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On the pyrazine and pyrazine-pyrimidine dimers^{a)}

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Spectra of the pyrazine-*d*₄, pyrazine-*h*₄-pyrazine-*d*₄, and pyrazine-*d*₄-pyrimidine dimer are obtained and analyzed with the help of Lennard-Jones-hydrogen-bonding (LJ-HB) potential energy calculations. The pyrazine isotopic hetero and homo dimers possess nearly identical spectra with the exception that the perpendicular dimer features are displaced to the red by ~ 11 cm^{-1} . Exchange or exciton interactions in this system are vanishingly small (less than 1 cm^{-1}). The geometries suggested by the isotopically substituted pyrazine dimer spectra are the same as those found for the pyrazine-*h*₄ homo dimer: a parallel planar hydrogen bonded and a perpendicular dimer. The pyrazine-*d*₄- and pyrazine-*h*₄-pyrimidine dimer spectra are quite complicated. These spectra can be assigned as arising from one parallel stacked head-to-tail displaced dimer, one parallel planar dimer, and three perpendicular dimers based on comparisons with spectra of the pyrazine and pyrimidine dimers.

I. INTRODUCTION

The study of dimers of simple organic systems has a number of motivations. Dimers are of interest in their own right for the investigation of geometry, energy levels, intermolecular interactions, and vibrational dynamics. In addition, dimers can serve as models for various condensed phase systems and nonrigid, flexible molecules. Dimer formation must be an essential process in the early stages of the nucleation and growth of condensed phases. Condensed phase dynamics and molecular rearrangements can be elucidated through dimer intramolecular vibrational redistribution and vibrational predissociation studies. Various types of dimers have been studied by supersonic molecular jet laser optical spectroscopy.¹⁻³

Among the various supersonic molecular jet optical techniques available for the study of clusters in general, we have invariably employed two color time of flight mass spectroscopy (two-color TOFMS) for the investigation of dimers. The two-color TOFMS technique allows the optical spectrum of a species belonging to a particular mass to be recorded. This is essential for the spectroscopic characterization of isotopic species and for dimers with different geometries but identical masses. The two-color TOFMS technique yields both mass and wavelength resolution in a single experiment. The spectra of (benzene)₂,² (toluene)₂,^{1(a)} (toluene-benzene),^{1(a)} (pyrazine)₂,³ (pyrimidine)₂,³ and many of their deuterated analogs have been recorded and analyzed with this technique. Along with the experimental data, potential energy calculations employing Lennard-Jones (LJ, 1-6-12) potential functions are used to generate minimum energy configurations for the dimers. A hydrogen bonding term of the form (10-12) replaces the LJ (6-12) form if a hydrogen bonding interaction is possible for a pair of atoms. Details of this procedure, atom-atom potential

parameters, and the calculational techniques are discussed in previous publications from our laboratory.^{3,4}

In the case of protonated pyrazine, both the experimental results and the potential energy calculations generate a consistent set of conclusions for the dimer geometries. The calculations produce three distinct geometries for the pyrazine dimer: a hydrogen bonded planar configuration with a nitrogen of each pyrazine coordinated to a hydrogen of its partner; a perpendicular configuration with two hydrogens of the stem pyrazine oriented toward the nitrogens of the base pyrazine; and parallel stacked pyrazine with the two pyrazines rotated $\pi/4$ with respect to one another. Observed spectral features can be assigned to the first two configurations, but not the third. The latter configuration can form an excimer and may well have no sharp observable features within thousands of wave numbers of the pyrazine 0_0^0 .

The experimental observations for the pyrimidine dimers are much more complex than those of pyrazine, but, nonetheless, the calculations still render an accurate, logical, and self-consistent assignment of these data. Calculations find a head-to-tail parallel stacked and displaced configuration, another parallel stacked configuration but with the two pyrimidine molecules rotated $\pi/4$ with respect to one another, and four distinct, hydrogen bonded planar configurations. Unlike the case of pyrazine, no perpendicular configurations can be calculated with the potential employed. The four planar configurations are expected to be blue shifted from the pyrimidine origin and can be readily identified in the spectrum. The parallel stacked displaced, head-to-tail configuration can be assigned to a single feature with a large red shift ($\Delta \sim -170 \text{ cm}^{-1}$). The stacked and rotated configuration is not assigned to a spectroscopic feature and is presumed to form an excimer.

Since both spectroscopic data and calculational results present a consistent picture of the pyrazine and pyrimidine dimers, the LJ potential form proves of great value in making assignments and in understanding the nature of the dimers in general.

^{a)} Supported in part by grants from ONR and the Philip Morris Corporation.

The set of experiments reported herein are designed to examine further the pyrazine and pyrimidine dimers. Of particular interest with regard to the above results for the individual dimers, is the existence of perpendicular dimer structures for pyrimidine with other molecules. The dimers of pyrazine and pyrimidine, as well as their mixed dimers, all have the same mass and thus the most useful experiment for the mixed dimer employs pyrazine- d_4 rather than pyrazine- h_4 . The selective use of isotopically enriched molecules displays another significant advantage of two-color TOFMS techniques. Pyrazine- d_4 is chosen rather than pyrimidine- d_4 because of its ready commercial availability.

As a consequence, pyrazine- d_4 and pyrazine- d_4 - h_4 dimers are also studied and reported. These latter dimers have spectra similar to the pyrazine- h_4 dimer, as would be expected based on the LJ potential calculations.

