

# Electronic Spectra and Excited-State Dynamics of van der Waals Clusters of Anthracene with Aliphatic and Aromatic Ethers: Dependence of Exciplex Formation on Donor (Ether) Ionization Potential

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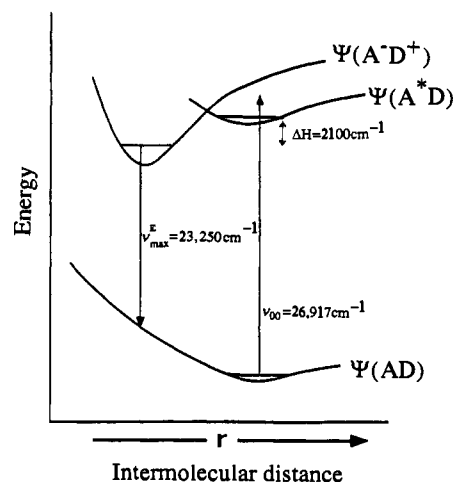
Received January 18, 1994. Revised Manuscript Received June 3, 1994<sup>⊙</sup>

**Abstract:** We have carried out a systematic study of exciplex formation from photoexcited van der Waals complexes of anthracene with a variety of ethers, under collision-free conditions of a supersonic jet. Unlike some of the previously reported results, we have observed only narrow bands in the fluorescence excitation spectra. The exciplex fluorescence was observed only from the complex containing donor moiety with the lowest ionization potential (viz., 1,4-dimethoxybenzene), thus providing clear evidence for the dependence of exciplex formation on the ionization potential of the donor (ether) moiety. These results indicate that the energy of the charge transfer state relative to that of the initially prepared locally excited state determines the efficiency of the exciplex formation. In contrast to the previous report of exciplex formation in anthracene/diethyl ether and anthracene/anisole systems, we have observed only van der Waals type emissions from the locally excited states.

## Introduction

Charge transfer interactions between an electronically-excited molecule of one kind and a ground-state molecule of another, leading to the formation of an exciplex, have extensively been studied since the pioneering work of Weller<sup>1</sup> and Mataga.<sup>2</sup> Although the basic spectroscopic features and dynamics of exciplex formation are well-known from the condensed-phase studies, the effective merger between laser and supersonic jet has recently renewed active interest in the study of exciplexes. The reason for this is that in the collision-free environment of supersonic jets, exciplex formation can only be initiated by photoexcitation of a component (electron donor or acceptor) molecule in the pre-formed ground-state van der Waals (vdW) complex.<sup>3</sup> The exciplex formation in a supersonic jet can therefore be considered to be a "half-collision" by comparison to the "full" collision in which reactants approach from large separation.<sup>4</sup> Thus, important questions pertaining to the dynamics of gas-phase reactions, such as vibrational energy and mode dependence of the product formation, can be addressed to the laser-excited half-collision studies of gas-phase exciplexes in supersonic jets.

A systematic study of the vdW complexes of 1-cyanonaphthalene (CNN) with aliphatic amines, by Saigusa and Lim,<sup>5</sup> has shown that the efficiency of the exciplex formation in the photoexcited vdW complexes depends on both the ionization potential (IP) of the amine (electron donor, D) and the excess vibrational energy of the electronically excited CNN (electron acceptor, A) moiety. Thus, the complex involving the donor molecule with the highest IP (viz., ammonia) does not exhibit exciplex formation even at high excess energies, whereas that involving the donor molecule with the lowest IP (viz., tributylamine) forms an exciplex even at zero excess energy. For donors



**Figure 1.** A schematic potential energy diagram illustrating various energy parameters of the vdW complex and exciplex of anthracene with 1,4-dimethoxybenzene.

with intermediate IPs (dimethylamine, diethylamine, trimethylamine and tripropylamine), the exciplex formation from the locally excited (LE) state A\*D of the vdW complex requires excess energy above a certain threshold value.<sup>5</sup> These results indicate that the exciplex formation in these systems is driven primarily by charge-transfer (CT) force, and the energy of the CT state A<sup>-</sup>D<sup>+</sup> relative to that of the initially excited LE state of the complex determines the efficiency of the exciplex formation. A schematic diagram illustrating the exciplex formation in a supersonic jet is given in Figure 1.

In contrast to the above results the vdW complexes of anthracene with different aliphatic and aromatic ethers, studied by several groups,<sup>6-8</sup> do not exhibit a simple dependence on donor strength for the exciplex formation. Thus, while 1:1 complexes of anthracene with diethyl ether (IP = 9.60 eV) and anisole (IP

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<sup>⊙</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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= 8.21 eV)<sup>6,7</sup> have been reported to form exciplexes, those having donors with much smaller IPs like 1,2-dimethoxybenzene (IP = 8.05 eV) and 1,3-dimethoxybenzene (IP = 8.00 eV) are reported not to form exciplexes.<sup>8</sup> The formation of an exciplex from the vdW complex of anthracene with diethyl ether, if real, is truly remarkable since photoexcited anthracene in neat aliphatic ethers does not form an exciplex in the condensed phase. Even more remarkable is the report<sup>9</sup> that the vdW complex of anthracene with ammonia (IP = 10.85 eV) exhibits exciplex formation in a supersonic jet. Since the electron affinities (or reduction potentials) of anthracene and CNN are very similar and the LE state of CNN lies above that of anthracene, it is difficult to account for the lack of the exciplex formation in the 1-cyanonaphthalene complex with ammonia,<sup>5</sup> if the interpretation of Anner and Haas is correct.

In view of these discrepancies and unexpected results and because of the spectral similarity of the "exciplex fluorescence" of Anner and Haas to our recently reported excimer fluorescence of anthracene,<sup>10</sup> we have reinvestigated the photophysical properties of the vdW complexes of anthracene with diethyl ether, anisole, and two dimethoxybenzenes (1,2- and 1,4-). We show here that only the vdW complex of anthracene with 1,4-dimethoxybenzene (IP = 7.5 eV) forms an exciplex upon electronic excitation. In all other cases only the fluorescence from the LE state of the vdW complex is observed. These observations demonstrate, once again, that the efficiency of the exciplex formation in the photoexcited vdW complexes is intimately related to the ionization potential of the donor molecule. The "exciplex fluorescence" reported by Anner and Haas<sup>6,7,9</sup> appears to be due to the excimer fluorescence from anthracene dimer, solvated by ethers.

