ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 150 (2002) 159–165

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Supersonic jet spectroscopy of naphthalene–fluorene bichromophoric cluster

David Groswasser, Gershon Rosenblum, Shammai Speiser*

Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

Received 29 October 2001; received in revised form 12 February 2002; accepted 26 March 2002

Abstract

We have investigated the supersonic jet spectroscopy and photophysics of 1-methylnaphthalene–fluorene (1MN–FL) cluster, and looked for indications of intramolecular electronic energy transfer (Intra-EET) from the FL (donor, D) to 1MN (acceptor, A). The clusters were identified by their time of flight (TOF) mass spectra. We observed clusters bands in the LIF spectrum near the region of 1MN origin. We have also observed cluster TOF–resonance enhanced multi-photon ionization (REMPI) spectrum near the electronic origin of the fluorene moiety. However, this spectrum was almost independent of the excitation wavelength, and was not observed in the LIF spectrum. This is probably due to fast Intra-EET resulting in lifetime broadening of the donor chromophore cluster spectrum, similar to that observed previously for the naphthalene–anthracene bichromophoric system. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Supersonic jet spectroscopy; Bichromophoric cluster; Intra-EET

1. Introduction

Supersonic jet spectroscopy of hetero-molecular clusters and its related photophysics is a well-studied area [1]. One of the possible decay routes in these bichromophoric van der Waals molecular complex clusters is the intramolecular electronic energy transfer (Intra-EET) process between donor (D) and acceptor (A) chromophores. Intra-EET in the jet involves interaction between specific vibronic states of the donor and acceptor molecules. However, intramolecular exciplex formation and the limited chemical stability of the complex, which introduces dissociative channels, might interfere with observation of the Intra-EET process, thus complicating the interpretation. On the other hand, study of Intra-EET in bichromophoric clusters is interesting as a source of information on the relative importance of these competing processes in the photophysics of such molecular systems. In an ideal case, one should be able to study the dependence of the transfer efficiency on the particular vibronic excitation of the donor moiety in the bichromophoric cluster and to determine the transfer mechanism.

Intra-EET in a bichromophoric cluster was evidenced by Young et al. [2] in T-shape dimers of tetrazine following excitation of the $6a_0^2$ vibrational levels of the dimer. The first reported study of Intra-EET under supersonic jet conditions was that by Poeltl and McVey [3] on hydrogen-bonded dimers of benzoic acid. In particular, the mixed dimer composed of bezoic-d_0 acid and benzoic-d_5 acid was studied. From the measurements of the dispersed fluorescence spectra, they concluded that efficient EET process involving transfer from the deuterated moiety to the non-deuterated one took place. However, due to limited spectral resolution no detailed quantitative interpretation was offered.

Tomioka et al. [4] did similar measurements on a mixed dimer of benzoic acid and *p*-toluic acid. They have concluded that Intra-EET in the cluster from specific vibronic donor states competes efficiently with IVR within the donor manifold. The relative rates of energy transfer and of the IVR process were discussed in terms of the vibrational density of states of the bichromophoric complex.

Lahmani et al. [5] studied Intra-EET in the bichromophoric system composed of perdeuterated and non-deuterated *p*-xylene (*p*xd and *p*x, respectively) and *p*-difluorobenzene (*p*df). Dispersed fluorescence resulting from excitation of the *p*df was indicative of EET from the excited *p*df moiety to the *p*x (or *p*xd) chromophore.

Intra-EET in naphthalene–anthracene clusters was observed by Bigman et al. [6,7] and by Rosenblum and Speiser [8]. In this system, the energy gap between the donor (naphthalene) and acceptor (anthracene) is ∼5000 cm^{-1}. The excitation of the naphthalene chromophore is followed by fast EET to a quasi-continuum of anthracene states. Such a fast EET is not always observed due to lifetime broadening

---

* Corresponding author. Tel.: +972-4-8293-735; fax: +972-4-8233-735.
E-mail address: speiser@tx.technion.ac.il (S. Speiser).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00149-1

