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# Analysis of the Origin Band of Acridine Dimer Fluorescence Excitation Spectrum — Conformations of Jet-Cooled Acridine Dimer

I. DEPERASIŃSKA AND J. PROCHOROW

Institute of Physics, Polish Academy of Sciences  
al. Lotników 32/46, 02-668 Warsaw, Poland

*(Received August 8, 2001)*

The analysis of rotational band contour for the origin transition of fluorescence excitation spectrum of acridine dimer, earlier observed under conditions of jet-cooling in supersonic helium expansion, has been performed. An optimized ground-state equilibrium structure of acridine dimer fits the approximation of asymmetric top rigid rotor. In this approximation rotational constants were determined and an A-type rotational band was computed. It has turned out that the computed rotational band contour is much narrower than the experimental one. In search for the reasons of this discrepancy between calculations and experiment, an analysis of relative rotational motion of acridine moieties of the dimer was carried out. It was found that minima of potential energy curves for rotational motion, although very flat, under conditions of supersonic expansion can acquire (in their shallow local minima) non-vanishing population of slightly different conformations of the dimer. It was shown that in terms of non-statistical distribution of such populations, the origin bands of individual conformations may contribute to the experimental band contour.

PACS numbers: 33.20.Sn, 33.70.-w

## 1. Introductory review and problem formulation

With the help of high-resolution laser spectroscopy in supersonic molecular beams expansions, the long-lasting search and dispute of the mechanisms of very large (and sometimes extreme) sensitivity of aza-derivatives of aromatic polycyclic hydrocarbons to the solvation process — as either due to the solvent-dependent

gap between close-lying singlet excited states of different electronic character (connected with their  $\pi$ ,  $\pi^*$  and  $n$ ,  $\pi^*$  origin), or due to inversion of these  $^1(\pi, \pi^*)$  and  $^1(n, \pi^*)$  electronic states upon formation of hydrogen-bonded complexes with solvent molecules [1–5] — though not yet terminated, have been driven toward much better understanding in the last decade (for a review see for instance [6]). Recently, even in the case of such a troublesome member of this family as acridine, some progress has been reached due to the application of laser-induced emission spectroscopy of acridine cooled in a supersonic jet. A fairly efficient fluorescence emission of acridine (ACD) molecules observed in protic solvents, which becomes extremely weak and is not at all observed in aprotic nonpolar solvents (and in the gas phase), neither shows up under supersonic expansion conditions. Instead, in a supersonic helium jet seeded with ACD molecules, the fluorescence due to acridine dimers,  $(\text{ACD})_2$ , which are being formed under jet cooling conditions, was observed [7].

Since an ACD molecule, a monoaza-derivative of anthracene, contains a nitrogen heteroatom in a central aromatic ring of anthracene skeleton (cf. Fig. 1), its capability to the formation of hydrogen-bonded complexes by the interaction of nitrogen lone-pair electron density with molecules of protic solvents, seems to be obvious. Hence, a huge enhancement of the fluorescence quantum yields of ACD in hydrogen-bonding solvents, could safely be explained as due to changes of radiative properties of the lowest excited state caused by the inversion of nearly-resonant,  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$ , singlet states of ACD in hydrogen-bonded complex. On the other hand, quite a large body of experimental evidence seems to indicate that the lowest excited singlet state of ACD is of  $\pi, \pi^*$  origin, with clear-cut observations of ACD fluorescence and phosphorescence in rigid crystalline and inert matrices (see for instance [8, 9] and references therein). As a matter of fact, the assignment of the lowest excited electronic states of ACD is not definitive as yet.

In this context an identification of laser-induced fluorescence from acridine-seeded supersonic helium jet as the emission of acridine dimer [7] has added to the old question (about the reasons of virtual lack of fluorescence of the ACD molecules in aprotic solvents and in the gas phase) the new questions about a possible stable structure of the  $(\text{ACD})_2$  dimer formed under jet-cooling conditions and of course about the physical cause of the opening of radiative relaxation channel within the dimer unit.