## Experimental Section

The apparatus used for measuring fluorescence excitation and dispersed fluorescence spectra was fully described previously.<sup>11</sup> Anthracene, dimethoxybenzenes, anisole, and diethyl ether were the highest purity Aldrich samples, used without further purifications. The sample compartment containing one-refined anthracene was heated only to 100–110 °C to minimize the formation of pure anthracene clusters. Helium at a pressure of 20 psi was first passed through a reservoir containing ether. The vapor pressure of the ether was carefully regulated by maintaining the fixed temperature of the container. The gas mixture was finally passed through the heated anthracene compartment and expanded through a pulsed pinhole nozzle (General Valve) of diameter 0.5 mm and operated at a frequency of 12 Hz. The fluorescence excitation spectrum was measured by collecting fluorescence after eliminating the stray laser lights by optical filters, whereas the dispersed fluorescence spectrum was measured with a 0.64 m monochromator (Jovin Yvon). The excitation source was a frequency-doubled output of an excimer-pumped dye laser (Lambda Physik LPX110i+FL3002E). The signal from the photomultiplier was processed by a boxcar integrator (Stanford Research Systems SR 250). For measuring the hole burning spectrum the source of a second laser was the frequency mixed output of a dye laser (Quanta Ray PDL-1) with YAG fundamental. The dye laser was pumped by the second harmonic of a Nd:YAG laser (Continuum NY61-10). An autotracking system (Quanta Ray WEX-1) was used to maintain efficient frequency mixing during wavelength scan. The pump and the probe lasers were introduced into the chamber in an anticollinear direction and the probe laser was softly focused at the crossing region with the molecular beam.

The hole burning spectrum was recorded by scanning the pump laser with the time delayed probe laser fixed on a strong transition of the vdW complex.<sup>12</sup> The experiment starts with initial excitation of the complex by the strong pump laser. Subsequently, spontaneous fluorescence and internal conversion populate vibronic levels of the electronic ground state. Since many of these levels are no longer resonant at the probe wavelength, there is a depletion of the fluorescence signal induced by the delayed probe laser at all vibronic transitions involving the originally excited ground-state complex. Scanning the pump laser with the fixed probe

laser then generates the hole burning spectrum, which corresponds to an inverted absorption spectrum of the complex. In order to avoid any leakage from the strong pump laser signal, the probe laser was delayed by several lifetimes of the complex from the pump laser. Because of a finite velocity of the helium jet the pump laser was spatially shifted by a few millimeters toward the nozzle. This spatial separation was optimized to obtain maximum depletion.

## Results

Owing to the weak intensity of the single-vibronic-level (SVL) fluorescence from the locally excited (LE) states of the vdW complexes, it was not possible to disperse this SVL emission well for any of the systems we have studied. Thus, the question of the presence or absence of the LE fluorescence was determined on the basis of the spectral region of emission (deduced by the use of a combination of color filters) and the measured fluorescence lifetime. When the wavelength region and the lifetime of fluorescence are very similar to those of bare anthracene (370–420 nm and ~20 ns), the emission is considered to be the LE (A\*D) type. Conversely, a strongly Stokes shifted structureless fluorescence with a long lifetime (>>20 ns) is taken to be an exciplex (A-D<sup>+</sup>) type. In what follows, we describe the electronic spectra of various anthracene/ether vdW clusters in the order of increasing ionization potential of the donor (ether) molecule.

**Anthracene/1,4-Dimethoxybenzene.** Figure 2 shows the fluorescence excitation spectrum of the vdW complex of anthracene with 1,4-dimethoxybenzene in the spectral region lower in energy than the electronic origin band of anthracene. The spectrum was obtained by using an optical filter (LF 399) that transmits light of wavelength longer than 380 nm. The longest wavelength feature in the spectrum appears at 371.514 nm. To the higher energy side of this longest wavelength feature, the spectrum exhibits a progression of a low-frequency vibration of frequency ca. 20 cm<sup>-1</sup>, which can only be assigned to an intermolecular vdW mode of the complex (denoted by A in Table 1). The same progression repeatedly appears throughout the spectrum as combinations over other vibronic origins. The first two of these vibronic origins appear at 371.13 and 370.63 nm, respectively. The spacings of these origins from the longest wavelength feature at 371.514 nm are 28 and 63 cm<sup>-1</sup>, respectively (Figure 2). These small frequency separations indicate that other intermolecular vdW modes serve as the vibronic origins of the additional progressions. A clean progression involving the same vdW mode starts again from 366.26 nm, at 386 cm<sup>-1</sup> above the longest wavelength feature. Since the 386 cm<sup>-1</sup> spacing is the same as the excited-state frequency of  $\nu_{12}$  in bare anthracene, we assign the longest wavelength band at 371.514 nm as the origin of the S<sub>1</sub>-S<sub>0</sub> absorption system of the 1:1 vdW complex and the band at 0 + 386 cm<sup>-1</sup> to 1<sub>2</sub><sup>1</sup>.

At about 200 cm<sup>-1</sup> above the electronic origin of the complex, strong features due to the vdW complex appear over an underlying Gaussian shaped background. The intensity of this background, relative to the strong sharp features, increases with increasing concentration of 1,4-DMB, suggesting that the background might be due to a higher cluster of anthracene with more than one 1,4-DMB molecule.

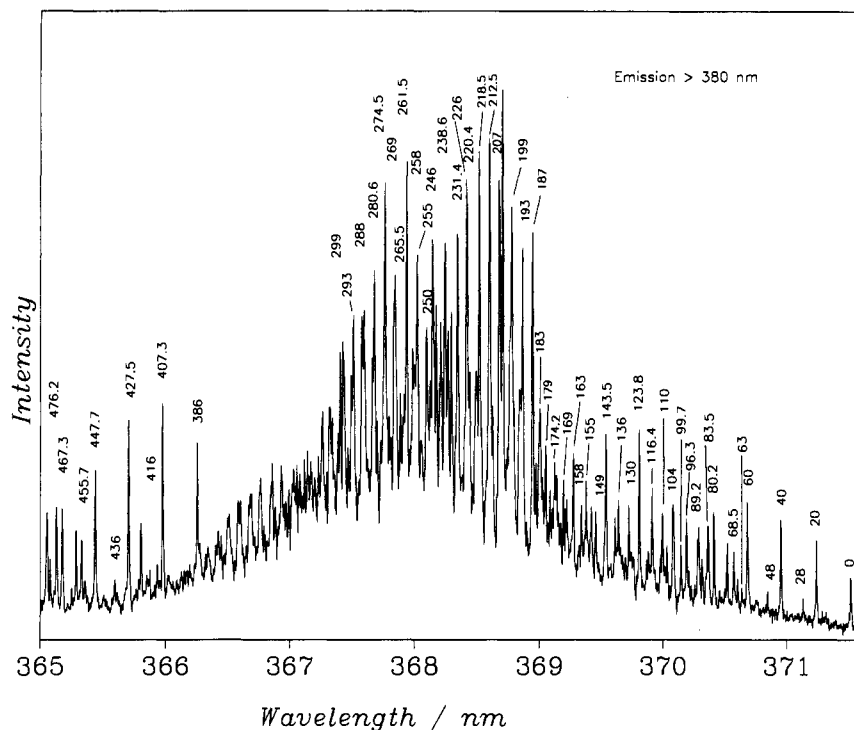
When the excitation spectrum is measured using a filter transmitting light of wavelengths longer than 480 nm, the intensities of the lower energy (>369 nm) features decrease dramatically relative to those of the higher-energy features, as shown in Figure 3. This indicates that the excitation in the low-energy region of the spectrum leads to fluorescence which has major intensities at wavelengths substantially shorter than 480 nm, whereas excitation at the higher energy region produces mainly red-shifted emission. Consistent with this conclusion, excitation of the 212.5 cm<sup>-1</sup> band (and other bands at higher energies) leads to a strongly Stokes shifted, structureless fluorescence in Figure 4, which bears no features attributable to emission from the initially excited vibronic level. This, together with the long decay time (~100 ns) of the emission, leads us to assign the red-shifted structureless emission to the exciplex