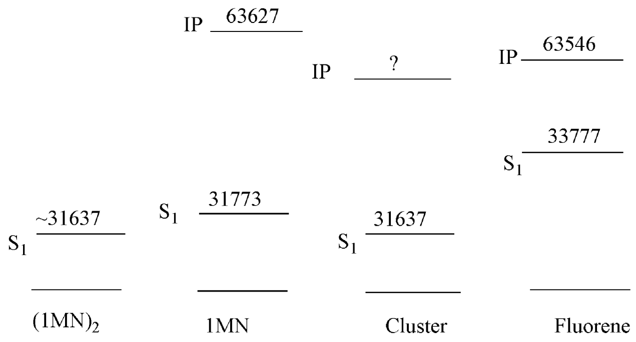

Fig. 1. Energy level diagram of 1MN, 1MN dimer, fluorene, and the 1MN–FL cluster (IP denotes the ionization potential, all energies are given in cm^{-1}).

effect. In fact, EET was observed only in one conformer that does not favor fast EET [9]. Similar results were obtained for the benzene–biacetyl cluster where Intra-EET due to exchange interaction between specific vibronic levels of the benzene $^1B_{2u}$ state and vibronic levels of the biacetyl ^1B_g state was observed [7]. A dual fluorescence spectrum induced by excitation of the benzene chromophore in the cluster was indicative of the Intra-EET process.

We decided to try and see if we can detect Intra-EET in 1-methylnaphthalene–fluorene (1MN–FL) clusters. In this system, the energy gap between the $S_0 \rightarrow S_1$, 0–0 transition of naphthalene, and fluorene is only 2000 cm^{-1} (Fig. 1). Furthermore, 1MN shows spectral activity in the spectral region of fluorene 0–0 transitions (unlike the case of naphthalene–anthracene clusters). We chose to use 1MN and not naphthalene since our calculations predicted two stable conformations of this (1:1) cluster (Fig. 5). The observation of Intra-EET will be based on the difference in fluorescence wavelength and lifetime of the two molecules (~300 ns for 1MN and ~16 ns for fluorene). The goal of the experiment is to excite the fluorene moiety of the cluster and to observe a long-lived and “red” fluorescence ($\lambda > 350$ nm) from 1MN. There are two problems in this scheme, the first is to identify cluster lines, and the second is to verify whether the excitation is really localized on the fluorene site, or on the 1MN site. However, due to the relatively small energy gap between the origins of the two chromophores absorption spectra significant mixing might destroy this localization, resulting in line broadening and no observable Intra-EET.

2. Experimental

The molecules were seeded in helium in a supersonic jet using a pulsed nozzle apparatus described elsewhere [6,8]. Briefly, 6 atm helium was passed over a heated cell containing liquid organic sample. The temperature was chosen so as to produce an organic vapor pressure of about 0.2 Torr. The gas containing the organic vapor was expanded through a 1.1 mm orifice into an evacuated chamber. The pressure in the vacuum chamber was typically 2×10^{-4} Torr. The jet was crossed with a laser beam (<1 mm spot size) 33 mm down stream. About 10% of the resulting fluorescence was collected by a lens to a photomultiplier.

The laser beam (~5 mW) was produced by frequency doubling or mixing an Nd:YAG (continuum) second harmonic pumped dye laser. The resulting laser bandwidth was about 0.2 cm^{-1}. The experimental uncertainties of absolute frequencies are ±2 cm^{-1} and those of relative frequencies are 0.2 cm^{-1}.

Resonance enhanced multi-photon ionization (REMPI) spectrum was measured using excitation with the same laser system. 1MN was heated to 82 °C and the signal was collected using a time gate suitable for the flight time of the dimer. For many aromatic molecules, the ionization potential is 6–9 eV, and the $S_0 \rightarrow S_1$ transition energy is 3–5 eV. Hence, if the $S_0 \rightarrow S_1$ transition system is over half the ionization threshold, then resonant two photons are sufficient for ionization (one color two photons (1C2P) process). In this case, one laser is enough for the experiment. The ionization of the molecular beam was possible by directing the laser beam perpendicular to the molecular beam, or counter propagating to it, and by so ionizing a larger volume. The 1MN–FL cluster was studied under similar conditions.

An important feature of the experimental set up is that we could measure simultaneously LIF and time of flight (TOF) spectra, this was done by splitting the excitation laser beam with a quartz plate, and directing the 4% reflected beam to the first chamber. The nozzle pulse is long enough to observe both signals simultaneously, thus we measured LIF in the first chamber as described. Both LIF and TOF signals were recorded on digital oscilloscopes (Tektronics TDS 220 and Tektronics 2430) and transferred to a computer via GPIB card. All signals were normalized to the laser power.