Under supersonic jet conditions only two types of intermolecular interactions, that could result in the formation of Van der Waals complexes, are of importance. The first one, i.e. aggregation or clustering of acridine with helium carrier gas, can safely be excluded as not strong enough to change the electronic transitions in acridine molecule. The second one is an interaction between the ACD molecules and this may result in the formation of  $(\text{ACD})_2$  dimer (or other aggregates) stabilized by weak Van der Waals interactions in the ground state (presumably of sandwich type structure, in undisplaced or displaced parallel or anti-parallel configuration,

as in many other known cases [10–14]). However, the presence of nitrogen atom in the ACD molecule could also lead to the stabilization of the ground-state dimer via hydrogen-bonded complex in planar configuration (as in the case of pyrazine and pyrimidine [13], benzonitrile [14] or carbazole [15]). This has turned out to be the case for  $(ACD)_2$ , as inferred from calculations of its equilibrium geometry, first performed within the framework of the AM1, and subsequently cross-checked and verified by the PM3, semi-empirical parametric methods [7, 16]. The results of both methods are qualitatively the same: an optimized ground-state equilibrium configuration of acridine dimer has a head-to-tail configuration in which nitrogen atom of one acridine molecule is located directly above C–H bond in the central ring of the second acridine molecule in almost coplanar orientation of aromatic skeletons of both molecules and colinear orientation of the short NCH molecular axes of both ACD moieties in the  $(ACD)_2$  unit (cf. Fig. 1; see also Fig. 3 in Ref. [7] and Fig. 3 in Ref. [16]). Such a structure of  $(ACD)_2$  facilitates the formation of a weak  $N \cdots H-C$  hydrogen-bond between both ACD molecules. Furthermore, it also facilitates a very effective enhancement of the transition dipole moment for electronic transition to the first excited singlet state of the dimer (polarized along the short molecular axis in the ACD molecule), which results in a large increase in the oscillator strength (from 0.002 for monomer ACD molecule to 0.213 for  $(ACD)_2$  acridine dimer [7, 16]). And this accounts for virtual lack of fluorescence emission

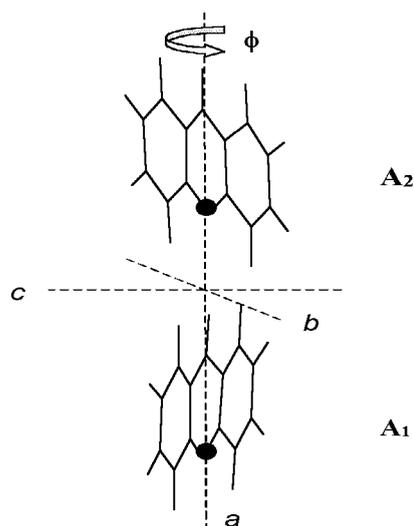


Fig. 1. The optimized ground-state equilibrium structure of acridine dimer in an arbitrary chosen perspective projection. Black dots in central rings of anthracene aromatic skeletons stand for nitrogen atoms (in acridine molecules).  $a$ ,  $b$  and  $c$  axes of the coordinate system are the principle axes of inertia of the molecular system.

of acridine monomer and fairly measurable fluorescence of acridine dimer under jet-cooling conditions. In this context, it should be mentioned that detailed singly excited configuration interaction (CI) calculations of MO energy diagrams for the ACD molecule and its (ACD)<sub>2</sub> dimer always indicate that the lowest-lying excited states are of  $\pi, \pi^*$  electronic origin for both, the ACD molecule and its (ACD)<sub>2</sub> dimer [16].

