+$, although high pressure mass spectrometry provided a higher value of 0.77 eV.¹⁹ This discrepancy is not crucial to the following discussion.

Most of the condensed-phase studies suggested or supposed a parallel sandwich structure for $(C_{10}H_8)_2^+$. The appearance of the intense CR band implies that the positive

charge is shared with the two naphthalene molecules within $(C_{10}H_8)_2^+$ in the ground state and that the two moieties should be equivalent to each other. Here the question arises about the conformation of $(C_{10}H_8)_2^+$ whether it has a fully overlapped structure or a partially overlapped structure. When one links two naphthalene molecules by a C_3 methylene chain, one can control the mutual conformation of the two naphthalene parts. Both a fully overlapped and a partially overlapped conformations are allowed for 1,3-di(2-naphthyl)propane (abbreviated as 22Np). While 1-(1-naphthyl)-3-(2-naphthyl)propane (12Np) can have only a partially overlapped form. Yamamoto and co-workers measured transient absorption spectra of these intramolecular dimeric compounds in solution by nanosecond laser photolysis.⁶⁻⁸ For 22Np, two distinct absorption bands were obtained at 580 and 660 nm in the visible region. While for 12Np, only one absorption band was observed at ≈ 580 nm. Therefore they ascribed the 580- and 660-nm bands to the partially and fully overlapped intramolecular dimer cations, respectively. Since the intermolecular dimer cation in the glassy solutions showed the absorption band at around 580 nm,¹⁻⁵ they suggested a partially overlapped conformation for $(C_{10}H_8)_2^+$. Badger and Brocklehurst also proposed a distorted (partially overlapped) conformation of $(C_{10}H_8)_2^+$.²⁰ For free $(C_{10}H_8)_2^+$ in the gas phase, the corresponding band is located at 580 nm in our spectrum. The spectrum shows no indication of another band in the 600–800 nm range. The methylene chain and the surrounding solvent (acetonitrile) may show a little influence on the position of the LE band. Thus we deduce that $(C_{10}H_8)_2^+$ has a partially overlapped conformation in the gas phase.

The conformation of the two naphthalene molecules is thought to have a greater effect on the position of the CR band. Yamamoto and co-workers observed a strong CR band in the transient absorption spectra of 22Np and 12Np in near IR region.^{7,8} The CR band of 12Np is located at ≈ 1050 nm. For 22Np, we expect two CR bands corresponding to the two different conformations. However, only one CR band was found at ≈ 1250 nm. In contrast to the case of the LE band, the position of the CR band does not seem to uniquely correspond to a possible conformation. Molecular orbital calculations for 1,3-di(1-naphthyl)propane (11Np) show that the CR band due to the fully

overlapped conformation appears at wavelengths longer than that of the partially overlapped one.⁷ However, coverage of the CR band region expected for the fully overlapped conformation is prohibited by the wavelength restriction on the present laser system. Thus we can not completely rule out the existence of the fully overlapped conformer of $(C_{10}H_8)_2^+$ in the gas phase.

The photodissociation spectrum of $(C_{10}H_8)_2^+$ in the gas phase exhibits two bands at 580 and 1180 nm. The positions and the relative intensity of these bands are consistent with those of the absorption spectra previously obtained in condensed phase. The 580-nm band also coincides with the band for the partially overlapped conformation of the intramolecular dimeric compounds. We expect that $(C_{10}H_8)_2^+$ takes a partially overlapped conformation in the gas phase.

Acknowledgment

We are grateful to Mr. S. Nakagawa for his help at the initial stage of this work. We wish to thank Dr. Saigusa and Prof. Lim for sending a copy of their manuscript prior to publication. This work was supported in part by a Grant-in-Aid for New Program "Intelligent Molecular Systems with Controlled Functionality" (06NP0301) and general research program (04403002) from the Ministry of Education, Science and Culture of Japan.