The first chamber was pumped by Edwards E903 8 in. diffusion pump. The second chamber was pumped by an air cooled Edwards E06 6 in. diffusion pump. During operation, the pressure in the first chamber was 10^{-6} Torr and in the second 10^{-7} to 10^{-8} Torr. The two diffusion pumps were backed with one Alcatel 2033 pump. HPS cold cathode (CC) gauges monitored the pressure in the chambers, and Pirani gauges measured the pressure in the before the rotation pump.

3. Results and discussion

TOF signals of 1MN–FL mixture are shown in Fig. 2. The TOF is proportional to the square root of the mass, $T = C(m^{1/2})$. The constant C can be calculated by calculating the flight time in the two acceleration fields and in the field-free region, or measured from the flight time of a known mass as shown in Fig. 2. For mass of ~300 a.u., the flight time is ~12 μs, and FWHM of the signal is ~30 ns (Fig. 2). The TOF–REMPI spectrum shows the existence of 1MN dimers and trimers and of 1MN–FL 1:1 cluster.

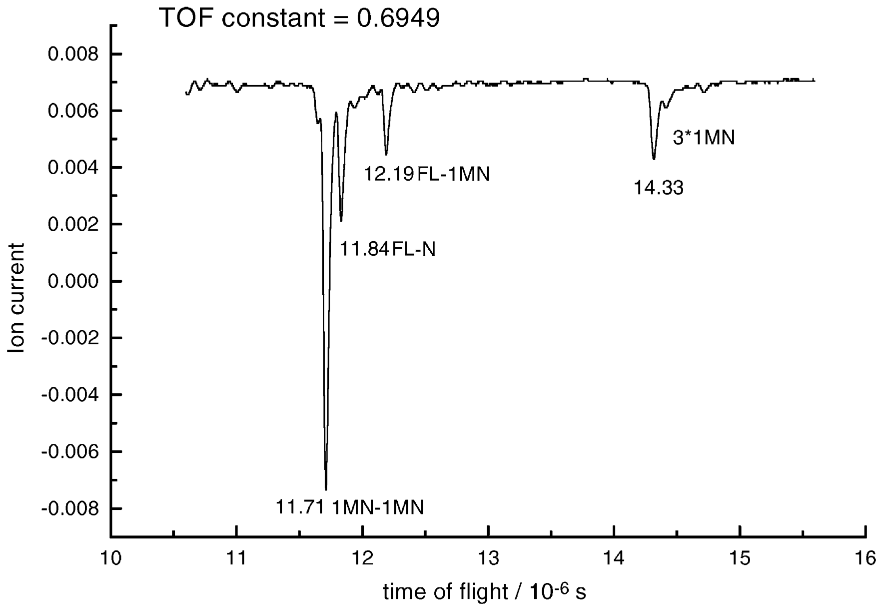

Fig. 2. TOF signals of 1MN cluster dimers, and 1MN–FL cluster complex. Excitation frequency is 33444 cm^{-1}, the sample temperature was 100 °C.

We measured the 1MN dimer ionization spectrum from ~32300 cm^{-1} and scanned to the red, expecting to find transitions associated with the $8b_{1g}$ mode. The only signal that we observed in this spectral range is between 31620 and 31680 cm^{-1} (Fig. 3). The signals in the spectrum were weak (as seen from the signal to noise ratio) and it is possible that three photons are required for the ionization. The origin of the dimer spectrum is shifted ~140 cm^{-1} to the red with respect to the monomer origin. The band is rather broad due to low frequency interchromophore progressions and possibly due to excimer formation. The major difference between this spectrum to that of naphthalene dimer is the absence of the $8b_{1g}$ transition from the spectrum, this transition has higher oscillator strength and higher probability for two-photon ionization. Such a spectrum is typical of our observations in naphthalene bichromophoric systems [10]. It remains an open question why the $8b_{1g}$ transition is absent or weak in these systems but is present in the spectrum of naphthalene dimer.

