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Electronic excitation spectra of radical anions of cyanoethylenes and cyanobenzenes: Symmetry adapted cluster–configuration interaction study

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Electronic excitation spectra of the radical anions of cyanoethylenes (*trans*-dicyanoethylene and tetracyanoethylene) and cyanobenzenes (1,2-dicyanobenzene: *o*-DCNB, 1,3-dicyanobenzene: *m*-DCNB, and 1,4-dicyanobenzene: *p*-DCNB) were studied by the symmetry adapted cluster–configuration interaction (SAC-CI) method. Theoretical calculations predicted positive electron affinities for all the molecules in good agreement with the experimental observations. Electronic excitation spectra of open-shell radicals is a topic that has not been studied as much as such spectra of closed-shell molecules, but this can be easily addressed using SAC-CI theory. The present paper systematically describes the calculation procedures for radical anions by investigating several basis sets, including anion diffuse and Rydberg functions. The calculated excitation energies were in good agreement with the experimental UV/NIR (near infrared region) spectra, which had been observed by one of the present authors in 2-methyltetrahydrofuran matrix frozen to transparent glassy solids at 77 K. For *p*-DCNB, the SAC-CI theoretical spectrum agreed particularly well with the experimental spectrum. An extremely weak $\pi^*(\text{SOMO}) - \pi^*$ excitation at 1.41 eV predicted in the present work, but had been overlooked in the previous experimental spectrum published in 1988, was confirmed to be real by a careful re-examination of the old spectrum. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4722335>]

I. INTRODUCTION

In organic material science, cyano compounds are recognized as good electron acceptors due to the large electronegativity of the cyano group and the possible extension of the π -conjugation through C=C and CN π -orbitals. Their charge-transfer complexes have been widely used for organic molecule-based conductors and molecular magnets, etc.^{1–11} For instance, tetracyanoethylene (TCNE), having the four hydrogen atoms of ethylene replaced by four cyano groups, is a key compound in molecular engineering, and can be utilized as an excellent electron acceptor for the preparation of charge-transfer complexes.^{12–19} Recent studies from our laboratory have examined, on a theoretical basis, the photo-induced phase-transition mechanism of the TTF (tetrathiafulvalene) – TCNE crystal,^{19,20} and we have proposed an interesting phase-transition mechanism as an alternative to the so-called “domino” mechanism.¹⁹ Cyanobenzene compounds also have useful possibilities as materials¹¹ with 1,4-dicyanobenzene (*p*-cyanobenzonitrile) being a basic compound that is similar to *p*-benzoquinone.²¹

Several theoretical and experimental studies have been reported for the ground states of the radical anions of cyano

compounds.^{1–11,22,23} However, there are only a limited number of studies on their excited states.^{15,22,23} Experimentally, it is generally difficult to maintain radical anions in a stable state for a long time. One of the present authors (T.S.), however, developed a method to generate radical anions of target molecules by gamma ray irradiation in combination with a matrix isolation technique.²⁴ As for the matrix, 2-methyltetrahydrofuran (MTHF) was mainly used which freezes to a transparent glassy solution of parent neutral molecules. Upon irradiation, ejected electrons migrate thermally until they reach the parent molecules to give their radical anions. Thus, it may be regarded as the simplest one-electron reduction of parent molecules, or a gentle electron migration and trapping as in N-type semiconductors. Use of this matrix has allowed observations of the UV/NIR (near infrared region) absorption spectra of hundreds of radical anions since 1970s.²⁴ Fortunately, matrix molecules of MTHF ionized by gamma irradiation leave byproducts which absorb only in the deep UV region so that they do not interfere seriously the absorption of radical anions in the longer wavelength region of UV/NIR.

Some of these spectral data were subjected to theoretical analysis by computation coded by Iwata and co-workers.^{25–28} However, the analysis in those days was necessarily limited to some π electron systems of planar molecules. Thus, the electronic excited states were treated by a self-consistent-field configuration-interaction (SCF-CI) procedure on the

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basis of Pariser-Parr-Pople (P-P-P) type approximation. Only limited numbers of one- and two-electron configurations were taken into account in combination with some modifications to empirical parameters for nitrogen and oxygen atoms.^{25–28} The study along this line includes the systems of aromatic nitro-substituted radical anions,²⁵ the dianthracene radical anion and anthracene dimer anion,²⁶ radical anions of aromatic hydrocarbons,²⁷ and radical anions of aromatic and unsaturated aliphatic carbonyl compounds.²⁸ Since then, of course, remarkable progress in theory and computational technique for spectral analysis has been made. Among many others,^{29–36} CASSCF and CASPT2 studies have been performed recently for several anionic species.^{22,30,31,34–36} But, even with recent advances in quantum chemistry theory, it is not easy to calculate dependable electronic excited states of radical anions compared with calculations for the closed-shell neutral molecules.

In this paper, we study the electronic excitation spectra of the radical anions using the symmetry adapted cluster-configuration interaction (SAC-CI) method.^{37–41} The SAC-CI method is based on a powerful electron-correlation theory^{37–41} that is applicable to both ground and excited states with similar accuracy even for radical species. This property that originates from the transferability of electron correlations among different electronic states is particularly important to investigate the excited states with high reliability. In the present article, we have systematically studied the ground and excited states of radical anions of several cyanoethylenes and cyanobenzenes, that is, *trans*-dicyanoethylene, *t*-DCNE; tetracyanoethylene, TCNE; cyanobenzene, CNB; 1,2-dicyanobenzene, *o*-DCNB; 1,3-dicyanobenzene, *m*-DCNB; and 1,4-dicyanobenzene, *p*-DCNB, Fig. 1 shows the chemical structures of these six radical anions. As a result of the study, the observed excitation energies, intensities, and the nature of the electronic transitions for all the systems are satisfactorily understood. A very feeble electronic excitation in the near IR region for the radical anion of *p*-DCNB overlooked in the previous experiment but predicted in the present work is confirmed to be real.²⁴ This

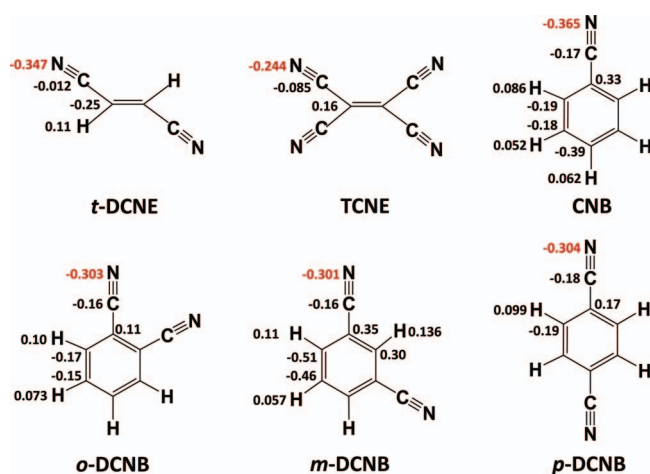


FIG. 1. Target radical anions studied in the present paper and Mulliken atomic charges of the anion ground states from the SAC-CI wave functions with basis set (1).

successful result represents predictive power of the present theoretical analysis.

II. THEORETICAL AND COMPUTATIONAL BACKGROUND

We performed the SAC-CI singles and doubles (SD-R) calculations, where one- and two-electron excitation operators (indicated by R) are considered as linked operators, to obtain the radical anion (doublet) ground and excited states. Since the SAC-CI wave function is based on the closed-shell SAC wave function,^{37–41} both the ground and excited states of the doublet anion radical are calculated with the SAC-CI method. We classified the excited states of the anions into three types to describe doublet-to-doublet excitations as follows:²¹ type I, the excitation from the singly occupied molecular orbital (SOMO) to the unoccupied orbital; type II, the excitation from the doubly occupied orbital to SOMO; and type III, the excitation from the doubly occupied orbital to the unoccupied orbital (Fig. 2). The excited states belonging to types I and II are accurately evaluated by the SAC-CI SD-R method, but the excited states of type III are less accurately estimated with the SAC-CI SD-R method. This is because type III excitations are a two-electron process viewed from the closed shell SAC state and, in principle, the SAC-CI general-R method^{41,42} is required to obtain accuracy similar to the ground state, (where “general-R” means that more than two electron-excitation operators are used). In a higher energy region, which the experimental observations cannot detect, there may be a small number of contributions of type III excited states. However, since our interests in the present study lie in the excited states appearing below about 7 eV (especially below 5 eV), no important type III states would be found in this energy region so that we did not employ the general-R method. To retain the one-electron process in the SD-R framework, we required two different calculations one for type I and the other for type II. For type I, we first calculated the closed-shell SAC wave function with the number of electrons the same as the neutral molecule, and then one electron was attached to the closed-shell SAC wave function in the SAC-CI level. On the other hand, for type II, the closed-shell SAC wave function with the number of electrons the same as the dianionic molecule was calculated, and then one electron detachment from that SAC wave function was done in the SAC-CI level. After performing two independent calculations of types I and II, all the excited states can be obtained, theoretically, from the sum of the resultant states. This

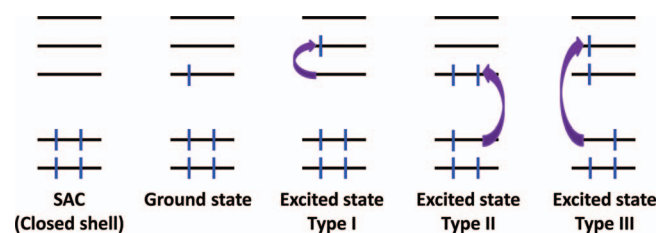


FIG. 2. Three types of excitations from the ground state of the radical anion: type I, from SOMO to unoccupied; type II, from occupied to SOMO; and type III, from doubly occupied to unoccupied.