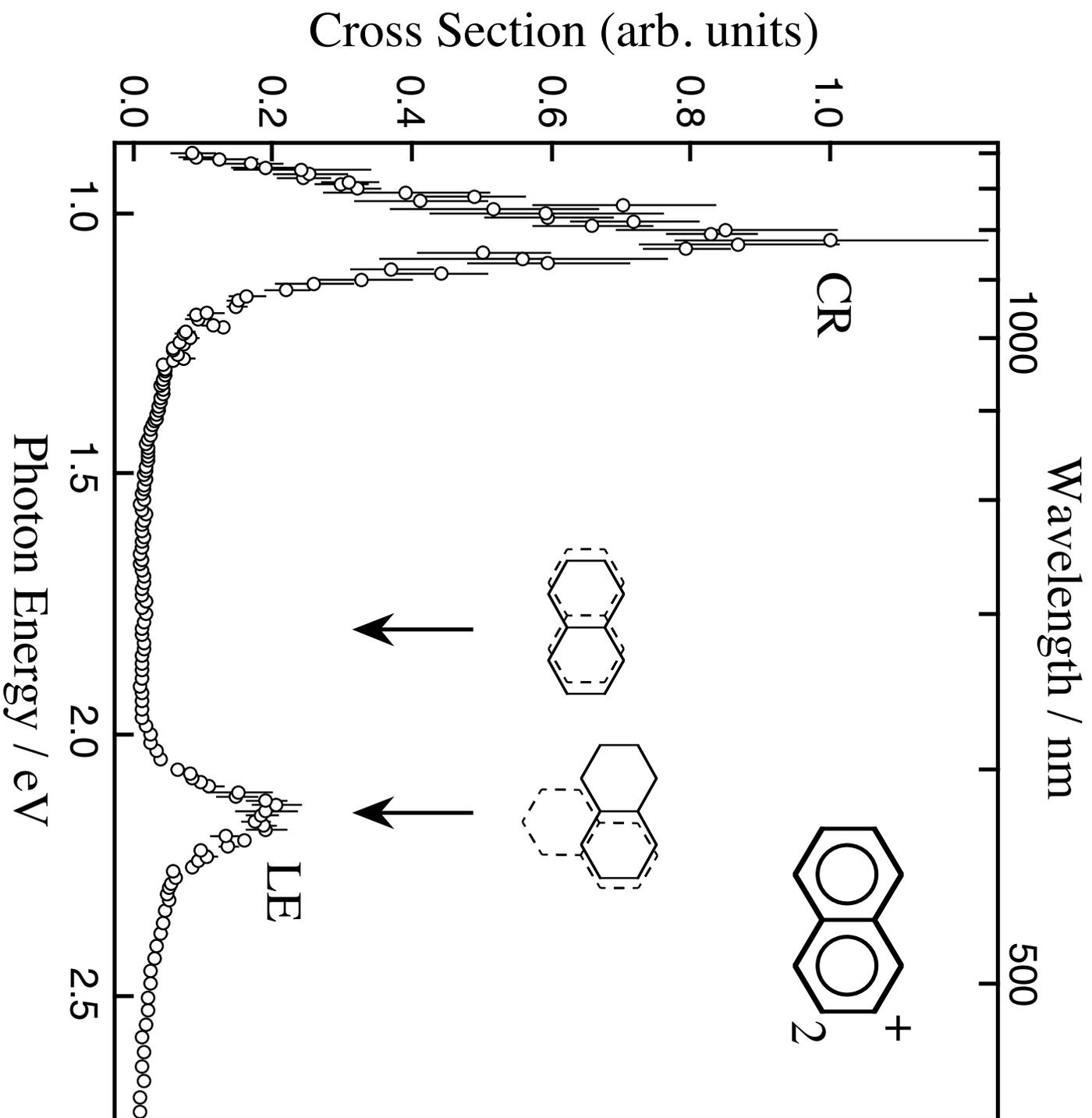
References

1. Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, 65, 2588.
2. Badger, B.; Brocklehurst, B.; Russell, R. D. *Chem. Phys. Lett.* **1967**, 1, 122.
3. Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, 95, 3473.
4. Kira, A.; Imamura, M.; Shida, T. *J. Phys. Chem.* **1976**, 80, 1445.
5. Kira, A.; Imamura, M. *J. Phys. Chem.* **1979**, 83, 2267.
6. Tsuchida, A.; Tsujii, Y.; Ito, S.; Yamamoto, M.; Wada, Y. *J. Phys. Chem.* **1989**, 93, 1244.
7. Tsujii, Y.; Tsuchida, A.; Yamamoto, M.; Momose, T.; Shida, T. *J. Phys. Chem.* **1991**, 95, 8635.
8. Tsujii, Y.; Tsuchida, A.; Ito, S.; Yamamoto, M. *Macromolecules* **1991**, 24, 4061.
9. Saigusa, H.; Lim, E. C. *J. Phys. Chem.* in press.
10. Beck, S. M.; Hecht, J. H. *J. Chem. Phys.* **1992**, 96, 1975.
11. Zeman, H. D. *Rev. Sci. Instrum.* **1977**, 48, 1079.
12. Farley, J. W. *Rev. Sci. Instrum.* **1985**, 56, 1834.
13. Dresch, T.; Kramer, H.; Thurner, Y.; Weber, R. *Z. Phys. D* **1991**, 18, 391.
14. Okuno, K. *J. Phys. Soc. Jpn.* **1986**, 55, 1504.
15. Yeh, L. I.; Okumura, M.; Myers, J. D.; Price, J. M.; Lee, Y. T. *J. Chem. Phys.* **1989**, 91, 7319.
16. Andrews, L.; Kelsall, J.; Blankenship, A. B. *J. Phys. Chem.* **1982**, 86, 2916.
17. Ohashi, K.; Nakai, Y.; Shibata, T.; Nishi, N. *Laser Chem.* **1994**, 14, 3.
18. Ernstberger, B.; Krause, H.; Kiermeier, A.; Neusser, H. J. *J. Chem. Phys.* **1990**, 92, 5285.
19. Meot-Ner (Mautner), M. *J. Phys. Chem.* **1980**, 84, 2724.
20. Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1970**, 66, 2939.