Our observations conform with previously published works on naphthalene clusters [11–14]. Excitonic splitting in naphthalene clusters were reported by Syage and Wessel

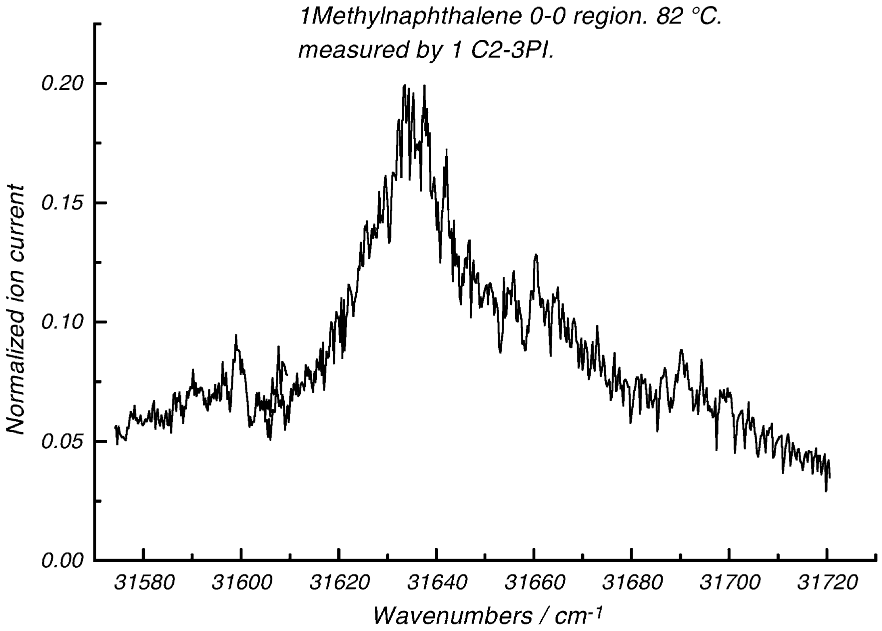

Fig. 3. REMPI spectrum of 1MN dimer.

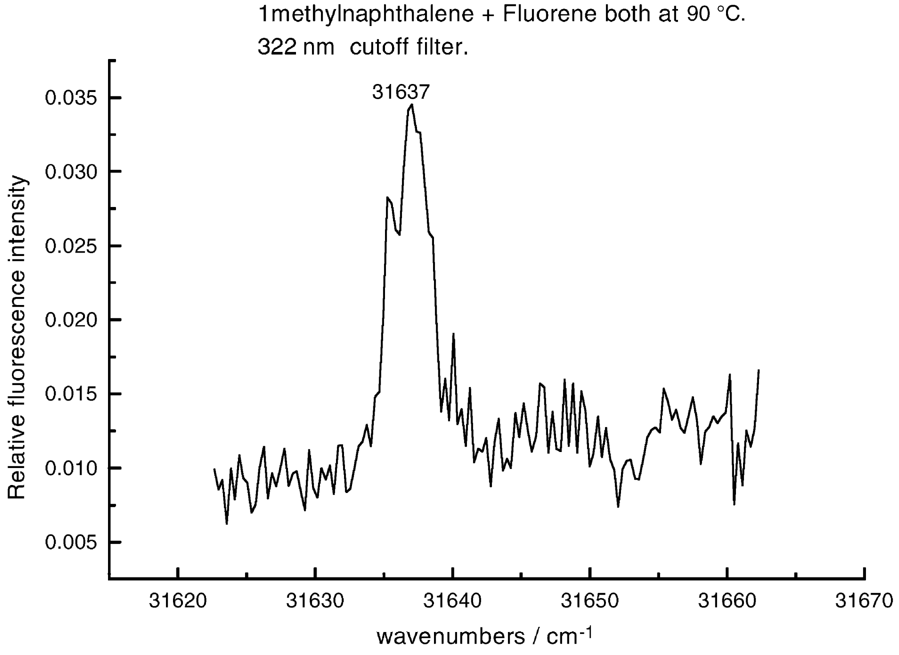

Fig. 4. The 1MN origin LIF excitation spectrum of 1MN–FL cluster.

[11] and later interpreted as site shifts by Schaffer et al. [12] and by Saigusa and Lim [14]. The spectrum of the naphthalene dimer is inherently broad, but with the general features of the monomer spectrum. The broadening may be due to the formation of an excimer or due to low frequency interchromophoric vibrational modes.