TABLE I. Definition of the basis sets (1) to (4) used in the present calculations. (Detailed definitions are given in the text.)

Basis set	Valence	Polarization	Anion diffuse	Rydberg
(1)	Double zeta	Single (<i>d,p</i>)	Single (<i>p</i>)	None
(2)	Triple zeta	Double (<i>d,p</i>)	Single (<i>p</i>)	None
(3)	Triple zeta	Double (<i>d,p</i>)	Double (<i>s,p</i>)	None
(4)	Triple zeta	Double (<i>d,p</i>)	Double (<i>s,p</i>)	Single (3 <i>s</i> ,3 <i>p</i>)

is possible because the SAC-CI method has the transferability of the electron correlations.

The present calculations were performed using the SAC-CI program in the GAUSSIAN 09, Revision B01 program package.⁴³ The basis sets used here are summarized in Table I. Four different basis sets were prepared: Basis set (1): “DZ + single polarization (*d,p*) + single diffuse (*p*)”; basis set (2): “TZ + double polarization (*d,p*) + single diffuse (*p*)”; basis set (3): “TZ + double polarization (*d,p*) + double diffuse (*s,p*)”; and basis set (4): “TZ + double polarization (*d,p*) + double diffuse (*s,p*) + single Rydberg (3*s*,3*p*)” (where, DZ: double zeta; TZ: triple zeta). In the ground-state calculations of the radical anions, we employed basis set (1) for the geometry optimization and electron affinity calculations. For the excited states of radical anions, however, a larger basis space than the ground state is required to describe more flexible electronic wave function in terms of both the valence orbital relaxation and diffuse property. We examined the former case with basis set (2) by extending valence orbitals, and the latter case with basis set (3), which includes further diffuse functions in addition to basis set (2). Rydberg states may not be important in comparison with the experimental spectra observed in a frozen MTHF matrix, where Rydberg excited states might be quenched.⁴⁴ From a theoretical point of view, however, it is necessary to introduce the Rydberg functions for basis set completeness, i.e., nature is expressed only with the complete basis. The effect of such a Rydberg basis was examined with basis set (4).

To ensure the reproducibility of the calculations, we have summarized further details of the basis sets. Basis set (1) is composed of Huzinaga-Dunning’s (9*s*5*p*/4*s*)/[4*s*2*p*/2*s*] (D95) basis set⁴⁵ plus polarization functions, 1*d* for C and N, 1*p* for H,⁴⁶ plus Dunning’s diffuse anion basis, [1*p*: $\zeta = 0.034$] for C, [1*p*: $\zeta = 0.048$] for N, and [1*s*: $\zeta = 0.048273$] for H.⁴⁷ This basis set is also available through the web on a Gaussian basis set order form⁴⁸ as “DZP” and “anion basis.” In basis set (2), Dunning’s triple-zeta functions (11*s*6*p*/5*s*)/[5*s*3*p*/3*s*] (TZ) were employed. It can be also taken from the Internet on a Gaussian basis set order form⁴⁸ as “TZ.” A single polarization function was divided into a double by using the factors 1.9 and 0.75, and the same diffuse function as basis set (1) was used. For basis set (3), the additional diffuse functions (*s* and *p* types) were obtained by using the factor 1.5 from Dunning’s diffuse anion basis⁴⁷ for C and N. Their exponents are [2*s*, 2*p*: $\zeta = 0.034, 0.051$] for C, [2*s*, 2*p*: $\zeta = 0.048, 0.072$] for N, and [1*s*: $\zeta = 0.048273$] for H. For basis set (4), the single Rydberg basis (3*s* and 3*p* type functions) was introduced for each C and N atom center. The exponents were also taken from the

literature:⁴⁷ [3*s* type: $\zeta = 0.023$ and 3*p* type: $\zeta = 0.021$] for C and [3*s* type: $\zeta = 0.028$ and 3*p* type: $\zeta = 0.025$] for N.

The molecular geometry of the radical anions was optimized using the unrestricted B3LYP method with basis set (1). To calculate the electron affinity, we also performed the optimization for the neutral molecules. The symmetry option was used in the calculations, with C_{2h}, D_{2h}, C_{2v}, C_{2v}, C_{2v}, and D_{2h} for *t*-DCNE, TCNE, CNB, *o*-DCNB, *m*-DCNB, and *p*-DCNB anions, respectively. In the SAC-CI calculations, “AnionDoublet” and “CationDoublet” keywords were used to calculate types I and II excited states, respectively. The direct algorithm was employed with the keyword “Direct.”⁴⁹ The number of calculated excited states for each irreducible representation was set to 10, with the keyword “Nstate = 10” for basis set (1), 15 (“Nstate = 15”) for basis sets (2) and (3), and 20 (“Nstate = 20”) for basis set (4). The restricted open-shell Hartree-Fock (ROHF) molecular orbitals of radical anions were used as reference orbitals and all the orbitals except for the 1*s* cores were used in an active space. All of the single excitation operators, including electron attachment and detachment, and part of the double excitation operators selected by the perturbative selection technique were used^{50–52} in which “LevelThree” (default) threshold was employed.

It is worth noting the effects of the choice of the reference orbitals and the perturbation selection. An alternative choice of the reference orbitals may be the restricted closed-shell Hartree-Fock (RHF) molecular orbitals of neutral and dianionic molecules for types I and II excited states, respectively. When one does not want to use the perturbation selection technique, all the double excitation operators are included by the “NoLinkedSelection” keyword instead of “LevelThree.” Figure 3 illustrates the SAC-CI excitation spectra of the *t*-DCNE anion by basis set (1) with four different computations: (a) reference orbital, RHF, perturbation selection, “LevelThree”; (b) ROHF, “LevelThree”; (c) RHF, “NoLinkedSelection”; and (d) ROHF, “NoLinkedSelection”. Orbital pictures (especially orbital energies) were quite different between the RHF and ROHF. The total dimensions of the linked operators of the closed-shell SAC wave function were 71 061 (RHF, “LevelThree”), 68 501 (ROHF, “LevelThree”), and 26 0248 (“NoLinkedSelection”). Thus, the dimension with “NoLinkedSelection” was almost three times larger than that with “LevelThree” threshold. Despite this difference, the four spectra look almost identical. Thus, in the theoretical framework of the SAC-CI method, the excitation spectra should not be highly dependent on the choice of the reference orbitals and the perturbation selection technique due to the balanced descriptions between the ground and excited states.^{38–41} The former, i.e., the independence on the reference orbitals, can guarantee safe calculations even for the doublet-doublet excitations. Due to the perturbation selection, we can deal with large molecules and a large basis set without loss of accuracy, as has already been published in many cases.⁵³

III. ELECTRON AFFINITIES

To investigate both vertical and adiabatic electron affinities of the cyano compounds in this study, the geometry optimization was performed for both the neutral molecule and

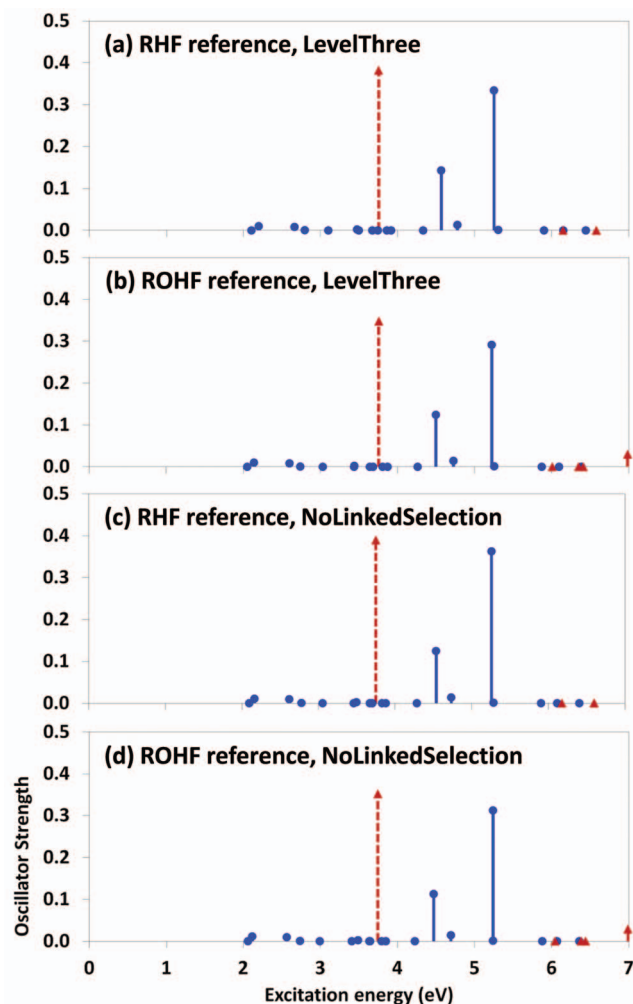


FIG. 3. SAC-CI excitation spectra of the *t*-DCNE anion by basis set (1) with four different calculations: (a) reference orbital: RHF, perturbation-selection level = “LevelThree”; (b) ROHF, “LevelThree”; (c) RHF, “NoLinkedSelection”; and (d) ROHF, “NoLinkedSelection.” The filled circle and solid line with blue color shows type I excitation and the triangle and dotted line with red color shows type II excitation.