As was mentioned above, the main characteristic of the equilibrium configuration of acridine dimer (either AM1- or PM3-optimized) is its colinearity along the axis which contains the N · · H–C hydrogen-bond and short molecular axes of both ACD moieties (an  $a$  axis in Fig. 1). There is, however, a structural difference between AM1- and PM3-optimized equilibrium configurations of (ACD)<sub>2</sub>. In the case of PM3 optimization method the head-to-tail structure of the dimer is ideally coplanar — the molecular planes of both ACD molecules lie in the  $ac$  plane of coordinate system (cf. also Fig. 3 in Ref. [16]). In the AM1-optimized structure the molecular planes are rotated from coplanarity by an angle of  $\sim 40^\circ$  about  $a$  axis of the coordinate system (cf. also Fig. 3c in Ref. [7]). From the point of view of above-described mechanism of enhancement of the oscillator strength for radiative transition between the ground and excited singlet states in (ACD)<sub>2</sub> dimer, rotation of molecular planes of ACD moieties in the dimer about the common axis, seems to be of minor importance, provided such a rotation does not destroy the colinearity of short molecular axes of both ACD moieties. However, the “rigidity” of this axis of rotation is assured in the equilibrium structure of the dimer by the weak N · · H–C hydrogen-bond only, and thus the relative stability of the dimer becomes a crucial factor.

Binding energies of optimized configurations of (ACD)<sub>2</sub> were found to depend strongly on the used optimization procedure ( $\sim 600$  and  $\sim 1900$  cm<sup>-1</sup> for AM1 and PM3, respectively). However, these results are of limited significance, as demonstrated by the “cross-optimization” analysis [16], and the cited absolute values should be treated as the lower and upper limits of binding energies of the optimized structure of (ACD)<sub>2</sub>.

The above review of previous findings and conclusions of the analysis of (ACD)<sub>2</sub> dimer formed in jet-cooled expansion was aimed at the demonstration that in the case of such extended and loosely-bounded molecular system, as (ACD)<sub>2</sub> dimer under consideration, which are characterized by several additional internal degrees of freedom (for relative motion between dimer’s components), the fine details of the geometry and stabilization of equilibrium configurations depend much on the optimization procedures employed, even if the general features (or qualitative results) are for all practical purposes much the same. The most suitable for the verification of calculated geometry of equilibrium configuration of molecular Van der Waals clusters formed under jet-cooling conditions, and for analysis of its fine details, is the method of rotational contour analysis of observed bands in high-resolution fluorescence and fluorescence excitation spectra. The rotational spectrum

depends strongly on relative orientation of molecular components of the cluster (dimer) and on its rotational temperature, and computer simulations of rotational band contour (based on an appropriate molecular rotor) can justify postulated equilibrium configuration with, sometimes, great accuracy, or yield necessary information for its improvement in the case when the rotational structure of the observed rovibronic bands is not resolved. Advantages of rotational contours analysis and simulations have been clearly demonstrated with numerous examples of isolated molecules, various types of Van der Waals complexes, hydrogen-bonded complexes, etc. (see for instance [6, 13, 14, 17, 18]).

In this paper we report the results of rotational contour analysis of the origin (0-0) band of fluorescence excitation spectrum of jet-cooled acridine dimer, registered in the course of our earlier experiments [7]. The analysis is aimed at a refinement of geometry of equilibrium configuration of acridine dimer obtained within the framework of AM1 and PM3 optimization procedures [7, 16]. In particular we expect to gain information concerning coplanarity of the molecular components of the dimer stabilized by the formation of the weak  $N \cdots H-C$  hydrogen-bond in the head-to-tail configuration. To this end we will also perform calculations and analysis of the potential energy curve for rotation of the acridine moieties in the  $(ACD)_2$  unit, in the hope of getting a deeper insight into the freedom of such rotational motion (and/or getting an idea about presumable energy barriers that could inhibit the rotation).

## 2. Origin band of fluorescence excitation spectrum of acridine dimer

The dispersed laser induced fluorescence and its excitation spectra for acridine-seeded helium supersonic expansion have been observed with the use of molecular beam supersonic apparatus, laser system, and data acquisition methods, which have been all described in detail earlier [7].