The existence of the 1MN–FL cluster is evidenced from our TOF–REMPI mass spectrum of Fig. 2. The LIF excitation spectrum of the cluster at the spectral region of the 0–0 transition of 1MN is shown in Fig. 4. We have identified the 0–0 ($31637\,\mathrm{cm}^{-1}$) transition of the 1MN moiety of the cluster by changing the partial vapor pressure of the constituents

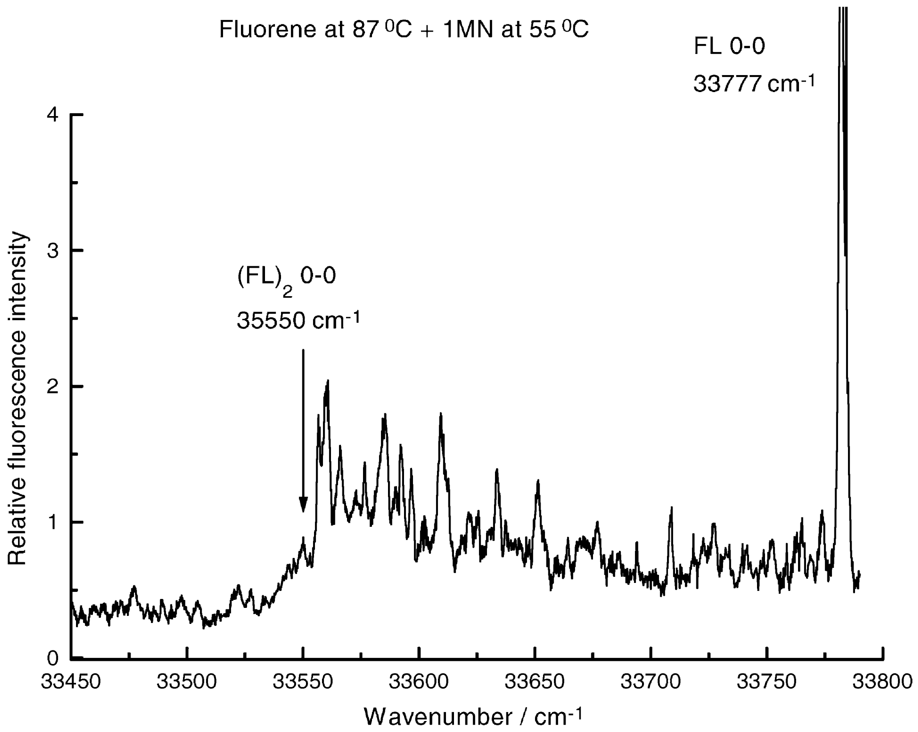

Fig. 5. LIF excitation spectrum of fluorene dimer (excimer).

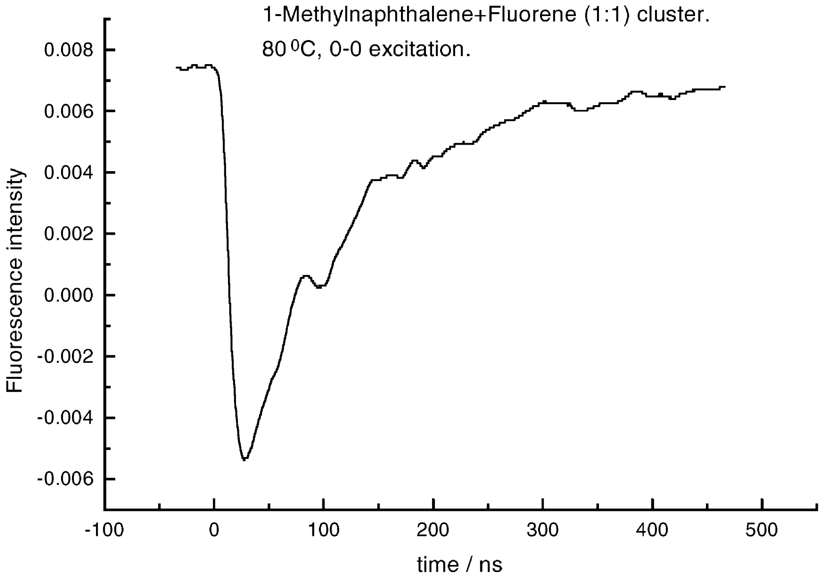

Fig. 6. Fluorescence decay of the 0–0 band of the naphthalene moiety of 1MN–FL.

and monitoring the transition intensity. Fig. 6 shows the decay of the 1MN 0–0 fluorescence. The lifetime of the 0–0 transition of the cluster is 140 ± 10 ns, this is much shorter than the 300 ns lifetime of 1MN. The spectrum, however, is not very different from what was observed for the 1MN dimer.