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**Figure 2.** Fluorescence excitation spectrum of the van der Waals complex of anthracene with 1,4-dimethoxybenzene. The band positions are denoted in wavenumber unit relative to the electronic origin of the complex at 371.514 nm.

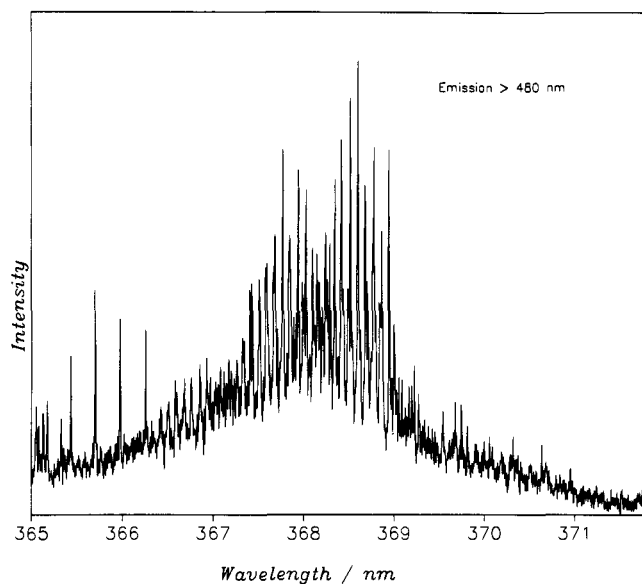
**Table 1.** Vibrational Assignment of the Fluorescence Excitation Spectrum of a 1:1 vdW Complex of Anthracene with 1,4-Dimethoxybenzene

band position (nm)	freq rel to the original band (cm <sup>-1</sup> )	assign	band position (nm)	freq rel to the original band (cm <sup>-1</sup> )	assign	band position (nm)	freq rel to the original band (cm <sup>-1</sup> )	assign
371.514	0	A <sub>0</sub> <sup>0</sup>	369.45	149	E <sub>0</sub> <sup>1</sup>	368.09	250	J <sub>0</sub> <sup>1</sup>
371.23	20	A <sub>0</sub> <sup>0</sup>	369.38	155	F <sub>0</sub> <sup>1</sup>	368.03	255	A <sub>0</sub> <sup>1</sup> I <sub>0</sub>
371.13	28	B <sub>0</sub> <sup>1</sup>	369.34	158	G <sub>0</sub> <sup>1</sup>	367.98	258	A <sub>0</sub> <sup>3</sup> G <sub>0</sub> <sup>1</sup>
370.95	40	A <sub>0</sub> <sup>2</sup>	369.22	163	A <sub>0</sub> <sup>3</sup> C <sub>0</sub> <sup>1</sup>	367.94	261.5	A <sub>0</sub> <sup>2</sup> H <sub>0</sub> <sup>1</sup>
370.84	48	A <sub>0</sub> <sup>3</sup> B <sub>0</sub> <sup>1</sup>	369.19	169	A <sub>0</sub> <sup>4</sup> E <sub>0</sub> <sup>1</sup>	367.88	265.5	A <sub>0</sub> <sup>0</sup> F <sub>0</sub> <sup>1</sup>
370.68	60	A <sub>0</sub> <sup>3</sup>	369.12	174.2	A <sub>0</sub> <sup>1</sup> F <sub>0</sub> <sup>1</sup>	367.84	269	A <sub>0</sub> <sup>1</sup> J <sub>0</sub> <sup>1</sup>
370.63	63	C <sub>0</sub> <sup>1</sup>	369.05	179	A <sub>0</sub> <sup>1</sup> G <sub>0</sub> <sup>1</sup>	367.76	274.4	A <sub>0</sub> <sup>2</sup> I <sub>0</sub> <sup>1</sup>
370.57	68.5	A <sub>0</sub> <sup>2</sup> B <sub>0</sub> <sup>1</sup>	369	183	A <sub>0</sub> <sup>0</sup> C <sub>0</sub> <sup>1</sup>	367.68	280.7	A <sub>0</sub> <sup>3</sup> H <sub>0</sub> <sup>1</sup>
370.41	80.2	A <sub>0</sub> <sup>3</sup>	368.95	187	A <sub>0</sub> <sup>2</sup> E <sub>0</sub> <sup>1</sup>	367.58	288	A <sub>0</sub> <sup>2</sup> J <sub>0</sub> <sup>1</sup>
370.36	83.5	A <sub>0</sub> <sup>1</sup> C <sub>0</sub> <sup>1</sup>	368.86	193	A <sub>0</sub> <sup>2</sup> F <sub>0</sub> <sup>1</sup>	367.49	296.3	A <sub>0</sub> <sup>3</sup> I <sub>0</sub> <sup>1</sup>
370.29	89.2	A <sub>0</sub> <sup>3</sup> B <sub>0</sub> <sup>1</sup>	368.78	199	A <sub>0</sub> <sup>2</sup> G <sub>0</sub> <sup>1</sup>	367.43	299	A <sub>0</sub> <sup>4</sup> H <sub>0</sub> <sup>1</sup>
370.19	96.3	D <sub>0</sub> <sup>1</sup>	368.68	207	A <sub>0</sub> <sup>3</sup> E <sub>0</sub> <sup>1</sup>	366.26	386	ν <sub>12</sub>
370.14	99.7	A <sub>0</sub> <sup>3</sup>	368.6	212.5	A <sub>0</sub> <sup>3</sup> F <sub>0</sub> <sup>1</sup>	365.97	407.3	ν <sub>12</sub> A <sub>0</sub> <sup>1</sup>
370.08	104.0	A <sub>0</sub> <sup>2</sup> C <sub>0</sub> <sup>1</sup>	368.52	218.5	A <sub>0</sub> <sup>3</sup> G <sub>0</sub> <sup>1</sup>	365.86	416	ν <sub>12</sub> B <sub>0</sub> <sup>1</sup>
369.99	110.5	A <sub>0</sub> <sup>4</sup> B <sub>0</sub> <sup>1</sup>	368.49	220.4	H <sub>0</sub> <sup>1</sup>	365.7	427.5	ν <sub>12</sub> A <sub>0</sub> <sup>2</sup>
369.91	116.4	A <sub>0</sub> <sup>4</sup> D <sub>0</sub> <sup>1</sup>	368.428	226	A <sub>0</sub> <sup>4</sup> E <sub>0</sub> <sup>1</sup>	365.59	436	ν <sub>12</sub> A <sub>0</sub> <sup>3</sup> B <sub>0</sub> <sup>1</sup>
369.87	119.7	A <sub>0</sub> <sup>4</sup>	368.34	231.4	A <sub>0</sub> <sup>4</sup> F <sub>0</sub> <sup>1</sup>	365.43	447.8	ν <sub>12</sub> A <sub>0</sub> <sup>3</sup>
369.81	123.8	A <sub>0</sub> <sup>3</sup> C <sub>0</sub> <sup>1</sup>	368.29	235	I <sub>0</sub> <sup>1</sup>	365.33	455.7	ν <sub>12</sub> A <sub>0</sub> <sup>2</sup> B <sub>0</sub> <sup>1</sup>
369.72	130	A <sub>0</sub> <sup>3</sup> B <sub>0</sub> <sup>1</sup>	368.25	238.6	A <sub>0</sub> <sup>4</sup> G <sub>0</sub> <sup>1</sup>	365.17	467.4	ν <sub>12</sub> A <sub>0</sub> <sup>4</sup>
369.65	136.0	A <sub>0</sub> <sup>4</sup> D <sub>0</sub> <sup>1</sup>	368.21	241.2	A <sub>0</sub> <sup>4</sup> H <sub>0</sub> <sup>1</sup>	365.055	476.4	ν <sub>12</sub> A <sub>0</sub> <sup>3</sup> B <sub>0</sub> <sup>1</sup>
369.54	143.5	A <sub>0</sub> <sup>4</sup> C <sub>0</sub> <sup>1</sup>	368.15	246	A <sub>0</sub> <sup>4</sup> E <sub>0</sub> <sup>1</sup>			