Figure Captions

Figure 1. Photodissociation spectrum of $(C_{10}H_8)_2^+$ in the 455–1400 nm region. The two naphthalene parts of 1,3-di(2-naphthyl)propane for fully and partially overlapped conformations are schematically shown at the positions of the respective LE bands determined by the transient absorption spectroscopy.⁶⁻⁸

Figure 2. Energy level diagram of $(C_{10}H_8)_2^+$ and $C_{10}H_8^+$. Transition energies of $(C_{10}H_8)_2^+$ are determined from the photodissociation spectrum. The energy for the $D_2 \leftarrow D_0$ transition of $C_{10}H_8^+$ is taken from the literature.¹⁶ The binding energy of $(C_{10}H_8)_2^+$ is tentatively set to half the energy of the CR transition (see text).



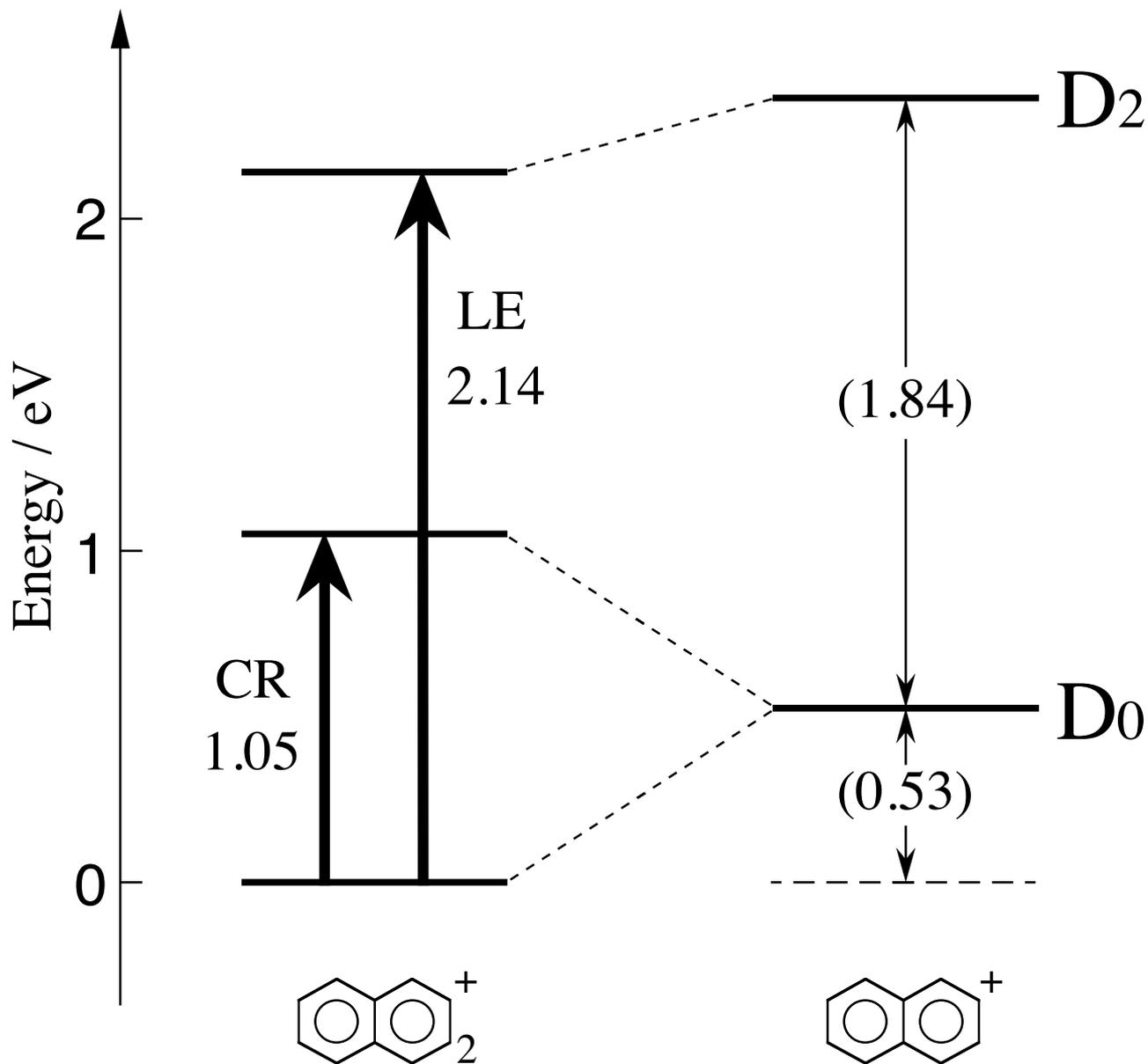


Figure 2 Inokuchi *et al.*