The low-energy part (from  $\sim 26\,900$  to  $\sim 27\,300$   $\text{cm}^{-1}$ ) of fluorescence excitation spectrum, shown in Fig. 2, begins with the most intense band located at  $27\,018 \pm 2$   $\text{cm}^{-1}$ . This band has been identified as an origin (vibrationless) transition in the laser induced fluorescence (LIF) excitation spectrum of  $(ACD)_2$  acridine dimer [7]. Relatively intense bands located within 0–150  $\text{cm}^{-1}$  of the spectrum origin (the range, where there are no active vibrations of acridine molecule) are of intermolecular character. The subsequent normal mode analysis of vibrations, performed for the whole recorded range of the LIF excitation spectrum, has confirmed such an assignment of low-frequency vibrations as intermolecular vibrations of  $(ACD)_2$  dimer — the forms of the normal vibrations are clearly showing that they are connected with a movement of counterparts of  $(ACD)_2$  as a whole, without changes of molecular bonds and angles in the ACD molecules [19]. Their presence in the observed fluorescence excitation spectrum was the most conclusive experimental evidence of the formation of  $(ACD)_2$  acridine dimer under jet-cooling conditions.

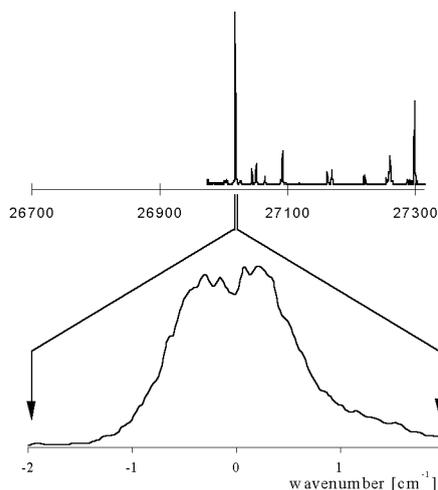


Fig. 2. (Top) low-energy part of the fluorescence excitation spectrum of acridine dimer formed in a supersonic jet expansion (after [7]). Transition at  $27\,018\text{ cm}^{-1}$  is the electronic vibrationless 0–0 transition — the origin band of the dimer excitation spectrum. (Bottom) observed rotational band contour of the 0–0 transition (zero of the scale is centred at  $27\,017.5\text{ cm}^{-1}$ ); arrow-ended vertical lines show the magnified region of the upper spectrum.

The dispersed fluorescence spectrum of  $(\text{ACD})_2$  excited in the band origin ( $27\,018\text{ cm}^{-1}$ ) starts with the 0–0 transition which is resonant with the 0–0 origin band of LIF excitation spectra (see Fig. 2 in Ref. [7] or Fig. 2 in Ref. [16]) and contains most of the intensity of fluorescence emission (recorded in our experiments down to  $\sim 24\,000\text{ cm}^{-1}$ ). We note that these observations may indicate that geometry of acridine dimer is to a large degree retained in its excited state.

Figure 2 shows also a fluorescence excitation spectrum recorded over the rotational contour of the origin 0–0 band. This band contour is characterized by the relatively low width, of  $\sim 1.5\text{ cm}^{-1}$  fwhm, which is smaller than the observed one of the anthracene 0–0 band under comparable experimental conditions [17], still however it seems to be wider than expected for such a relatively large and massive molecular system as  $(\text{ACD})_2$  dimer. The rotational structure is not resolved and the observed band contour is the envelope of rovibronic transition. However, there are distinct and regular traces of the structural features within the band profile. They are especially regularly spaced at the region of a double-headed band maximum where each of the two, *P*- and *R*-like branches (separated by the distinct minimum at  $27\,017.5\text{ cm}^{-1}$ ) is additionally split by  $0.15\text{ cm}^{-1}$  into two maxima. Furthermore, the wings of the contour are not smooth and bear the traces of the structure. In this respect, the observed origin band contour of  $(\text{ACD})_2$  dimer is different from the rotational contours, rich of dense and fully irregular structural

features, usually observed for large molecules [20]. Therefore, although quick inspection of the origin band of fluorescence excitation spectrum given in Fig. 2 suggests that it looks like a B-type rotational contour of asymmetric top rigid rotor, such a classification is not definite and subsequent computer simulations should be carried out with great care.