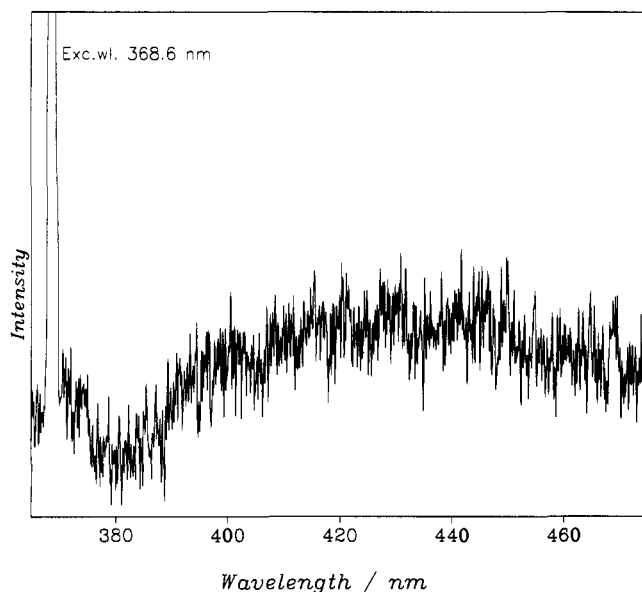
fluorescence of the complex. Although it was not possible to disperse the shorter-wavelength fluorescence produced by the low-energy excitations, due to low intensities, the similarity of its spectral position and short decay time to the SVL fluorescence from the bare anthracene allow us to assign it to the LE emission of the vdW complex. The excitation spectrum of vdW type fluorescence (in the 380–410 nm region) and that of the exciplex fluorescence (in the wavelength region longer than 480 nm) are compared in Figure 5. A number of hot bands are observed in the former case and are marked by asterisks. It is evident that the emission is primarily of LE type for excitations up to about 183 cm<sup>-1</sup> above the electronic origin of the complex, and mostly of exciplex type for vibrational energies greater than about 183 cm<sup>-1</sup>. Thus, there is a threshold excess vibrational energy associated with the exciplex formation.

Figure 6 compares the fluorescence excitation spectrum with

the hole-burning spectrum which measures the inverted absorption spectrum of a selected single species. The hole-burning spectrum was obtained by fixing the probe laser at 368.6 nm (12<sub>0</sub><sup>1</sup> transition of the complex) and scanning the pump laser throughout the region of the absorption spectrum. Several conclusions can be made from the comparison. First, it clearly distinguishes the complex bands from the hot monomer bands marked by asterisks. Second, all of the bands appearing in the fluorescence excitation spectrum also appear in the hole-burning spectrum, indicating that all the distinct bands in the excitation spectrum belong to a single species of the complex (with definite stoichiometry and conformation). Third, the intensity distribution over the different energy region of the hole-burning spectrum, which resembles the genuine intensity distribution in an absorption spectrum, is different from that of the excitation spectrum. Comparing the



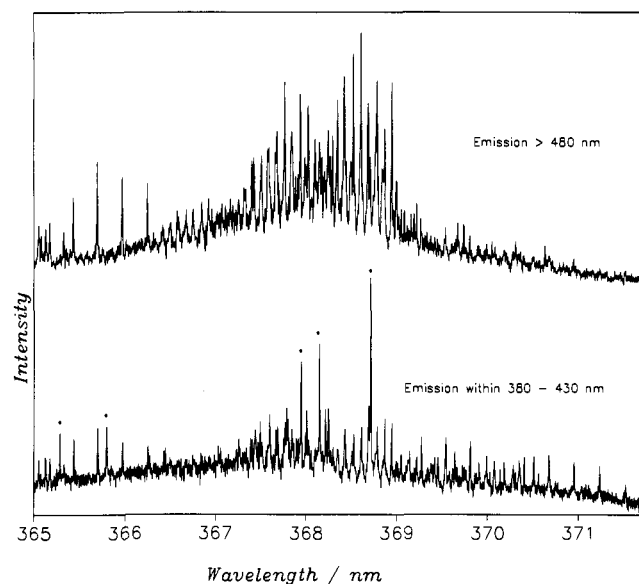
**Figure 3.** Fluorescence excitation spectrum of the vdW complex of anthracene with 1,4-dimethoxybenzene for emission above 480 nm. Expansion conditions are the same as for Figure 2.