The identification of the 0–0 transition on the 1MN chromophore proved the existence of the cluster. But in order to confirm the existence of an Intra-EET process we had to look for the excitation spectrum of the fluorene moiety (the donor) monitored via the appearance of naphthalene (acceptor moiety) emission. We scanned the region from the 0–0 transition of fluorene (33777 cm^{-1}) for more than towards 700 cm^{-1} to the red and monitored the resulting emission through a red pass filter (Schot WG345) and looked for long-lived transitions. We were able to observe lines corresponding to fluorene dimer (excimer, Fig. 5) [15–17], but we did not find any discrete fluorene moiety cluster bands. However, the mere fact that we have observed naphthalene like emission is indicative of an Intra-EET process, as was the case for other bichromophoric clusters. The observed TOF cluster signal (Fig. 2) did not depend strongly on the excitation wavelength, but indicates that the cluster can be excited at the fluorene chromophore. It is very probable that LIF discrete spectrum due to fluorene moiety excitation of the 1MN–FL complex is either masked by the FL dimer signal or that it very broadened due to fast Intra-EET to the naphthalene chromophore, and thus is missing from the LIF spectrum of Fig. 5. Similar observation and conclusion was made for the Intra-EET of jet expanded naphthalene–anthracene bichromophoric molecule where the naphthalene-donor lines are very broadened due to ultrafast EET process to the anthracene chromophore [18].

The experimental observations were supported by calculations of the conformations and binding energies of the clusters. Using our previously developed *anisotropic method* [9,19], we have calculated the geometries of the 1MN dimer, of the fluorene–naphthalene cluster and of that of 1MN–FL cluster. The method is illustrated in detail for the fluorene–naphthalene cluster.

The most stable conformations of the 1MN dimer are shown in Fig. 7. The binding energy of the most stable conformation is $-2262\,\mathrm{cm}^{-1}$. In this “sandwich” conformation, the distance between the planes of the chromophores is 3.6 Å. Other sandwich conformations are less stable by $\sim 30\,\mathrm{cm}^{-1}$. The calculation confirm that indeed a stable dimer can be formed under our jet expansion conditions which should resemble the spectra observed for the dinaphthalene bichromophoric molecules.

We have calculated the geometry of the fluorene–naphthalene cluster by the anisotropic method [19]. In addition, zero-point (ZP) intermolecular vibrational frequencies were calculated. This calculation was performed by diagonalizing the 6 × 6 normalized matrix of second derivatives of the potential energy in the minimum point [20,21].

The global minimum structure (Table 1) is a crossed sandwich in which the molecular planes are nearly parallel

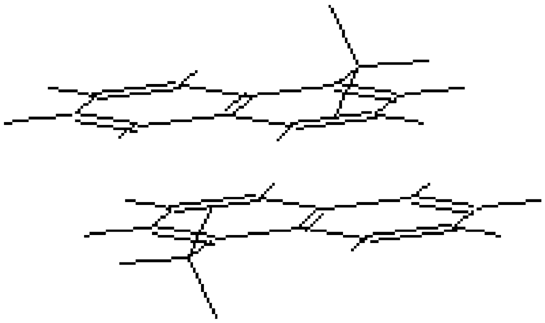

Fig. 7. The most stable conformation of 1MN dimer.

Table 1
Geometry parameters and frequencies of global potential minimum

Intermolecular coordinate	Global minimum value	ZP vibration frequency (cm^{-1})
x	0.00 Å	26.4
y	0.72 Å	15.5
z	3.58 Å	136.9
φ	90°	2.7
χ	1°49′	39.3
ψ	0°	56.5
Potential energy	$-2401\,cm^{-1}$	
$1/2\,\Sigma h\nu_0$	$138.7\,cm^{-1}$	

(Fig. 8). The deviation from planarity is in the χ coordinate, which is the relative rotation of the naphthalene molecule around its short axis. The obvious reason for this deviation is the out-of-plane hydrogen atom in the fluorene molecule. This interference lowers the barrier for intermolecular rotation around the normal axis. The global minimum is very shallow with respect to this coordinate (φ), compared to other inter-aromatic clusters [19,22,23].