### 3. Simulations of rotational contour of the origin band

The most important feature in geometry of ground-state equilibrium configuration (besides the fact that for all practical purposes it does not depend on the choice of optimization method) is a colinear arrangement of short molecular axes of both acridine moieties (depicted as  $A_1$  and  $A_2$  in Fig. 1, which illustrates an AM1-optimized version of the dimer structure). As discussed earlier in Sec. 1, this colinearity is responsible for a huge enhancement (by two orders of magnitude) of the oscillator strength for electronic transition from the ground to the first excited singlet state in the dimer, as compared to the monomer acridine molecule (which, by the same token, accounts for the virtual lack of fluorescence emission of acridine, hardly observed in the gas phase or in aprotic solutions). This was a very strong physical argument in favour of equilibrium structure of  $(ACD)_2$  dimer, predicted by both AM1 and PM3 methods [7, 16].

TABLE  
Rotational constants of AM1- and PM3-optimized ground-state equilibrium structure of acridine dimer.

	Rotational constants [ $\text{cm}^{-1}$ ]		
	$A$	$B$	$C$
AM1	0.007773	0.003557	0.002624
PM3	0.007688	0.003851	0.002591

Within the framework of both optimization procedures, we have calculated the inertia moments along the principle inertia axes  $a$ ,  $b$ , and  $c$ , and from these, in a usual manner the corresponding rotational constants  $A$ ,  $B$ , and  $C$  were derived for both optimized structures of  $(ACD)_2$  dimer (see Table). It is seen that the rotational constants for AM1- and PM3-optimized structures of  $(ACD)_2$  practically do not differ (only in the case of  $B$  rotational constant this difference exceeds 5%). It is also seen that for both optimized equilibrium structures, all three rotational constants are different ( $A > B > C$ ) and the principle  $a$  axis of the dimer is an axis of the largest rotational constant  $A$ . If we recall that the transition dipole moment for the origin 0–0 transition from the ground to the excited singlet states of the dimer is polarized along the  $a$  axis (whose direction, as discussed on several occasions earlier, also coincides with the directions of short molecular axes of both

$A_1$  and  $A_2$  acridine moieties and of the  $N \cdots H-C$  hydrogen bond) then we arrive at the conclusion that the rotational contour of the origin band must be of A-type (within the asymmetric top rigid rotor approximation).

Computer simulations of the rotational band contour have been carried out with the use of modified ASYROT asymmetric rotor code [21]. In the first approximation of these stimulations we have assumed that the equilibrium geometry in the first excited singlet state of  $(ACD)_2$  is not changed relatively to its geometry in the ground state. This assumption seems to be largely justified by the fact that the observed 0–0 origin transition in the fluorescence spectrum is strictly resonant with the 0–0 transition in its fluorescence excitation spectrum and both these transitions are the most intense (cf. earlier discussion in Sec. 2).

The result of computer simulated rotational contour, for the AM1-optimized structure, is given in Fig. 3 (for PM3-optimized dimer geometry, the computer simulated rotational contour is quantitatively the same and in the following we will stick to the results of AM1 model). The computed A-type band shows all three,  $P$ ,  $Q$ , and  $R$  branches but its comparison with experimental rotational contours clearly shows that it is much narrower than the observed one (approx. by the factor of 2). As expected, the computed contours are dependent on the rotational temperature, as shown by the results given in Fig. 4, but even at a higher rotational temperature (10 K) the computed contour is still not wide enough. Similarly, as shown in Fig. 5, the simulated band contour is getting wider upon an increase in the used half-width  $\Gamma$  of the Lorentzian profile for the rotational lines, but also in this case, the gain of the width of simulated rotational band contour is not satisfactory from the point of view of the observed contour. And what is probably more important, the shape of simulated rotational band contour does not resemble the experimental shape, even qualitatively. It seems that one should look for the