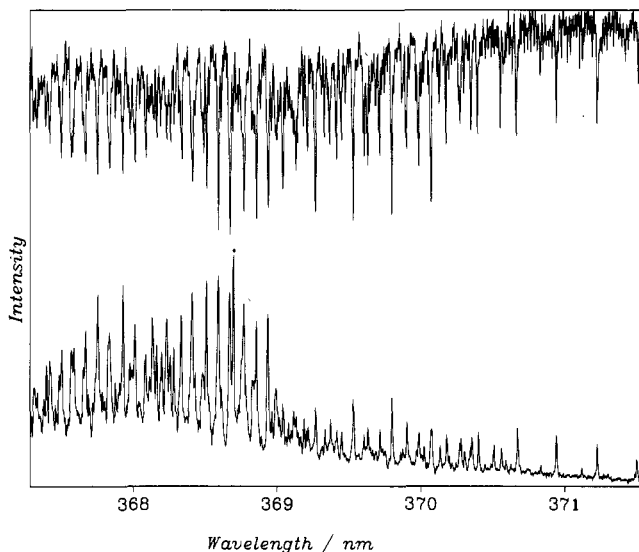
**Figure 4.** Dispersed fluorescence spectrum of the anthracene/1,4-dimethoxybenzene vdW complex for excitation at the 212.5  $\text{cm}^{-1}$  band (368.6 nm).

relative intensity distributions in the two spectra, it is clear that the quantum yield of the exciplex fluorescence (and hence that of the exciplex formation) exhibits a sharp increase at the threshold excess vibrational energy of 183  $\text{cm}^{-1}$ . This is especially evident when the excitation spectrum of the exciplex fluorescence in Figure 3 is compared to the hole-burning spectrum in Figure 6. Finally, it is apparent from both the fluorescence excitation spectrum and the hole-burning spectrum that the 20  $\text{cm}^{-1}$  mode is the only active progression forming intermolecular vibration in the anthracene/1,4-DMB vdW complex (Figure 2). A partial listing of the frequencies and tentative assignments of the observed bands in the first 500  $\text{cm}^{-1}$  of the fluorescence excitation spectrum is given in Table 1.

**Anthracene/1,2-Dimethoxybenzene.** Figure 7 shows the fluorescence excitation spectrum of the vdW complex of anthracene with 1,2-dimethoxybenzene (1,2-DMB), measured by collecting the total emission ( $\lambda > 380$  nm). The first 200  $\text{cm}^{-1}$  of the excitation spectrum was reported previously by Tramer and co-workers.<sup>8</sup> As in the earlier work, the fluorescence excitation spectrum displays a long progression in a low-frequency ( $\sim 23$   $\text{cm}^{-1}$ ) mode. Concentration dependence of the intensities indicates



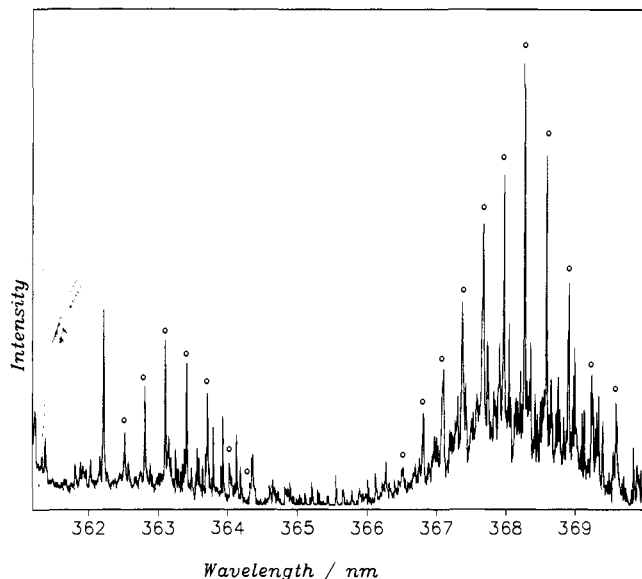
**Figure 5.** A comparison of the fluorescence excitation spectra obtained by detecting different fractions of emission of anthracene/1,4-dimethoxybenzene vdW complex. The lower trace is for the detection of local emission (380–430 nm) and the upper one is for the detection of exciplex emission above 480 nm.



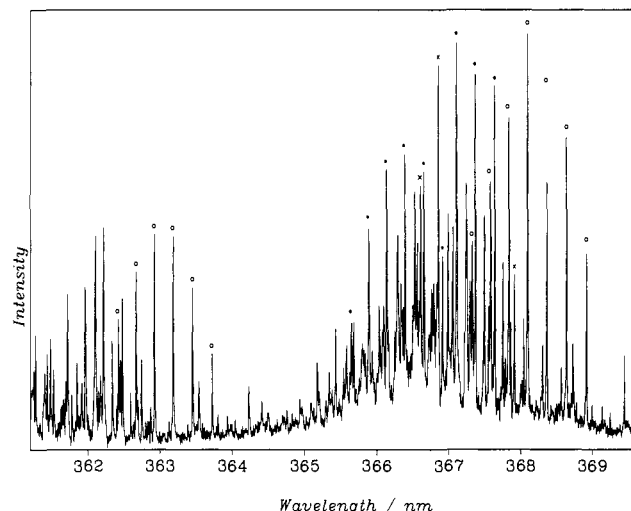
**Figure 6.** A comparison between the fluorescence excitation and the hole-burning spectra of the anthracene/1,4-dimethoxybenzene vdW complex measuring under the same expansion conditions. The probe laser frequency of the hole-burning spectrum was fixed at the transition frequency of the 212.5  $\text{cm}^{-1}$  band.

that this progression is due to a 1:1 complex of anthracene with 1,2-DMB. A weaker feature at 369.56 nm is assigned as the origin of the  $S_1-S_0$  system. This assignment is based on the observation that the same progression starts again at  $0 + 386$   $\text{cm}^{-1}$  (364.36 nm), which corresponds to the  $12_0^1$  transition of the vdW complex. In addition to these progressions involving an intermolecular vibration, the spectrum shows complicated spectral features due to a number of weaker bands around the origin and an underlying broad feature. These features grow in intensity faster than linearly with increasing 1,2-DMB concentration, and hence might be assigned to higher clusters.