the radical anion by the B3LYP method with basis set (1). When the perturbation selection technique is employed in the SAC-CI calculations, it may be difficult to compare the total energies of different geometries. In such cases, the keyword “GSUM” is recommended. Then the group-sum of the excita-

tion operators selected at different geometries is used for both geometries, and therefore should be equivalent for both geometries. In the present calculations, “GSUM” was employed together with the keyword “CPHF = Mod” to minimize the orbital deformation at different geometries.⁵⁴ Table II summarizes the calculated vertical (on the equilibrium geometries of the neutral molecule and the anion) and adiabatic electron affinities with basis set (1). The Koopmans values (negative of the LUMO orbital energy of the RHF calculation) are also listed in the table. The experimental data in gas phase is available in the literature.^{55–57}

The adiabatic electron affinities of *t*-DCNE and TCNE were 1.31 and 3.68 eV, respectively, from SAC-CI, which correspond to 1.24 and 3.17 ± 0.2 eV from the experimental observations. TCNE has an extremely large positive electron affinity arising from its four cyano groups. Therefore, the TCNE radical anion can exist quite stably and is widely used as one of the most efficient electron acceptors.

CNB has only one cyano group so that its radical anion might be considered not so stable. There have been several earlier discussions about the electron affinity of CNB in the literature.^{55–57} But, based on a report,⁵⁷ the electron affinity of CNB is considered slightly positive (0.26 ± 0.1 eV). In our calculations, the adiabatic electron affinity was 0.063 eV, which was also slightly positive and in agreement with the experimental expectations. However, it is interesting to note that the vertical electron affinity at the optimized geometry of the neutral molecule was slightly negative, i.e., -0.12 eV as given in Table II, whereas the vertical electron affinity at the anion geometry was positive, i.e., 0.27 eV. The result implies that the neutral geometry is destabilized, while the electron attached state is stabilized. Therefore, the geometry relaxation of the electron attached state is considered to stabilize the radical anion. So, the electron attached state of CNB is concluded to be somewhat stable (positive adiabatic electron affinity).

Table II also shows that the adiabatic electron affinities of *o*-, *m*-, and *p*-DCNB were calculated by SAC-CI as 1.21, 1.20, and 1.26 eV, respectively, which are in good agreement with the corresponding experimental values of 0.95, 0.91, and 1.10 eV. The order of the magnitude, i.e., $p > o > m$, is consistent with the general knowledge of the basic electronic nature of the three isomers, that is to say, in *p*- and *o*-DCNB, the negative charge prefers to be in the vicinity of the nitro-

TABLE II. Gas-phase vertical (with neutral and anion geometries) and adiabatic electron affinities (eV) calculated by the SAC-CI method.

Molecule	Vertical (Neutral)		Vertical (Anion)		Adiabatic (SAC-CI) ^a	Adiabatic (Expt.)
	SAC-CI ^a	Koopmans ^b	SAC-CI ^a	Koopmans ^b		
<i>t</i> -DCNE	1.13	-0.30	1.62	0.22	1.31	1.24 ^c
TCNE	3.60	1.86	3.97	2.26	3.68	3.17 ± 0.2 ^c
CNB	-0.12	-1.26	0.27	-1.24	0.063	0.26 ± 0.1 ^d
<i>o</i> -DCNB	0.95	-0.74	1.32	-0.33	1.21	0.95 ^c
<i>m</i> -DCNB	1.02	-0.85	1.34	-0.51	1.20	0.91 ^c
<i>p</i> -DCNB	1.09	-0.52	1.46	-0.11	1.26	1.10 ^c

^a“GSUM” and “CPHF = Mod” keywords and basis set (1) were used.

^bNegative sign of LUMO energy of RHF orbital with basis set (1).

^cReference 55.

^dReference 57.

gen atoms in the π -conjugative systems, whereas in *m*-DCNB such a resonance stabilization is suppressed. This tendency is also found in the calculated total energies of the radical anions (with “NoLinkedSelection”), which turn out to be $-415.580\ 535$, $-415.579\ 504$, and $-415.590\ 743$ a.u. with basis set (1) for the *o*-, *m*-, and *p*-DCNB anions, respectively. Thus, the *m*-DCNB anion is understood to be the most unstable.

As is seen from the 6th column of Table II, the order of the electron affinities in SAC-CI turns out to be $\text{TCNE} > t\text{-DCNE} > p\text{-DCNB} > o\text{-DCNB} > m\text{-DCNB} > \text{CNB}$, which is in complete agreement with the experiment not only for the order but also for the absolute values and their signs. Practically, the order of the electron affinities may simply be predicted from the Koopmans values. Actually, the order of the electron affinities of the present molecules was in the order of the Koopmans values, although the absolute values were far from agreement and even the sign was wrong for many molecules as seen from Table II.

IV. GROUND STATES OF RADICAL ANIONS

The ground states of all the radical anions studied here were calculated by the SAC-CI with their symmetries; B_g , B_{2g} , B_1 , A_2 , A_2 , and B_{3u} for *t*-DCNE, TCNE, CNB, *o*-, *m*-, and *p*-DCNB anions, respectively. In Tables III and IV, the first entry in each molecule is for the ground states from type I calculations. The main configurations of these ground states were the electron attachment to their π^* LUMO of neutral molecule. Therefore, the above symmetries correspond to the symmetries of the highest singly occupied orbitals (see Tables SI and SII in the supplementary material⁵⁸). We describe this orbital $\pi^*(\text{SOMO})$ or simply $\pi^*(S)$.

Figure 1 includes the illustrations of the Mulliken atomic charges of the ground states of the radical anions obtained from the SAC-CI wave functions with basis set (1). For all the molecules, the most negative atom is the nitrogen atom of the cyano group and the next most negative is the carbon atom of the cyano group. The stability of radical anions has some correlation with the total negative charges of the nitrogen atoms. The sums of the negative charges on nitrogen atom(s) were -0.694 , -0.976 , -0.365 , -0.606 , -0.602 , and -0.608 for *t*-DCNE, TCNE, CNB, *o*-, *m*-, and *p*-DCNB anions, respectively, and the order of their magnitude is $\text{TCNE} > t\text{-DCNE} > p\text{-DCNB} > o\text{-DCNB} > m\text{-DCNB} > \text{CNB}$, which is the same order as for the electron affinity (cf. Table II).

V. EXCITED STATES OF RADICAL ANIONS

We performed two different calculations for each molecule to obtain type I and type II excited states within the SD-R framework as shown in Fig. 2. The type I excitations only appeared in the radical anion because it is the excitation from the LUMO of the neutral molecule to the higher unoccupied MOs. On the other hand, the type II excitations can also be found in the neutral molecule. Generally speaking, the orbital energy gap between LUMO and higher unoccupied orbital is smaller than the HOMO-LUMO gap and therefore, the type I excitation energies are expected to be found at a lower

energy region than the type II ones. We found this to be true in many cases, but there were exceptions, which will be discussed below.

Tables III and IV summarize the important excited states of all the six radical anions calculated by the SAC-CI method with excitation energy, oscillator strength, second moment, and its perpendicular component to the molecular surface in basis sets (1) to (4). Figures 4 and 5 show the theoretical excitation spectra from basis sets (1) to (4) together with the experimental UV/NIR absorption spectra for each molecule. It is to be noted that the theoretical calculations are for the gas phase, whereas the experimental spectra were observed in the MTHF matrix.²⁴ Fortunately, however, the matrix shift was found to be not so serious. This is mainly because the randomly oriented MTHF molecules frozen at 77 K are immobilized so that the dielectric effect to the radical anion under study does not differ drastically whether the anion is in the ground electronic state or in the excited state.

Before discussing the excited states of each radical anion in detail, the basis set dependencies shown in Tables III and IV and Figs. 4 and 5 are reviewed. Since all the molecules under discussion are planar, the perpendicular component of the second moment is an important index for knowing the nature of the π -symmetry excited states. Whereas it is difficult to see them within the results in basis sets (1) to (3), it becomes clear in basis set (4) (see Tables III and IV). Figures 4 and 5 clearly show how the excited states change as the basis set space is extended.