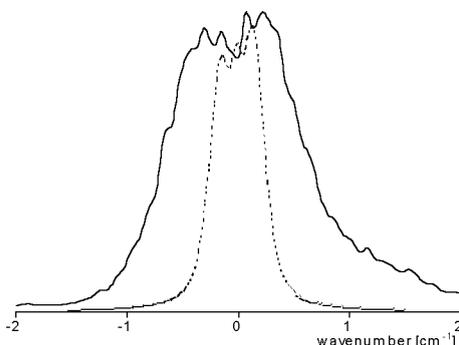


Fig. 3. Observed rotational band contour (solid line) and simulated rotational band contour (dashed line) computed as the A-type transition of asymmetric top rigid rotor (with the values of  $A$ ,  $B$ , and  $C$  rotational constants given in Table for AM1-optimized structure of the dimer; half-width of the Lorentzian line profiles  $\Gamma = 0.1 \text{ cm}^{-1}$ ,  $T = 2 \text{ K}$ ).

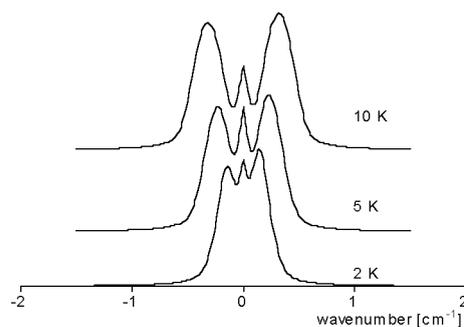


Fig. 4. Simulated rotational band contours computed for different rotational temperatures (as indicated);  $\Gamma = 0.1 \text{ cm}^{-1}$ .

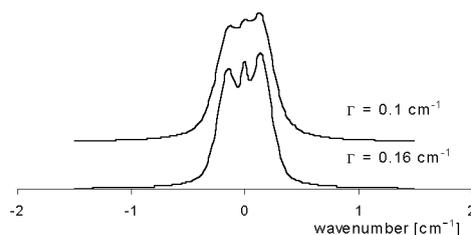


Fig. 5. Simulated rotational band contours computed for different half-widths of the Lorentzian line profiles  $\Gamma$  (as indicated);  $T = 2 \text{ K}$ .

reasons of this apparent failure of simulations of rotational contour for the origin band, beyond the drawbacks of simulation procedures itself.

#### 4. Discussion and conclusions

In order to rationalize our search for the troubles encountered during the first steps of the analysis of rotational band contour, we examine in more details energetics of internal rotational motion within the  $(\text{ACD})_2$  acridine dimer.

The potential energy of  $(\text{ACD})_2$  dimer has previously been analysed in a function of the  $\text{N} \cdots \text{H}$  hydrogen bond length, in connection with the check of validity of AM1 and PM3 optimization methods in handling a hydrogen bond problem [16]. As we mentioned earlier in Sec. 1, the binding energies of optimized configurations of  $(\text{ACD})_2$  along the  $\text{N} \cdots \text{H}$  reaction coordinate are strongly dependent on the applied optimization procedure ( $\sim 600$  and  $\sim 1900 \text{ cm}^{-1}$  for AM1 and PM3, respectively). However, it was also demonstrated that the absolute values of energies can only be treated as the lower and upper limits of binding energies for the optimized structure of  $(\text{ACD})_2$ . Moreover, these findings have not excluded the possibility of existence of different, noncoplanar or tilted conformations of  $\text{A}_1$  and  $\text{A}_2$  moieties within the  $(\text{ACD})_2$  unit.

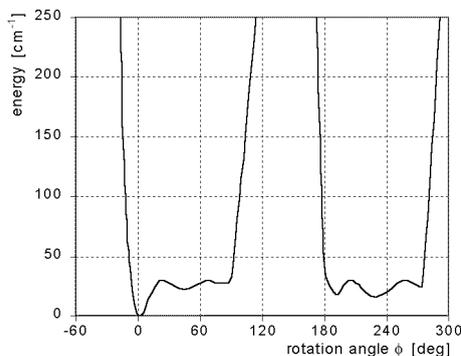


Fig. 6. Potential energy curve of acridine dimer for relative rotation (about principle  $a$  axis) of molecular planes of  $A_1$  and  $A_2$  acridine moieties in the AM1-optimized dimer structure in the ground-state.