Despite our inability to disperse the fluorescence, it is possible to assign the emission to LE fluorescence based on the fact that both the lifetime and the spectral position of emission are quite similar to those of the fluorescence of bare anthracene. Unlike the case of anthracene/1,4-DMB, no long wavelength emission attributable to exciplex fluorescence was detected from this vdW complex. We conclude therefore that the emission from the



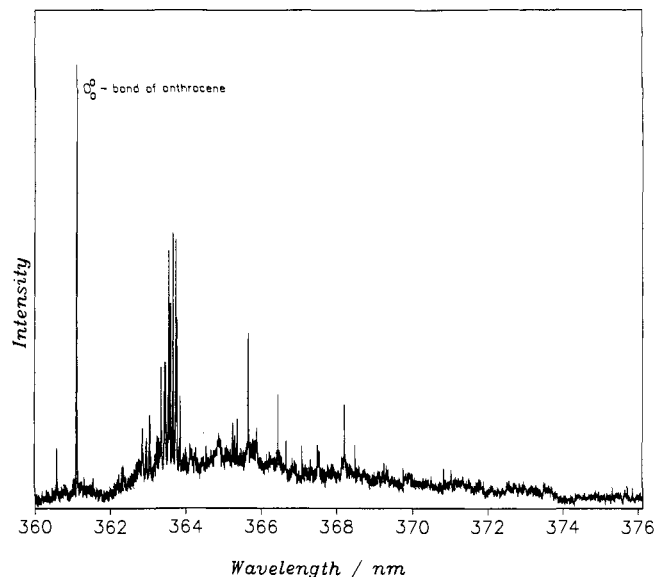
**Figure 7.** Fluorescence excitation spectrum of the vdW complex of anthracene with 1,2-dimethoxybenzene in a helium jet. The main progression in the spectrum is denoted by an open circle.



**Figure 8.** Fluorescence excitation spectrum of the vdW complex of anthracene with anisole. The temperature of anisole compartment was maintained at 0 °C. The main progression built on the electronic origin marked by small circles in the figure. The same progression built on other intermolecular modes is indicated by crosses and asterisks.

photoexcited anthracene/1,2-DMB vdW complex is fluorescence from the LE state of the species.

**Anthracene/Anisole.** Clusters of anthracene with anisole in the supersonic jet were studied previously by Anner and Haas.<sup>6,7</sup> They reported two types of features in the fluorescence excitation spectrum. One is the narrow band features which produce vdW type (i.e., LE) emission with a short decay time and the other is a broad feature with fwhm > 100 cm<sup>-1</sup>. The dispersed emission obtained by excitation of this broad band is structureless and highly Stokes shifted and shows a very long decay time, which they assigned to an exciplex fluorescence from the anthracene/anisole complex. Our fluorescence excitation spectrum for this system is quite different. Figure 8 shows the excitation spectrum obtained by detecting total fluorescence ( $\lambda > 380$  nm) and by maintaining the anisole compartment at ice temperature. As in the case of the anthracene/dimethoxybenzene complexes, the fluorescence excitation spectrum is dominated by a progression of frequency  $\sim 20$  cm<sup>-1</sup> in a vdW mode. The longest wavelength feature at 369.44 nm is assigned as the origin band of the 1:2 complex. The main progressions are assigned to the 1:1 complex whose origin band lies at 368.912 nm. The assignments are verified by measuring the excitation spectra at different partial

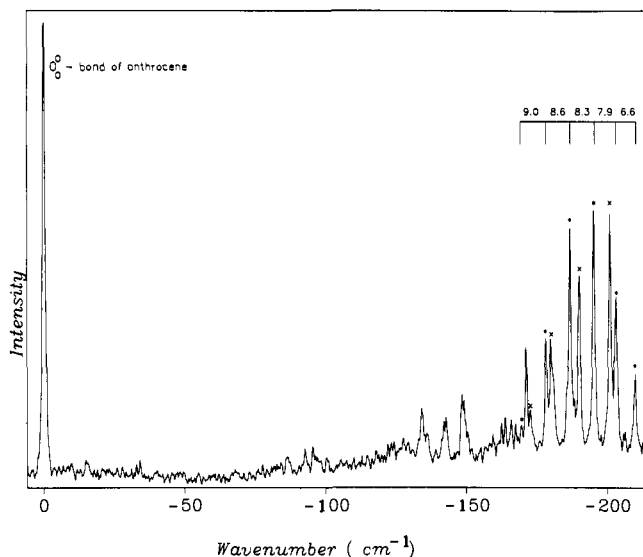


**Figure 9.** Fluorescence excitation spectrum of the vdW complex of anthracene with diethyl ether. The vapor pressure of ether was lowered by maintaining ether at dry ice temperature.

pressures of anisole and also by hole-burning spectroscopy. They are also supported by the observation of very similar features built on the respective  $12_0^1$  transitions, at 386 cm<sup>-1</sup> above the assigned origin of each complex. Unlike Anner and Haas, we did not observe any broad absorption feature in the spectral region longer than the assigned band origin. On the basis of the spectral region of fluorescence (which is similar to that of anthracene) and the fluorescence decay time (which is again similar to the anthracene fluorescence), we assign the emitting state to the LE state of the anthracene/anisole vdW complex.

**Anthracene/Diethyl Ether.** Clusters of anthracene with diethyl ether were also studied by Anner and Haas.<sup>6,7</sup> As in the case of the anisole complex, two types of bands were observed in their fluorescence excitation spectrum: a system of narrow bands that gives vdW type (LE) emission and a broad band showing exciplex type emission. The position of the broad band in the fluorescence excitation spectrum as well as the spectral position of the "exciplex fluorescence" are very similar to those reported for the anthracene/anisole complex. Figure 9 presents the fluorescence excitation spectrum we recorded for the anthracene/diethyl ether system. The spectrum was obtained by maintaining ether at dry ice temperature. Our result is very different from that of Anner and Haas, and the spectrum shows only narrow band structures. By using a combination of filters we have confirmed that the fluorescence emitted from these narrow bands is only LE type emission. The most prominent group of bands in the fluorescence excitation spectrum that appears at about 363.7 nm is assigned to the 1:1 complex, while the weaker bands in the lower energy region are assigned to the higher clusters. Figure 10 shows the fluorescence excitation spectrum of the 1:1 complex in an expanded scale. The lowest energy band in this group at about 210 cm<sup>-1</sup> to the red of the monomer origin band can be assigned to the origin of the  $S_1$ - $S_0$  absorption system of the complex. Two low-frequency vibrational modes of fundamental frequencies 6.6 and 8.8 cm<sup>-1</sup>, respectively, form progressions with distinct anharmonicity. Different shapes of the Franck-Condon envelopes for the two progressions indicate that the two progression-forming intermolecular vibrations undergo a different extent of distortions due to electronic excitation.