No significant differences appear between the results with basis sets (1) and (2) for all the radical anions under discussion, indicating that the valence basis functions inclusive of polarization are enough. On the other hand, the type I excited states assigned to anion diffuse or Rydberg states require more widespread basis functions. By extending the basis space to basis sets (3) and/or (4), the excitation energies and oscillator strengths of some such states changed significantly. The second moments and/or the perpendicular components also changed drastically.

In the theoretical calculations of a gas phase spectrum of common organic molecules, it is well known that inclusion of the Rydberg basis functions is inevitable, even for the discussion of valence main states.⁵⁹ If any Rydberg basis is not employed, the calculation process manages to describe such spread states within the given valence basis and it may cause a strong valence-Rydberg mixing, which is artificial and unphysical, due to the lack of a widespread Rydberg basis. By introducing Rydberg basis functions, these states are correctly separable, i.e., valence-Rydberg splitting. This should hold true for the case of radical anions. In the discussion that follows, we will give specific examples of each radical anion. In cases where the molecule is in a solvent matrix, however, Rydberg states might be prevented because of limited space for electron-free motion. It is difficult to give an answer to the question of how much diffuse is the function most appropriate to the given experimental conditions. From a theoretical point of view, however, it looks quite artificial, and the Rydberg basis functions are generally unavoidable to ensure the consistency of theoretical calculations for basis set completeness. Nature always has a complete basis.

TABLE III. Summary of the ground and important excited states of the *t*-DCNE, TCNE, and CNB radical anions. The excitation energy: ΔE (eV), oscillator strength: f , second moment: $\langle r^2 \rangle$ (a.u.), and its perpendicular component to the molecular surface: $\langle z^2 \rangle$ (a.u.) are compared within four different basis sets. More detailed tables including all the excited states below 7 eV with basis set (4) are given in the supplementary material (Tables SIII–SV).⁵⁸

State ^a	Nature ^a	Type	Basis set (1)				Basis set (2)				Basis set (3)				Basis set (4)				ΔE (Expt.) ^b
			ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	
<i>t</i>-DCNE																			
1B _g	(π^* anion)				120.1	30.2			120.1	30.1			120.0	30.1			120.0	30.0	
3A _u	$\pi^*(S) - \pi^*(\text{Ryd})$	I	4.50	0.124	161.8	50.5	4.54	0.129	164.7	51.2	4.05	0.053	190.8	61.6	3.54	0.021	235.1	85.6	(4.0)
4A _u	$\pi - \pi^*(S)$	II	3.76	0.345	122.0	30.7	3.72	0.338	121.7	30.6	3.73	0.339	121.7	30.6	3.72	0.336	121.7	30.6	3.26
6A _u	$\pi^*(S) - \pi^*$	I	5.22	0.291	137.2	37.7	5.24	0.286	138.8	38.6	5.07	0.320	149.9	41.9	5.09	0.345	151.4	37.3	4.51
TCNE																			
1B _{2g}	(π^* anion)				179.5	43.5			179.9	43.4			179.9	43.4			179.5	43.3	
1B _{3u}	$\pi - \pi^*(S)$	II	3.29	0.298	180.6	43.6	3.26	0.292	180.8	43.5	3.27	0.293	180.6	43.5	3.26	0.292	180.5	43.5	2.82
2B _{1g}	$\pi^*(S) - \pi^*$	I	4.82	Forbidden	184.5	44.9	4.78	Forbidden	184.6	44.4	4.72	Forbidden	187.0	44.8	4.76	Forbidden	190.2	49.6	
1A _u	$\pi^*(S) - \pi^*(\text{Ryd})$	I													4.78	0.033	311.9	101.4	
2A _u	$\pi^*(S) - \pi^*(\text{dif})$	I	5.43	0.279	69.6	47.4	5.44	0.283	191.4	46.6	5.33	0.254	202.6	51.0	5.53	0.256	210.3	59.1	
5B _{3u}	$\pi^*(S) - \pi^*(\text{Ryd})$	I	6.13	0.136	73.6	59.1	6.20	0.138	209.3	58.3	5.82	0.070	232.1	69.2	5.77	0.026	246.7	92.2	
3A _u	$\pi - \pi^*(S)$	II	5.89	0.102	64.9	43.9	5.82	0.108	179.3	43.8	5.81	0.111	179.1	43.8	5.80	0.110	179.0	43.8	
6B _{3u}	$\pi^*(S) - \pi^*(\text{dif})$	I	6.83	0.163	68.1	49.9	6.87	0.070	195.3	54.5	6.57	0.054	202.3	55.5	6.64	0.149	216.6	53.8	
CNB																			
1B ₁	(π^* anion)				142.7	42.4			142.5	42.2			142.4	42.2			142.4	42.2	
1A ₂	$\pi^*(S) - \pi^*$	I	0.97	0.002	143.3	43.7	0.98	0.002	142.7	43.4	0.97	0.002	144.1	43.9	0.94	0.001	148.6	45.4	
4B ₁	$\pi^*(S) - \pi^*(\text{Ryd})$	I	3.13	0.201	184.4	58.3	3.18	0.184	187.4	59.4	2.59	0.081	216.3	70.9	1.70	0.017	283.4	95.9	(3.06)
9B ₁	$\pi^*(S) - \pi^*(\text{Ryd})$	I	4.40	0.080	179.3	52.7	4.38	0.055	188.5	57.0	3.52	0.018	218.1	69.4	3.39	0.010	219.8	81.9	(3.06)
10B ₁	$\pi^*(S) - \pi^*$	I	4.13	0.116	166.7	57.8	4.12	0.153	165.4	56.0	3.95	0.293	161.5	48.7	3.69	0.294	182.6	53.5	3.91
11B ₁	$\pi - \pi^*(S)$	II	4.06	0.245	147.0	43.6	4.06	0.246	146.9	43.5	4.03	0.253	151.8	46.0	4.00	0.202	163.1	51.6	3.91
6A ₂	$\pi - \pi^*(S)$	II	5.45	0.150	157.1	48.5	5.46	0.130	167.2	54.0	5.40	0.122	155.2	45.9	5.41	0.069	161.9	48.3	

^aBasis set (4).

^bReference 24.

TABLE IV. Summary of the ground and important excited states of the *o*-, *m*-, and *p*-DCNB radical anions. The excitation energy: ΔE (eV), oscillator strength: f , second moment: $\langle r^2 \rangle$ (a.u.), and its perpendicular component to the molecular surface: $\langle z^2 \rangle$ (a.u.) are compared within four different basis sets. More detailed tables including all the excited states below 7 eV with basis set (4) are given in the supplementary material (Tables SVI–SVIII).⁵⁸

State ^a	Nature ^a	Type	Basis set (1)				Basis set (2)				Basis set (3)				Basis set (4)				ΔE (Expt.) ^b
			ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	ΔE	f	$\langle r^2 \rangle$	$\langle z^2 \rangle$	
<i>o</i>-DCNB																			
1A ₂	(π^* anion)				173.5	48.6			173.7	48.5			173.5	48.5			173.4	48.5	
1B ₁	$\pi^*(S) - \pi^*$	I	0.93	0.007	174.7	49.6	0.92	0.006	174.4	49.3	0.92	0.006	174.9	49.5	0.90	0.006	175.3	49.6	
3A ₂	$\pi^*(S) - \pi^*(\text{Ryd})$	I													2.54	0.015	321.3	104.7	(3.32)
6A ₂	$\pi^*(S) - \pi^*(\text{dif})$	I	3.51	0.200	214.4	63.3	3.64	0.214	211.0	61.8	3.31	0.111	241.0	74.0	3.87	0.186	234.7	79.0	(3.32)
8B ₁	$\pi - \pi^*(S)$	II	4.05	0.194	176.1	49.1	4.01	0.202	176.0	49.0	3.99	0.189	175.9	49.0	3.99	0.187	176.0	49.0	3.94
7A ₂	$\pi^*(S) - \pi^*(\text{Ryd})$	I	4.42	0.094	200.7	64.2	4.47	0.090	204.6	65.1	4.14	0.150	205.8	64.9	4.04	0.102	261.4	88.0	
9A ₂	$\pi - \pi^*(S)$	II	4.83	0.091	177.4	49.2	4.81	0.105	177.3	49.0	4.78	0.093	177.3	49.1	4.77	0.090	177.5	49.1	
<i>m</i>-DCNB																			
1A ₂	(π^* anion)				184.2	48.8			184.1	48.6			184.0	48.5			184.1	48.5	
1B ₁	$\pi^*(S) - \pi^*$	I	0.67	0.005	182.8	49.2	0.67	0.005	182.7	49.0	0.65	0.005	183.0	49.1	0.63	0.005	183.4	49.2	
4B ₁	$\pi^*(S) - \pi^*(\text{Ryd})$	I													2.58	0.028	308.6	98.1	(2.76)
7B ₁	$\pi^*(S) - \pi^*(\text{Ryd})$	I	3.36	0.311	199.1	54.5	3.38	0.302	199.3	54.8	3.23	0.244	216.5	61.5	3.32	0.127	264.9	92.8	2.76
8B ₁	$\pi^*(S) - \pi^*(\text{dif})$	I	4.35	0.026	218.3	64.8	4.32	0.025	222.9	66.5	3.83	0.077	229.0	67.6	3.48	0.141	232.6	74.6	2.76
6A ₂	$\pi - \pi^*(S)$	II	4.29	0.186	187.6	49.8	4.26	0.182	187.5	49.6	4.24	0.182	187.5	49.7	4.23	0.178	189.0	50.2	3.84
11B ₁	$\pi - \pi^*(S)$	II	4.84	0.002	189.5	49.9	4.83	0.014	189.3	49.7	4.79	0.033	209.9	62.0	4.76	0.007	232.9	71.0	
<i>p</i>-DCNB																			
1B _{3u}	(π^* anion)				190.3	48.6			190.6	48.5			190.4	48.4			190.2	48.4	
1A _u	$\pi^*(S) - \pi^*$	I	1.43	Forbidden	185.7	49.8	1.42	Forbidden	185.5	49.5	1.41	Forbidden	185.8	49.6	1.41	Forbidden	186.4	49.8	
1B _{2g}	$\pi^*(S) - \pi^*(\text{Ryd})$	I	2.77	0.062	244.9	74.3	2.97	0.087	244.2	73.5	2.71	0.051	261.4	82.0	2.06	0.013	331.2	113.1	(2.90)
1B _{1g}	$\pi^*(S) - \pi^*(\text{Ryd})$	I	3.17	0.024	217.4	69.9	3.29	0.019	221.1	71.5	2.85	0.015	238.5	79.6	2.17	0.007	286.9	100.6	(3.14)
4B _{2g}	$\pi^*(S) - \pi^*(\text{dif})$	I	3.71	0.495	200.5	51.9	3.69	0.453	202.3	53.1	3.64	0.480	202.0	52.9	3.48	0.394	242.9	71.6	3.60
5B _{2g}	$\pi - \pi^*(S)$	II	3.78	0.348	192.5	49.0	3.76	0.343	192.5	48.9	3.73	0.356	192.5	48.9	3.73	0.353	192.5	48.9	3.7
6B _{2g}	$\pi^*(S) - \pi^*(\text{Ryd})$	I													4.00	0.132	291.2	92.8	(3.8)
3B _{1g}	$\pi - \pi^*(S)$	II	5.12	0.099	199.7	49.0	5.08	0.099	199.8	48.9	5.03	0.093	199.8	48.9	5.03	0.093	199.7	49.8	