In Fig. 6 we present the potential energy curve, for the ground state AM1-optimized equilibrium configuration, calculated as a function of dihedral angle of rotation  $\phi$  about an  $a$  axis (a coordinate that measures coplanarity of molecular planes of  $A_1$  and  $A_2$  within  $ac$  plane of coordinate system; cf. Fig. 1). The potential energy curve for rotation is characterized by two minima, which are separated by an energy barrier of  $\sim 700 \text{ cm}^{-1}$  height — this is not a surprising result, in view of the earlier mentioned close equivalence of geometry of equilibrium structures optimized with two different (AM1 and PM3) methods. Both minima, of only slightly different depth (ca.  $15 \text{ cm}^{-1}$ ), are very wide (up to  $\sim 100 \text{ deg}$ ) and flat, although some shallow local minima, separated by equally low barriers, can be spotted on the bottom of each of these two. Although, such shallow minima seem to be of no importance, one should remember that under efficient cooling in supersonic jet, at very low rotational temperatures, the presence of such minima may indicate the possibility of non-statistical distribution of population among some number of slightly different (rotational) conformations (at 2 K even  $10 \text{ cm}^{-1}$  barrier can be considered as a high barrier). The question is, as to whether such a non-statistical distribution of populations could account for the observed rotational band contour, which is an envelope of rovibronic transition. In order to check further this issue, we have examined an influence of relative rotation of molecular moieties of  $(\text{ACD})_2$  dimer, on some other parameters, characteristic of the system and transition under consideration. The results of relevant calculations are collected in Fig. 7. It is seen that the rotational constants  $B$  and  $C$  are changing upon rotation, however, the rotational constant  $A$  is not sensitive to rotation and remains all the time fairly constant (Fig. 7a). On the other hand, changes of the 0–0 electronic transition energy (Fig. 7b) seem to be pronounced on the scale of width of the observed origin band of fluorescence excitation spectra (as they reach ca.  $10 \text{ cm}^{-1}$  in the range of angular width of minima of the potential energy curve of Fig. 6. Also the changes of oscillator strength for this transition (Fig. 7c), display the same

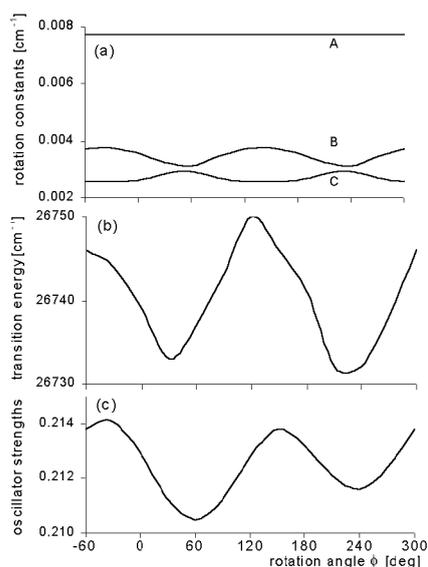


Fig. 7. Changes of the rotational constants (a), energy of electronic transition between the ground and excited singlet states (b) and of the oscillator strength for electronic transition (c) upon the relative rotation of molecular planes of  $A_1$  and  $A_2$  acridine moieties in the dimer.

periodic character upon the rotation as changes of energy of electronic transition (although the amplitude of changes is small).