A local minimum was found for parallel sandwich geometry, but the barrier for crossing to the global minimum via intermolecular rotation was less than $20\,cm^{-1}$. This barrier was much lower than the zero-point intermolecular vibrational energy (ZPE), estimated from the calculated frequencies. This implies that no separate quantum-vibrational state can exist for this structure, so that the "real" quantum-mechanical potential that should take into account the ZPE would not exhibit any local minimum. Similar observations were made in the case of benzene–fluorene cluster [19,22].

Similar calculations were performed for the 1MN–FL cluster. The most stable conformations of the 1MN–FL cluster are shown in Fig. 9. The binding energy of the "sandwich" conformation is $-2629\,cm^{-1}$, and the separation between the planes of the chromophores is 3.55 Å. The binding energy of the "T" conformer is only $-1994\,cm^{-1}$, the center of the 1MN chromophore is more than 5 Å above the plane of the fluorene chromophore.

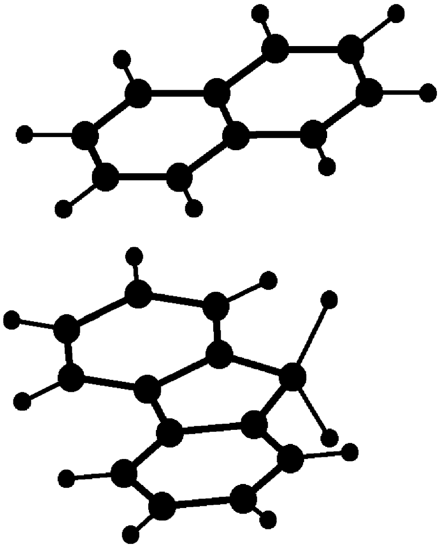

Fig. 8. Global minimum structure (crossed sandwich) of the fluorene–naphthalene cluster.

For both 1MN–FL and naphthalene–fluorene clusters the disturbance by the out-of-plane hydrogen couples strongly the intermolecular vibrations with one another. This means that no long equidistant progressions should be expected in a vibronic excitation spectrum. Also this disturbance can be expected to couple efficiently some *intra*molecular fluorene vibrations to the *inter*molecular vibrations of the cluster, which would promote IVR in fluorene. It may also enhance the "dark" deactivation processes in the cluster after vibronic excitation of the fluorene moiety. This may explain why in this cluster Intra-EET is either masked by IVR and cannot

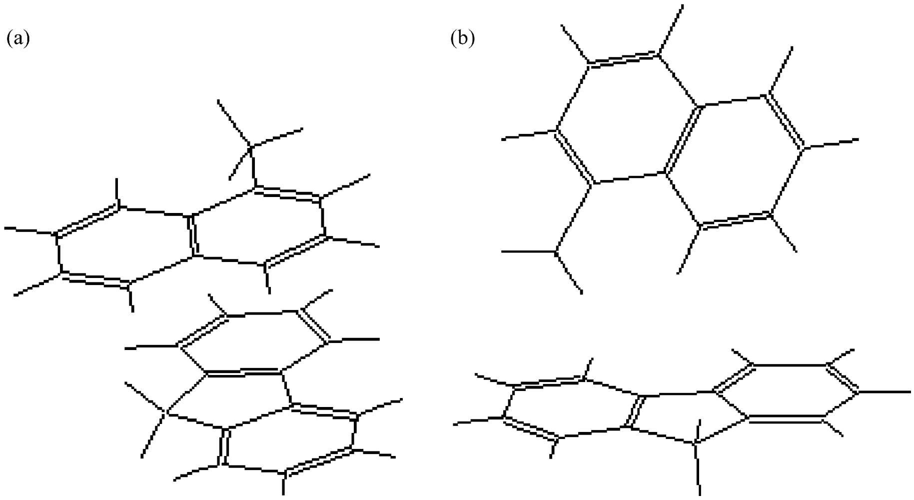

Fig. 9. The two predicted conformations of the 1MN–FL cluster: (a) the most stable, "sandwich" conformation; (b) the less stable, "T" conformation.

be observed directly or that it is so fat as to broaden the fluorene moiety excitation bands.