^aBasis set (4).

^bReference 24.

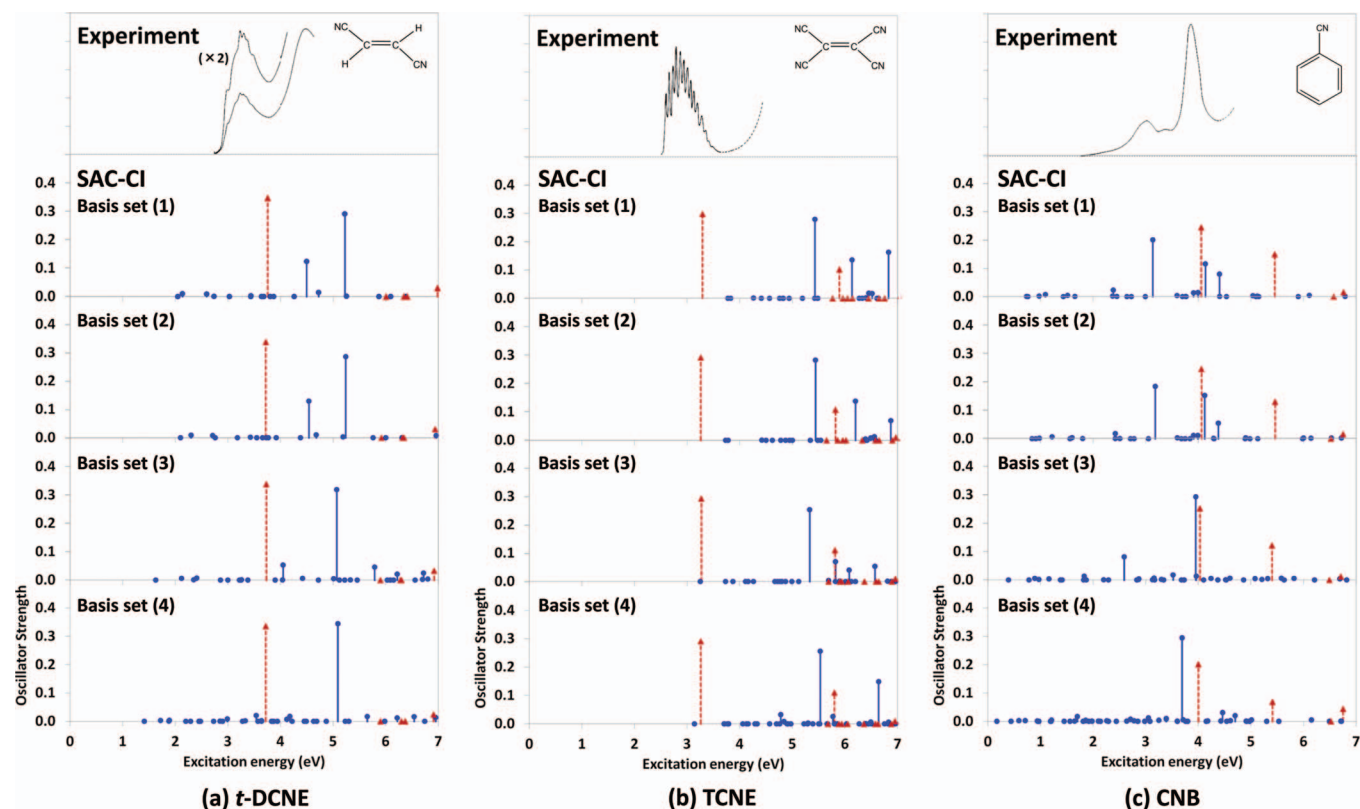


FIG. 4. SAC-CI (below) with basis sets (1) to (4) and experimental (upper) spectra of the radical anions: (a) *t*-DCNE, (b) TCNE, and (c) CNB. The blue circle and solid line in the SAC-CI spectrum show type I excitation, and the red triangle and dotted line show type II excitation. The dotted line in the experimental spectrum shows the uncertain observation.

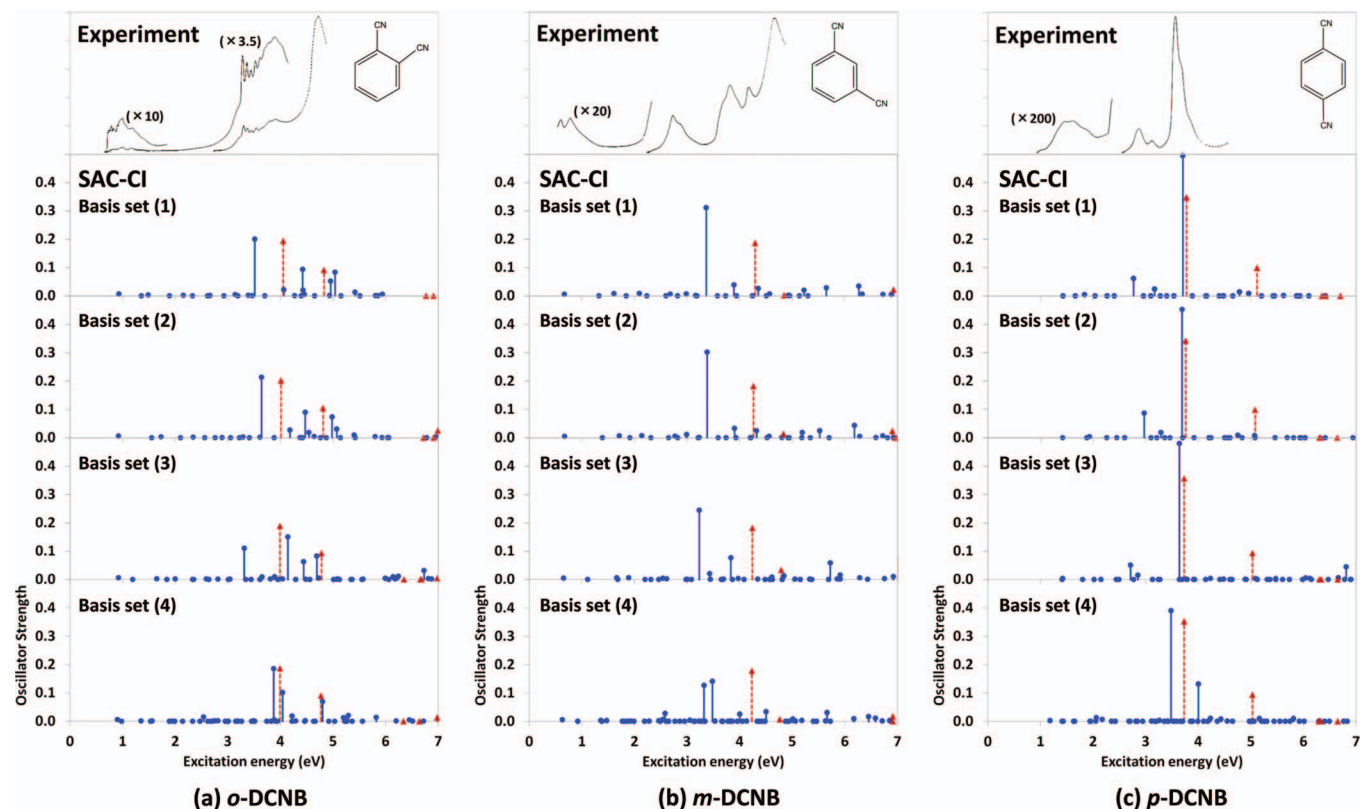


FIG. 5. SAC-CI (below) with basis sets (1) to (4) and experimental (upper) spectra of the radical anions: (a) *o*-DCNB, (b) *m*-DCNB, and (c) *p*-DCNB. The blue circle and solid line in the SAC-CI spectrum show type I excitation, and the red triangle and dotted line show type II excitation. The dotted line in the experimental spectrum shows the uncertain observation.