There are several notable differences in the fluorescence excitation spectrum of the diethyl ether complex as compared to those of the corresponding aromatic ether complexes. First, the frequencies of the progression-forming intermolecular vibration is much smaller in the diethyl ether complex (with smaller reduced mass) than in the aromatic ether complexes. Second, whereas the progressions in the aromatic ether complexes are nearly



**Figure 10.** Fluorescence excitation spectrum of the 1:1 vdW complex of anthracene with diethyl ether in an expanded scale. Two different low-frequency modes are assigned in the spectrum. The energy separation denotation is for the series of progression identified by asterisks.

harmonic, the progression in the diethyl ether complex exhibits a distinct anharmonicity. These observations suggest that the nature of the progression-forming modes is different in these two classes of compounds.

The most significant conclusion for the anthracene/diethyl ether system is that there is no long wavelength emission attributable to exciplex fluorescence. This is once again in clear contradiction to the conclusions of Anner and Haas.<sup>6,7</sup>

## Discussion

**Dependence of Exciplex Formation on Donor Ionization Potential.** The primary results of the present investigation are the observations that excitation spectra of the vdW complexes of anthracene with ethers always show narrow band excitations and transition of the photoexcited vdW state to the exciplex state depends on the ionization potential of the donor (ether) moiety. The complex involving the donor molecule with the lowest ionization potential, viz., 1,4-dimethoxybenzene, exhibits exciplex fluorescence for excitation to a certain threshold energy above the electronic origin. In all other cases, observed emission is from the locally excited state ( $A^*D$ ) of the vdW complex. Since the exciplex state is supposed to arise from crossing (and mixing) of the locally excited state to (and with) the charge transfer state, the occurrence of exciplex formation will depend on the energy separation between the potential minima of the LE and the CT states. Assuming the general case of smaller D–A separation of the CT state relative to the corresponding LE state, a simple one-dimensional potential energy profile of these two states of the complex along the reaction coordinate (an intermolecular coordinate) is shown in Figure 1. According to this model, vibrational energy of the complex in excess of a certain threshold value is required for the internal rearrangement of the complex leading to exciplex configuration. The magnitude of this threshold energy is again expected to be determined by the energy of the CT state relative to the LE state.

The energy of the charge transfer (CT) state is given by<sup>13</sup>

$$E(\text{CT}) = I_D - E_A - \frac{e^2}{r} \quad (1)$$

where  $I_D$  and  $E_A$  represent respectively the ionization potential of the donor and the electron affinity of the acceptor and  $r$  is the separation between donor and acceptor at equilibrium. For a

**Table 2.** Dependence of Exciplex Formation on Donor Ionization Potential for van der Waals Complexes of Anthracene with Various Amines and Ethers

donor	$I_D$ (eV)	$I_D - E_A$ (eV)	exciplex fluorescence	ref
ammonia	10.85	10.30	no	21
tetrahydrofuran	9.74	9.19	no	this work
diethyl ether	9.60	9.05	no	this work
anisole	8.21	7.66	no	this work
1,2-dimethoxybenzene	8.05	7.50	no	8, this work
1,3-dimethoxybenzene	8.00	7.45	no	8
aniline	7.70	7.15	yes	8, 22, 23
1,4-dimethoxybenzene	7.50	6.95	yes	this work
<i>N</i> -methylaniline	7.32	6.77	yes	8, 22
<i>N,N</i> -dimethylaniline	7.12	6.57	yes	8, 22, 24
<i>N,N</i> -diethylaniline	7.05	6.50	yes	23, 24

given acceptor molecule the energy gap between the zero-order CT state and the locally excited (LE) state of the complex is therefore determined by the donor ionization potential, provided that neither the energy of the LE state nor the donor–acceptor separation is a sensitive function of the nature of the donor moiety. Since the energies of the LE states of the three vdW complexes of anthracene with aromatic ethers presented here are almost identical, the crucial parameter that determines the energy gap between the LE and the CT states is the ionization potential of the donor moiety. These considerations lead to a conclusion that the ability of the excited vdW complex to form exciplex should depend on the donor ionization potential in a homologous series of complexes with a common acceptor moiety. Table 2 presents a correlation between the donor ionization potential ( $I_D$ ) and exciplex fluorescence for the vdW complexes of anthracene with various amine and ethers. For reasons described in the previous section (and to be described later), the results of Anner and Haas have been left out in this compilation. It is seen from the table that only the vdW complexes with donor  $I_D$  less than 7.7 eV exhibit exciplex fluorescence.

When the LE and the CT states are in close proximity, the LE state is expected to be strongly perturbed by the CT state and to undergo a large distortion along the reaction coordinate. The appearance of long progressions in a low-frequency vibration in the fluorescence excitation spectra of the three aromatic ether complexes suggests that the complexes undergo a large distortion along this particular coordinate. Therefore, this low-frequency mode might represent the reaction coordinate along which the excited vdW complex isomerizes to form an exciplex. Conventionally, the intermolecular distance is considered as the coordinate of exciplex formation and we therefore assign the progression-forming low-frequency mode as an intermolecular donor–acceptor stretching vibration. In comparison with the 1,4-DMB complex, the inability of the 1,2-DMB and anisole complexes to form an exciplex is simply a consequence of the relatively high donor ionization potential which makes the barrier to exciplex formation high. On the other hand, diethyl ether shows much smaller frequencies in the intermolecular vibrational modes. Unlike those for aromatic ether complexes, motions along these coordinates are quite anharmonic. Such low-frequency intermolecular modes have been observed previously in the vdW complexes of large hydrocarbons with small solvent molecules.<sup>14</sup> Following such a report we may assign the low-frequency modes in our present system as the gliding motion of a small ether molecule along the planar surface of anthracene. Therefore these modes are different from the reactive intermolecular mode observed in the case of aromatic ethers. The ionization potential of diethyl ether is 9.69 eV, which is much higher than the limiting value of the donor ionization potential (7.7 eV) for exciplex formation. So the ionic surface for this complex (which can be obtained from eq 1) should be far above the vdW surface and there is little probability of surface crossing within the limit of binding distance.