In view of these findings, one could assume that the changes of energy of electronic transition, due to the relative rotational motion of molecular  $A_1$  and  $A_2$  moieties, might be treated as an equivalence of non-statistical distribution of populations of different (rotational) conformations of ground-state of  $(ACD)_2$  dimer of slightly different energies. Excitation of such conformations would bring about, as a net result, a broadening of the observed rotational band contour of the origin transition. It is clear, however, that such an assumption must be a subject to verification by the calculations of potential energy surface of the first excited singlet state of the dimer. A direct search for different ground-state-stable conformations of  $(ACD)_2$  with the use of high-resolution Fourier-transform microwave spectroscopy in a supersonic expansion [6], although basically capable of revealing their presence, would not be able to provide necessary information about radiative and radiationless relaxation paths in the excited electronic state, which are responsible for the observed fluorescence excitation spectra. Only an examination of relevant cross-section of excited state potential energy surface along the rotational coordinate ( $\phi'$  angle) might be able to show presumable distribution of electronic (vertical) transition energies connected with the presence of different ground- and excited-state conformations of acridine dimer (as demonstrated in studies of the role of orientational isomers of exciplex systems [22, 23]).

Still, however, it is interesting to check such a possibility in an exercise-like manner just in order to see if this might be a proper way for the description of the observed rotational band contour. To this end, the rotational contour was computed as an overlap of several individual rotational contours of Fig. 3, which were slightly shifted one from each other. The results of these exercise computations are collected in Fig. 8. They show that the observed envelope of rovibronic origin transition can be reconstructed as an overlap of computed rotational band contours that are slightly shifted on the energy scale and which would contribute to the overall profile with a slightly different intensity (following the trend in rotational dependence of the oscillator strength shown in Fig. 7c). The fit of experimen-

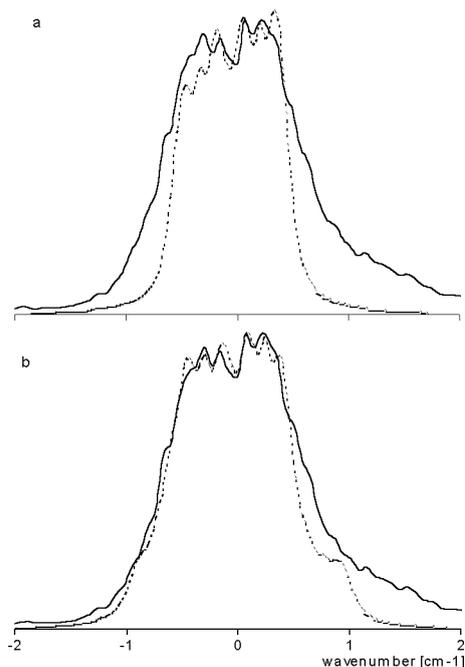


Fig. 8. Comparison of observed rotational band contour (solid line) with simulated rotational band contour (dashed line) computed under the assumption that the origin bands of different conformations of acridine dimer are contributing to the observed band contour (see the text). (a) Simulated band contour computed as a contribution from 2 conformations (with origin bands shifted from the central (0) position by  $-0.26$  and  $+0.28$   $\text{cm}^{-1}$ ; intensity ratio 1 : 0.84) and (b) simulated band contour computed as a contribution from 6 conformations (the best fit was achieved when the origin bands of individual conformations were shifted from the central (0) position by:  $-0.68$ ,  $-0.42$ ,  $-0.24$ ,  $+0.14$ ,  $+0.32$ , and  $+0.82$   $\text{cm}^{-1}$ , respectively, with the relative intensity ratio 1.05 : 1.15 : 3.45 : 1.0 : 4.05 : 1.0).

tal band profile is improving with an increasing number of contributing individual bands (of Fig. 3) and becomes reasonably good and acceptable for four (and more) overlapping bands.

The main conclusion, which comes out of this discussion, seems to be straightforward — there is a possibility that the origin bands of different conformations of acridine dimer, which may be populated under jet-cooling conditions, are contributing to the experimental band contour. And although this conclusion still requires more experimental and theoretical work for conclusive evidence, it seems to be supported, at least qualitatively, by recent investigations of large flexible organic molecules [24].

### Acknowledgments

We are grateful to Dr. Z. Kisiel for his PROSPE computational programs used in this work. We also want to acknowledge the fact that this work was in part financed by the State Committee for Scientific Research under project 5 P03B 136 20.

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