In the following discussion, we mainly make use of the results from basis set (4) (the largest basis, including Rydberg functions), unless otherwise specified. We provide a detailed discussion on the comparison of the results from the different basis sets, since such a comparison should be quite helpful to understand the true natures of the excited states. Detailed data with basis set (4) are provided in the supplementary material.⁵⁸ Tables SI and SII show the ROHF orbitals (MO number, symmetry, and nature). Tables SIII–SVIII provide information on all the calculated ground and excited states below 7 eV for *t*-DCNE, TCNE, CNB, *o*-DCNB, *m*-DCNB, and *p*-DCNB, respectively. In these tables, we distinguish between the anion diffuse (denoted by “dif”) and Rydberg (denoted by “Ryd”) natures, although there is no clear boundary between them. We assigned the excited state to Rydberg if its second moment (for π^* symmetry, its perpendicular component) is larger than the largest one calculated with basis set (3).

A. *t*-DCNE and TCNE anions

For the excited states of the *t*-DCNE and TCNE anions, the corresponding spectra are shown in Figs. 4(a) and 4(b), respectively. In Table III, for the *t*-DCNE anion, two important valence peaks are evident, that is, the first is $4A_u: \pi - \pi^*(S)$ belonging to type II at 3.72 eV, and the second strong peak is $6A_u: \pi^*(S) - \pi^*$ state at 5.09 eV, belonging to type I. With basis sets (1) to (3), another intense peak was found between $4A_u$ and $6A_u$. This peak indicated a redshift as a diffuse basis is introduced, and finally its intensity disappeared with the Rydberg functions in basis set (4). This state can be identified as $\pi^*(S) - \pi^*(Ryd)$ ($3A_u$ state), where a very large second moment was calculated with basis set (4). In the corresponding experimental spectrum, only two peaks appear at about 3.26 and 4.51 eV in contrast to the three peaks mentioned above. Unfortunately, however, the experimental spectral measurement was limited at about 4.7 eV because the residual parent neutral molecule of *t*-DCNE starts to absorb at about the same energies of >4.5 eV.

The table is instructive from the theoretical point of view: First, it should be noticed that the observed 3.26 eV peak, which has been corresponded to the theoretical $4A_u$ peak at 3.72 eV, is not of type I but type II with sizable oscillator strength of 0.336. This type II excited state $4A_u$ was found in a lower energy region than the valence type I excited state $6A_u$ because the $\pi^*(SOMO)$ orbital is comparably stable. Another point to note is that this first valence excited state is preceded by a number of states of type I (see Table SIII in the supplementary material⁵⁸): they mainly have $\pi^*(S) - dif$ or Ryd natures. Such states have a large second moment compared to the ground state and the valence excited states should have second moments with similar magnitude as the ground state. Since their magnitude of the oscillator strength is all minute, the detection of these states should be difficult. In fact, the spectrum in Fig. 4(a) shows no signal in the energy region of about 2.0–2.5 eV. According to the theoretical result, however, since some have small intensities, it was interesting to examine again the experimental spectra. The present calculation

predicts the occurrence of the valence state as $13A_g$ and $14B_u$ of $\sigma, n - \pi^*(S)$ and $8B_g$ and $8A_u$ of $\pi - \pi^*(S)$, belonging to type II, in the deep UV region.

The vertical electron affinity of *t*-DCNE at the anion geometry was 1.62 eV (Table II). Therefore, all the calculated excited states (except for $1A_g$) lie in the higher energy region than the ground state of neutral *t*-DCNE. Strictly speaking, these excited states are resonance state in nature. We assigned the first intense peak at about 3.26 eV in Fig. 4(a) to $4A_u: \pi - \pi^*(S)$ of type II. Therefore, several oscillatory structures on the 3.26 eV peak in the experimental spectrum should be considered as vibrational, which are likely to be observed for the type II excited state.

For the TCNE anion, the first valence excited state was calculated at 3.26 eV as $1B_{3u}: \pi - \pi^*(S)$ (type II) with large intensity (see Table III). The corresponding excited state should also be found for the neutral TCNE because it is of type II. Since the vertical electron affinity in anion geometry was 3.97 eV (see Table II), this state was considered to be a true bound state (although it was in an almost boundary region, approaching a resonance state). In the experimental spectrum of Fig. 4(b) (upper), the largest peak was found at 2.82 eV with many oscillating peaks, while in the SAC-CI spectrum of Fig. 4(b) (lower), there were no other electronic states below this excited state even with basis set (4), except for the $1A_g$ state (see Table SIV in the supplementary material⁵⁸), in contrast to the previous case of *t*-DCNE. Therefore, the many oscillating peaks in the experimental spectrum are considered to be vibrational. Type I peaks having diffuse or Rydberg natures, which appeared in the *t*-DCNE anion, were all blueshifted to a higher energy region in the TCNE anion. That is, the present type II excited state of TCNE anion is located in an energy region lower than any other type I states (except for $1A_g$). The large electron withdrawing nature of the four cyano groups must have made the first $\pi^*(SOMO)$ state very stable and the HOMO-LUMO gap very small. This explains why the type II excited state favorably exists in a lower energy region than the type I states. This explains also why the vibrational peaks are very clearly observed in the experimental spectrum.

The next excited state having a large intensity was calculated at 5.53 eV, which was $2A_u: \pi^*(S) - \pi^*(dif)$ belonging to type I. Interestingly, with basis sets (1) to (3), this state was calculated as the first state within A_u symmetry. With basis set (4), however, the lower A_u state ($1A_u$ state) was further obtained with $\pi^*(S) - \pi^*(Ryd)$ nature. This state arose from the valence-Rydberg splitting by introducing the Rydberg basis in basis set (4). The excitation energy of the $2A_u$ state gradually decreased as the basis set changed from (1) to (3); however, upon changing the basis from (3) to (4), this state showed a blueshift, again due to the existence of $1A_u$. Thus Rydberg functions are important not only for the Rydberg states but also for the valence or anion diffuse states.

We compared our results with other theoretical studies.^{22,23} The assignment of the first peak was in agreement with the CASPT2 result but the excitation energy was reported to be 2.90 eV.²² The excitation energy by the CIS method was reported as 3.40 eV.²³ For other intensive peaks larger than 5 eV, the CASPT2 calculations showed

5.56 ($b_{2g}-a_u$) and 5.89 eV ($b_{2g}-b_{3u}$). Our studies gave the same assignments, i.e., $2A_u: \pi^*(S) - \pi^*(\text{dif})$ with 5.53 eV ($b_{2g}-a_u$) and $5B_{3u}: \pi^*(S) - \pi^*(\text{dif})$ with 5.77 eV ($b_{2g}-b_{3u}$), both type I. In addition, we also identified one strong peak $3A_u: \pi - \pi^*(S)$ at 5.80 eV (a_u-b_{2g}) having type II nature. Another strong peak was found at 6.64 eV as $6B_{3u}$.

Furthermore, several other valence states with almost zero intensity or forbidden transition were also calculated: $2B_{1u}: \pi^*(S) - \sigma^*$ at 3.79 eV and $2B_{1g}: \pi^*(S) - \pi^*$ at 4.76 eV (type I); $4B_{3g}$, $9A_g$, $6B_{2u}$, $6B_{1u}$, $7B_{3g}$, $10B_{2u}$, $10B_{1u}: \sigma, n - \pi^*(S)$ (type II); and $4B_{1g}$, $5B_{2g}: \pi - \pi^*(S)$ (type II).