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**Stabilization Energy of the Exciplex.** The stabilization energy due to exciplex formation is commonly expressed as<sup>13,15</sup>

$$-\Delta H = h(\nu_{00} - \nu_{\max}^E) - E_r \quad (2)$$

where  $h\nu_{00}$  corresponds to the energy of the electronic origin transition of the vdW complex,  $h\nu_{\max}^E$  is the energy corresponding to the intensity maximum of the exciplex fluorescence, and  $E_r$  represents the energy of repulsive interaction between the donor and acceptor moieties in the ground electronic state. For a wide range of donor-acceptor pairs,  $E_r$  values have been found to be quite similar. For example, in hexane both pyrene/dimethylaniline and anthracene/dimethylaniline were assigned an  $E_r$  value of 4.4 kcal/mol.<sup>16</sup> Similar values of the repulsion energies have also been assigned to other exciplex systems.<sup>16</sup> Assuming that the repulsive interaction in the gas phase is similar to that in the hydrocarbon solvent,<sup>17</sup> we may therefore estimate the stabilization energy of the anthracene/1,4-DMB exciplex based on the  $E_r$  value of 4.4 kcal/mol (because of the smaller value of repulsive energy relative to the energy difference  $h(\nu_{00} - \nu_{\max}^E)$ , the uncertainty in estimating  $E_r$  will not much affect the stabilization energy.) The value of the stabilization energy so obtained is ca. -6 kcal/mol ( $\approx 2100 \text{ cm}^{-1}$ ), which is about a factor of 2 smaller than that obtained for various exciplexes of anthracene with different dialkylanilines in the condensed phase.<sup>13,15</sup> One possible reason for this smaller value of the stabilization energy in the present case is an incomplete vibrational relaxation of the exciplex which is formed from the photoexcited van der Waals complex, whereas in solution, energy dissipation takes place due to collisions with the solvent molecules and emission starts from the lowest vibronic level of the exciplex state. Figure 1 also shows various energy parameters appearing in eq 2.

**Charge Transfer Character of the Exciplex State.** The wave function for the exciplex state is commonly represented as a linear combination of the zero-order locally excited (LE) state  $\psi(A^*D)$  and the zero-order charge transfer (CT) state  $\psi(A^-D^+)$ ,<sup>13,18</sup>

$$\Psi_{\text{Ex}} = C_1\psi(A^*D) + C_2\psi(A^-D^+) \quad (3)$$

where  $C_1$  and  $C_2$  are mixing coefficients. The charge transfer character in the gas-phase exciplex can be estimated roughly by relating the value of  $C_2$  to the dipole moment of electronic transition from the ground state  $\Psi(AD)$  to the exciplex state  $\Psi_{\text{Ex}}$ .<sup>13,18</sup> The transition moment  $M$  in turn is related to the radiative decay rate for spontaneous emission  $k_r$  by

$$k_r = \frac{64\pi^4\nu_r^3}{3hc^3}|M|^2 \quad (4)$$

where  $\nu_r$  is the frequency for the radiative transition. Using eq 3, the radiative transition moment of the exciplex may be written as

$$\begin{aligned} M_E &= \langle \Psi_{\text{Ex}} | \vec{\mu} | \Psi(AD) \rangle \\ &= \langle C_1\psi(A^*D) + C_2\psi(A^-D^+) | \vec{\mu} | \Psi(AD) \rangle \\ &= C_1 \langle \psi(A^*D) | \vec{\mu} | \Psi(AD) \rangle + C_2 \langle \psi(A^-D^+) | \vec{\mu} | \Psi(AD) \rangle \\ &= C_1 M_{\text{LE}} + C_2 M_{\text{CT}} \end{aligned} \quad (5)$$

where  $M_{\text{LE}}$  and  $M_{\text{CT}}$  represent the moments of electronic transitions of the complex from the ground state to the zero-order LE state and CT state, respectively. For the anthracene/

1,4-DMB system, only the strong transition to the LE state is observed, so that  $M_E$  can be approximated by

$$M_E \cong C_1 M_{\text{LE}} \quad (6)$$

From eqs 4 and 6 one obtains (using the notations of eq 2 for the transition frequencies)<sup>17,18</sup>

$$|C_1|^2 = \left( \frac{k_r^E}{k_r^{\text{LE}}} \right) \times \left( \frac{\nu_{00}}{\nu_{\max}^E} \right)^3 \quad (7)$$

By using the inverse of the measured radiative lifetime ( $\sim 30 \text{ ns}$ )<sup>19,20</sup> of jet-cooled anthracene as  $k_r^{\text{LE}}$ , the reciprocal of the measured lifetime (100 ns) of exciplex fluorescence as  $k_r^E$  (because the quantum yield of exciplex fluorescence in the supersonic jet is larger than the vdW complex), and the corresponding transition frequencies, we obtain  $C_1 = 0.67$  and hence  $C_2 = 0.74$  by the normalization condition ( $|C_1|^2 + |C_2|^2 = 1.00$ ). We conclude, therefore, that the exciplex state of the anthracene/1,4-DMB complex is largely of CT character, as expected.

**Summary and Concluding Remarks.** Exciplex formation following the electronic excitation of the vdW complexes of anthracene with various ethers was studied under collision-free conditions in a supersonic jet and this was found to be strongly dependent on the ionization potential of the donor (ether) molecule. Thus, only the complex containing donor moiety with the lowest ionization potential (viz., 1,4-dimethoxybenzene) exhibits exciplex fluorescence. In all other cases, the observed emission is from the locally excited (LE) state of the vdW complex. The dependence of exciplex formation on the donor ionization potential is consistent with the previous results of the vdW complexes of 1-cyanonaphthalene with a variety of aliphatic amines.<sup>5</sup>

The observation of only LE (or vdW type) fluorescence from the vdW complexes of anthracene with diethyl ether and anisole is in direct conflict with the earlier report of Anner and Haas<sup>6,7</sup> in which an exciplex fluorescence with intensity maximum at about 450 nm is described. Interestingly, the position and the shape of their "exciplex fluorescence" from anthracene/anisole, anthracene/diethyl ether, and anthracene/ammonia<sup>9</sup> systems mimic the excimer fluorescence from the pure clusters of anthracene which we have recently reported.<sup>10</sup> Similarly, the excitation spectra corresponding to the "exciplex fluorescence" of these vdW clusters contain features that have been attributed<sup>10</sup> to a pure cluster of anthracene. These observations suggest that the emission assigned to the exciplex fluorescence of these complexes is actually excimer fluorescence from pure anthracene clusters, solvated with anisole and diethyl ether. Excitation of these solvated anthracene clusters leads to the excimer fluorescence that can be misinterpreted as the exciplex fluorescence from vdW complexes.

Finally, we wish to point out that quantitative comparison of the fluorescence excitation spectra of the LE and exciplex emissions in the anthracene/1,4-DMB system reveals mode selective exciplex formation.<sup>25</sup>

**Acknowledgment.** This work was funded by Grant DE-FG02-89ER14024 from the Office of the Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. The authors are grateful to Dr. Hiroyuki Saigusa for helpful discussions and suggestions.

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