4. Summary

Using laser induced excitation and complement conformation calculations, we identified the $S_0 \rightarrow S_1$, 0–0 transition of the 1MN chromophore of the 1MN–FL cluster. The spectrum of this chromophore resembles that of 1MN dimer. From TOF–REMPI measurements, we have indications that this cluster can also be excited close to the fluorene origin. However, this signal was not dependent on the excitation frequency. In addition, we did not detect any cluster bands in the LIF spectrum near the origin of fluorene (although we detected fluorene dimer transitions). There are two possible explanations for the absence of cluster bands in this spectral region: (1) They are weak and masked by the transitions of the fluorene dimer. (2) These transitions are not observed due to very fast Intra-EET processes that causes lifetime line broadening, similar to the case of the naphthalene–anthracene bichromophoric system [19]. The 0–0 transitions of 1MN dimer, and of the 1MN–FL cluster (at the 1MN spectral region) are very close. This is due to a similar perturbation of the 1MN chromophore in both cases.

Acknowledgements

This work was supported, in part, by the Technion VPR Fund for the Promotion of Research at the Technion and by the Technion VPR fund.

References

[1] S. Speiser, Chem. Rev. 96 (1996) 1953.
[2] L. Young, C.A. Hayman, D.H. Levy, J. Chem. Phys. 79 (1983) 1592.
[3] D.E. Poeltl, J.K. McVey, J. Chem. Phys. 40 (1984) 1801.
[4] Y. Tomioka, H. Abe, N. Mikami, M. Ito, J. Phys. Chem. 88 (1984) 5186.
[5] F. Lahmani, C. Lardeux-Dedoner, A. Zehnacker-Rentien, J. Chem. Phys. 92 (1990) 4159.
[6] J. Bigman, Y. Karni, S. Speiser, Chem. Phys. 177 (1993) 601.
[7] J. Bigman, Y. Karni, S. Speiser, J. Photochem. Photobiol. A: Chem. 78 (1994) 101.
[8] G. Rosenblum, S. Speiser, J. Photochem. Photobiol. A: Chem. 112 (1998) 117.
[9] G. Rosenblum, S. Speiser, J. Chem. Phys. 102 (1995) 9149.
[10] D. Groswasser, S. Speiser, J. Fluoresc. 10 (2000) 113.
[11] J.A. Syage, J.E. Wessel, J. Chem. Phys. 89 (1988) 5962;
J.E. Wessel, J.A. Syage, J. Chem. Phys. 94 (1988) 737.
[12] M.W. Schaffer, W. Kim, P.M. Maxton, J. Romascan, P.M. Felker, Chem. Phys. Lett. 242 (1995) 632.
[13] H. Saigusa, E.C. Lim, J. Chem. Phys. 98 (1994) 13470;
H. Saigusa, E.C. Lim, J. Chem. Phys. 99 (1995) 15738;
H. Saigusa, M. Itoh, J. Phys. Chem. 89 (1985) 5486.
[14] H. Saigusa, E.C. Lim, J. Chem. Phys. 103 (1995) 8793.
[15] M. Itoh, Y. Morita, J. Phys. Chem. 92 (1988) 5693;
H. Saigusa, E.C. Lim, J. Chem. Phys. 95 (1991) 1194;
H. Saigusa, E.C. Lim, J. Chem. Phys. 95 (1991) 2364.
[16] J.E. Wessel, S. Beck, C. Highstrete, J. Chem. Phys. 101 (1994) 10292.
[17] W.T. Yip, D.H. Levy, J. Phys. Chem. 100 (1996) 11539.
[18] X. Wang, D.H. Levy, M.B. Rubin, S. Speiser, J. Phys. Chem. 104 (2000) 6558.
[19] G. Rosenblum, S. Speiser, J. Chem. Phys. 102 (1995) 9149.
[20] B.E. Wilson, Molecular Vibrations, McGraw-Hill, New York, 1955.
[21] L.D. Landau, E.M. Lifshitz, Mechanics, 3rd Edition, Pergamon Press, Oxford, 1984.
[22] G. Rosenblum, S. Speiser, J. Nonl. Opt. Phys. Mat. 5 (1996) 695.
[23] G. Rosenblum, S. Speiser, Advances in Multi-Photon Processes and Spectroscopy, Vol. 12, World Scientific, Singapore, 1998, pp. 1–179.