B. CNB, and *o*-, *m*-, and *p*-DCNB anions

The important excited states of the radical anions of CNB, *o*-, *m*-, and *p*-DCNB are summarized also in Tables III and IV and their spectra in Fig. 4(c) for CNB and Figs. 5(a)–5(c) for *o*-, *m*-, and *p*-DCNB, respectively. The CNB anion is the most unstable among the cyano compounds examined in the present study because CNB has only one cyano group. In contrast to *t*-DCNE and TCNE, the CNB radical anion gave the type I purely valence state of $1A_2: \pi^*(S) - \pi^*$ calculated at 0.94 eV. This is in a lower energy region than the state of the type II at 4.00 eV. In the corresponding experimental spectrum of Fig. 4(c), the calculated peak at 0.94 eV of $1A_2$ was not detected. The first apparent peak is seen at about 3.06 eV. With basis set (4), however, the corresponding state with a strong intensity could not be obtained. On the other hand, this peak may correspond to the $4B_1$ state at 3.13, 3.18, and 2.59 eV with basis sets (1), (2), and (3), respectively. But, this state is characterized by a considerable mix of diffuse nature. With basis set (4), this $4B_1$ state is correctly described as a Rydberg state with very small oscillator strength. The experimental peak at 3.06 eV, however, might be assigned to $8B_1$ (3.05 eV) or $9B_1$ (3.39 eV) instead of $4B_1$ in basis set (4). Although one valence state, $8B_2: \pi^*(S) - \sigma^*(\text{dif})$, was calculated at 2.85 eV, it should not be seen because of the zero oscillator strength by symmetry.

The most intense peak in the experimental spectrum of Fig. 4(c) is seen at 3.91 eV. This peak is assigned to the valence state of $10B_1: \pi^*(S) - \pi^*$: type I with a calculated energy of 3.69 eV. Another surmise regarding the experimental spectrum of Fig. 4(c) is that the slope on the higher energy side of the observed peak at 3.91 eV may be attributable to the valence state of $11B_1: \pi - \pi^*(S)$: type II at 4.00 eV. Between the observed peaks at 3.06 and 3.91 eV, there is a small hump peaking at about 3.37 eV. This hump may comprise several theoretical states having Rydberg nature, for instance, $9B_1$ state: $\pi^*(S) - \pi^*(\text{Ryd})$ at 3.39 eV. Although there are no experimental information to be compared with the theoretical result, SAC-CI gave further predictive information on high-lying states such as the ones at 5.41 eV: $6A_2, \pi - \pi^*(S)$ and at 6.75 eV: $17B_1, \pi - \pi^*(S)$, both belongs to type II, and at 6.15 eV: $15B_1$ belonging to type I. A rare character of $\sigma, n - \pi^*$ of type II was also found at 6.52 eV as $18B_2$.

With respect to the excited states of *o*-, *m*-, and *p*-DCNB radical anions, $\pi^*(S) - \pi^*$ purely valence states belonging to type I were calculated as the first excited states in *o*- and

m-DCNB and the second lowest state in *p*-DCNB (see Tables SVI–SVIII in the supplementary material⁵⁸). This is in contrast to the case of CNB, where the corresponding purely valence state at 0.94 eV was not the first excited state but diffuse and Rydberg states were located in lower energy regions. In the radical anions of *o*-, *m*-, and *p*-DCNB, the symmetries of the first valence states were $1B_1$, $1B_1$, and $1A_u$ with the excitation energies being 0.90, 0.63, and 1.41 eV, respectively, which are in the near-infrared region. The second moments and the perpendicular components of these states were similar to those of the ground states. These excitation energies were unaffected by changing the basis from (1) to (4) because of their purely valence nature. Their intensities were small in *o*- and *m*-DCNB isomers and completely zero (Forbidden) in *p*-DCNB by symmetry. The experimental spectra of Figs. 5(a) and 5(b) show that the weak IR states for *o*- and *m*-DCNB are noticeable. However, in the spectrum of Fig. 5(c) for the *p*-DCNB anion, there seemed to be no corresponding IR states at the time of the experiment for the publication of the databook of Ref. 24. Now that the present theoretical calculation predicts the above valence state, $1A_u: \pi^*(S) - \pi^*$, and also very weak Rydberg states around it for the para isomer. The author (T.S.) re-examined the experimental spectrum to find an extremely weak signal as shown in the inset with a mark of amplification factor of 200 (see Fig. 5(c)). The *p*-DCNB anion belongs to D_{2h} symmetry and the excitation to $1A_u$ is optically forbidden and, therefore, the intensity should be smaller than those of the *o*- and *m*-DCNB that belong to C_{2v} and the excitation is not symmetry forbidden. In the experiment, it was quite difficult to distinguish whether this very small peak was a physical state or just noise. But, with the help of the present theoretical study, we determined the existence of the valence electronic state in this energy region. The rediscovery is regarded as a good example of demonstrating the predictive power of dependable calculation of excited electronic states.

In the three isomers, the next states associated with sizable oscillator strengths were calculated as $6A_2$, $7B_1$, and $4B_{2g}$ (all belonging to type I). In the *o*- and *m*-DCNB isomers, these states have the nature $\pi^*(S) - \pi^*(\text{dif})$. They showed slight redshifts with basis set (3) compared to the cases with basis sets (1) and (2), but, conversely, they showed blueshifts with basis set (4). In *o*-DCNB, the blueshift was quite drastic, i.e., basis set (3): 3.31 eV and basis set (4): 3.87 eV. They can be regarded as the valence (anion diffuse) – Rydberg state splitting, where the $6A_2$ state goes to $3A_2: \pi^*(S) - \pi^*(\text{Ryd})$ and $6A_2: \pi^*(S) - \pi^*(\text{dif})$ in *o*-DCNB, and the $7B_1$ state to $4B_1: \pi^*(S) - \pi^*(\text{Ryd})$ and $7B_1: \pi^*(S) - \pi^*(\text{dif})$ in *m*-DCNB. The latter states still have sizable intensities in both anions. On the other hand, in *p*-DCNB, such a state separation was not detected, and the $4B_{2g}$ state was calculated at 3.48 eV as $\pi^*(S) - \pi^*$ with basis set (4), and still with strong intensity. We assigned these states in the three isomers to the experimental peaks of 3.32, 2.76, and 3.60 eV, respectively. In *o*-DCNB, however, if the results with basis set (4) are accurately comparable, even with the spectrum in the matrix solvent, the oscillating peaks around 3.32 eV may be only showing the vibrational states. If this is true, then the $6A_2$ state may be assigned to the experimental peak around 3.94 eV. Good

experimental agreement was obtained for the *p*-DCNB anion but for the *m*-DCNB anion the theoretical value was somewhat blueshifted. The first type II excited states of the *o*-, *m*-, *p*-DCNB isomers were obtained as $8B_1$ at 3.99 eV, $6A_2$ at 4.23 eV, and $5B_{2g}$ at 3.73 eV, whose natures were $\pi - \pi^*(S)$. The experimental peaks we assigned are 3.94, 3.84, and 3.7 eV, respectively. Nice agreements with the experimental spectra were obtained for *o*- and *p*-DCNB, but for *m*-DCNB the theoretical excitation energy was blueshifted again with respect to the experimental value. In the following, further discussions on each isomer will be made.

First, in *o*-DCNB, although the experimental observation on the *o*-DCNB was limited at about 4 eV as shown in Fig. 5(a), the calculation shows that the states of $7A_2: \pi^*(S) - \pi^*(Ryd)$ (type I) at 4.04 eV, $9A_2: \pi - \pi^*(S)$ (type II) at 4.77 eV, and $10B_1: \pi^*(S) - \pi^*(dif)$ (type I) at 4.80 eV are associated with sizable oscillator strengths. The theory also predicts $13B_1: \pi - \pi^*(S)$ (type II) at 6.64 eV, $13A_2: \pi - \pi^*(S)$ (type II) at 6.98 eV, and an uncommon state of the nature of $\sigma, n - \pi^*$ (type II) at 6.34 and 6.64 eV as $21A_1$ and $18B_2$, respectively.

Second, in *m*-DCNB, the barely seen structured shoulder on the higher energy side of the observed 2.76 eV peak might be assigned to $8B_1: \pi^*(S) - \pi^*(dif)$ (type I) at 3.48 eV. The theoretical prediction on the *m*-DCNB anion gives information on states of high energy and medium intensity which, however, exceed the experimental states to be compared. Anyway, they include $11B_1: \pi - \pi^*(S)$ (type II) at 4.76 eV, $9A_2: \pi^*(S) - \pi^*(dif)$ (type I) at 5.66 eV, $10A_2: \pi^*(S) - \pi^*(dif)$ (type I) at 6.45 eV, and $16B_1: \pi - \pi^*(S)$ (type II) at 6.91 eV. $\sigma, n - \pi^*$ state is observed at 6.91 eV as $21A_1$.

Third, in *p*-DCNB, $5B_{2g}: \pi - \pi^*(S)$ (type II) at 3.73 eV was close to $4B_{2g}: \pi^*(S) - \pi^*$ (type I) at 3.48 eV. With basis set (4), one more sizable peak was calculated at 4.00 eV for $6B_{2g}: \pi^*(S) - \pi^*(Ryd)$ (type I), whose corresponding peak was not found with basis sets (1) to (3). Therefore, the experimental sharp peak in Fig. 5(c) in the range about 3.6–3.8 eV is regarded as being due to a superposition of the above two or three theoretical states. The experimental peak appears to have two shoulders on the higher energy side of the sharp peak at 3.60 eV, and the above three theoretical states may be the one-to-one correspondences to them. The third peak might be detected only in a gas phase, however, because it has Rydberg nature. Theoretical results also give detailed predictions for other remarkable states to be compared with the experimental spectrum in Fig. 5(c); there are several states between the first excited state of $1A_u$ at 1.41 eV and the prominent state $4B_{2g}$ at 3.48 eV. Except for those states forbidden by symmetry, such states were calculated as $1B_{2g}$ at 2.77, 2.97, and 2.71 eV, and $1B_{1g}$ at 3.17, 3.29, and 2.85 eV with basis sets (1) to (3), respectively. Both have diffuse natures belonging to type I. They might correspond to the experimental peaks of 2.90 and 3.14 eV, respectively. With basis set (4), however, these states showed large redshifts with very small oscillator strengths and they have Rydberg nature. Therefore, the experimental peaks at 2.90 and 3.14 eV might only be detected in the matrix solvent. In the energy region higher than $5B_{2g}$ at 3.73 eV, there is one state $3B_{1g}: \pi - \pi^*(S)$ (type II) at 5.03 eV with some oscillator strengths. Although the type II states

such as $10B_{3u}: \pi - \pi^*(S)$ at 6.29 eV, $8B_{3g}: \sigma, n - \pi^*(S)$ at 6.33 eV, and $11B_{2u}: \sigma, n - \pi^*(S)$ at 6.65 eV are of rare nature, they had no intensity by symmetry. As shown in Fig. 5(c), the theoretical spectrum of the *p*-DCNB anion was in good agreement with the experimental data.

Finally, when one reviews the experimental spectra of the cyanobenzene radical anions in Figs. 4(c) and 5(a)–5(c), one notices that the shapes of the spectra of CNB and *p*-DCNB look similar, but those of *o*-DCNB and *m*-DCNB are not similar to those of CNB and *p*-DCNB. The first type II peaks corresponding in these four radical anions were calculated at 4.00, 3.99, 4.23, and 3.73 eV as $11B_1$, $8B_1$, $6A_2$, and $5B_{2g}$, respectively (see Tables III and IV). The intense type I peaks were obtained at 3.69, 3.87, 3.32, and 3.48 eV as $10B_1$, $6A_2$, $7B_1$, and $4B_{2g}$. The nature of *o*- and *m*-DCNB has diffuse property but that of CNB and *p*-DCNB indicates almost valence. In the cases of *o*- and *m*-DCNB, the diffuse orbital from the second CN group mixes with the valence orbital, but in the case of *p*-DCNB they do not mix, due to the symmetry of D_{2h} . In the case of CNB, there is no second CN group. As a result, in *o*-DCNB and *m*-DCNB the present type I states are likely to be affected by the diffuse orbitals, but in CNB and *p*-DCNB, such a state of mixing is not crucial, and the above type I and type II states still appear in the near position. This is the reason for the similarity of the spectra of CNB and *p*-DCNB. The superposition of these states should produce highly intense peaks around 3.91 and 3.60 eV, as observed in the CNB and *p*-DCNB experiments, respectively.

C. Common features of the present radical anions

In the excited states of the radical anions studied in the present investigation, many diffuse and Rydberg states were obtained and the excited states of the valence excitations were found to be embedded in these states. A careful examination of the orbital nature and the second moment permitted us to distinguish the valence excitations from the excitations having diffuse or Rydberg natures. In the present molecules, the most important valence states having large intensities were mainly $\pi^*(S) - \pi^*$ in type I and $\pi - \pi^*(S)$ in type II, which is compatible with the experimental spectra. For the system containing the N and/or O lone pair orbital, the $n - \pi^*$ excited state should be found. For example, in the *p*-benzoquinone radical anion, $n - \pi^*$ excited states were found at 2.38 and 2.44 eV.²¹ In the present cyano compounds, however, $n - \pi^*$ excited states were calculated in higher energy regions (>5 eV) because the *n* orbital is independent from the *sp*-hybrid CN bond, allowing it to have lower orbital energy and, thus the excitation energy from this orbital should be higher. This is in contrast to the case of *p*-benzoquinone where the *sp*²-hybrid nature dominates.

When the vertical excitation energy exceeds the vertical electron affinity at the anionic geometry, the corresponding excited state should be of a resonance state. Such resonance states can be classified into three cases as illustratively shown in Fig. 6. The first case of Fig. 6(a) corresponds to excited states from type I. This can be always seen as a shape resonance because, when the singly occupied electron goes to infinity, the state M^{-*} asymptotically approaches to the ground

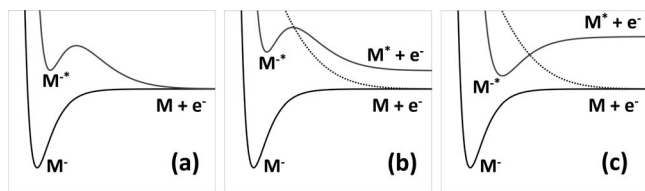


FIG. 6. Illustrations of three types of classifications of resonance: (a), shape resonance (type I); (b), core-excited shape resonance (type II); and (c), Feshbach resonance (type II). The vertical and horizontal axes denote the potential energy and the coordinate of an electron, respectively. $M^{\bullet-}$ and $M + e^-$ describe the radical anion and the neutral molecule + free electron, respectively, and $M^{\bullet-*}$ and $M^{\bullet-} + e^-$ show their corresponding excited states. Solid lines of dark and light colors represent the ground and excited states, respectively, and the dotted line represents the dissociation channel to the ground state of the neutral molecule, if it exists.

state of the neutral molecule, $M + e^-$. The type II excited state requires a two-electron process for the electron detachment to reach the state of $M + e^-$. One electron in the highest doubly occupied orbital goes to infinity as the first step and the other electron in this orbital needs to go down to the HOMO of the ground state of the neutral molecule as the second step. So, the process requires two potential curves, moving to a different channel. Such type II excited states can be divided into core-excited shape resonance (Fig. 6(b)) and Feshbach resonance (Fig. 6(c)). That classification depends on whether the energy position of $M^{\bullet-*}$ is higher or lower than the corresponding excited state of the neutral molecule, $M^* + e^-$. Generally, more stabilization is achieved in type II especially in the Feshbach resonance case.^{21,31} Therefore, the fine spectrum appearing as vibrational levels may be more likely to be observed in that case. In this sense, it is worth distinguishing the nature of the excited states of type I (shape resonance) and type II, and also type II to core-excited shape resonance and Feshbach resonance.

Finally, we wish to remark on the experimental spectra. All the experimental spectra discussed in Secs. V A and V B are reproduced from Shida,²⁴ a book that contains over 700 recorded spectra of radical cations and anions obtained by one of the present authors. Most of the spectra, including those discussed in the present article, have not yet been reported in scientific journals; hence these spectra can be regarded as a primary release of original scientific data. This is the first time that high-level theoretical assignments for them are provided by the SAC-CI method.

VI. SUMMARY

The ground and excited states of the radical anions of several cyano compounds were investigated by SAC-CI theoretical calculations in comparison with the experimental electronic absorption spectra. All the present cyano compounds are found to have positive electron affinities in good agreement with the experimental values in the gas phase. There have been very few comparative studies that present both theoretical and experimental electronic absorption spectra of radical anions even today. The present study has disclosed that the SAC-CI theoretical calculation can reproduce detailed features of the experimental spectra particularly for CNB, *o*-

DCNB, and *p*-DCNB. As for the systems of *t*-DCNE, TCNE, and *m*-DCNB anions, a general tendency is that the calculated energies are higher than the experimental by 0.3–0.5 eV. By comparing the results from the different basis sets, we were able to make conclusions about the valence, anion diffuse, and Rydberg excited states. After the examination of calculation conditions, especially for the basis set dependency, the usual excuse for such a discrepancy is to call for the effect of matrix. Although the authors do not exclude this possibility, they do not lean totally upon the matrix effect either on the basis of the reason mentioned briefly in Sec. V. The basis set completeness is surely important in theoretical calculations. Rydberg basis functions are important not only for anion diffuse and Rydberg excited states but also for valence-nature states due to valence-Rydberg splitting. Without including the Rydberg basis, not only the Rydberg states, but also the valence states, are not correctly described. This fact may not be well known, but the accurate excited states obtained from SAC-CI indicated its importance very clearly.

Type I excitations from $\pi^*(\text{SOMO})$ to unoccupied MOs are proper to anions and not to neutral closed-shell molecules. Such excitations should, in general, occur in lower energy regions than the type II excitation of occupied $-\pi^*(\text{SOMO})$. However, in the case of radical anion of TCNE, the type II excitation precedes type I excitations obviously due to the large stabilization of $\pi^*(\text{SOMO})$ orbital of the TCNE anion. The experimental spectrum shows clear vibrational structure, which is worthy of future study. By extending the present work, provocative problems as photo-related molecular designs of cyano compounds, for example, may be challenged.

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