The mixed pyrazine- d_4 -pyrimidine- h_4 dimers, on the other hand, do evidence spectra which are quite different from those of the homo dimers. In order to interpret and assign fully the mixed pyrazine- d_4 -pyrimidine- h_4 dimer spectra, use is also made of the pyrazine- h_4 -pyrimidine- h_4 dimer spectrum. While these latter spectra are even more congested than the pyrazine- d_4 -pyrimidine- h_4 spectra, the combination of the spectra of all four dimers is sufficient, in conjunction with the calculation, to assign self-consistently all features with reasonable certainty. The pyrazine-pyrimidine dimer system includes one planar, one stacked, and three perpendicular configurations.

II. EXPERIMENTAL PROCEDURES

The experimental apparatus and procedures for the supersonic molecular jet two-color TOFMS study of dimers have been described in earlier publications^{4,5} in considerable detail. Briefly, the dimers are generated with a pulsed valve having an 0.5 mm orifice. After the beam is skimmed, it is intersected by two pulsed laser beams 7.5 cm downstream from the valve. The two laser beams and the molecular beam intersect between the accelerator plates of the TOFMS; one laser excites the dimer to its first excited singlet state (S_1) and the second laser generates the dimer ion from S_1 . The signal from the mass detector is monitored on a transient digitizer or a boxcar averager. The output of these devices then goes to a computer for further averaging and storage. The computer scans the lasers and controls the time evolution of the experiment.

The lasers are two Nd-YAG pumped dye lasers, the outputs of which are doubled and/or mixed with the 1.064 μm pump beam to achieve the proper independent final frequencies for the $S_1 \leftarrow S_0$ and ion $\leftarrow S_1$ transitions. The pump dye laser employs DCM dye and the ionization dye laser employs R590 dye; both outputs are doubled.

The samples are treated as discussed in previous publications. The backing pressure for the nozzle is typically 120 psig.

The calculational procedure and potential energy terms have been given in an earlier publication⁴; the constants employed in the potential can be found in Refs. 4, 5, and 6. No parameter fitting is done in these calculations and thus they represent an independent set of data to aid in the spectral analysis.

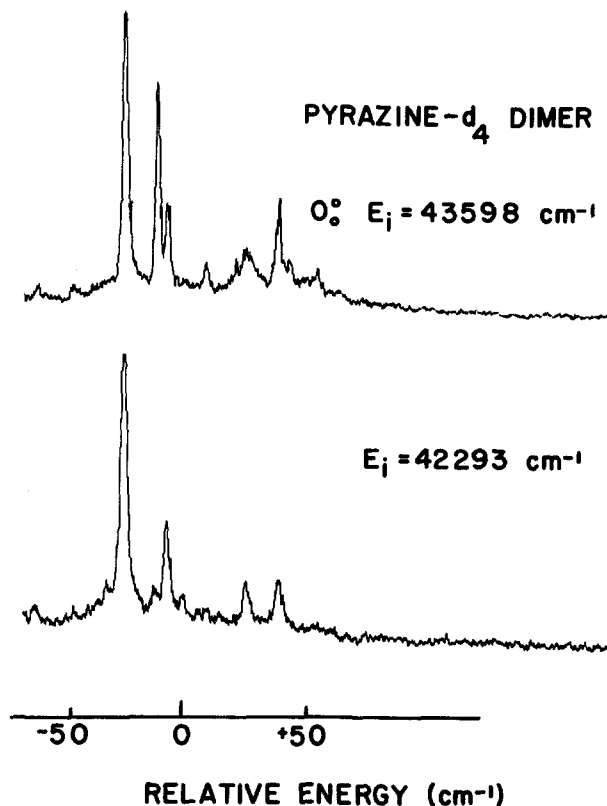


FIG. 1. Two-color TOFMS of pyrazine- d_4 dimer in the region of the pyrazine- d_4 origin. Spectra taken with two different ionization energies are presented. The pyrazine- d_4 monomer origin ($31\,030.4\text{ cm}^{-1}$) lies at 0 cm^{-1} on the scale of the figure. See Table I for absolute energies.

III. RESULTS

A. Pyrazine- d_4 dimer

The pyrazine- d_4 dimer spectra taken at two different ionization energies are shown in Fig. 1. Four features disappear in the spectrum of the dimer as the ionization energy is lowered from $\sim 43\,600$ to $42\,300\text{ cm}^{-1}$; these are located at shifts of -11.5 , $+11.5$, 25.5 , and 64.1 cm^{-1} from the pyrazine- d_4 monomer 0_0^0 transition at $31\,030.4\text{ cm}^{-1}$. The relatively intense features that remain at the lower ionization energy are located at shifts of -26.9 , -6.4 , $+31.0$, and $+45.9\text{ cm}^{-1}$ with respect to the pyrazine- d_4 0_0^0 transition. From this dependence of the spectrum upon ionization energy, one concludes that at least two configurations of the dimer are present in molecular jet expansion. A similar dependence on ionization energy has been reported for pyrazine- h_4 dimer.³ Table I summarizes these data.

Dimer spectra corresponding to the other pyrazine- d_4 vibronic origins 10_0^1 and $6a_0^1$ are shown in Fig. 2 along with the 0_0^0 spectrum. Note that a few of the features in these vibronic spectra do not appear to vary in shift or relative intensity as a function of the pyrazine vibronic transition observed. Comparing all three of these vibronic transitions to one another and those obtained for the pyrazine- h_4 dimer,³ one concludes that the features at -26.9 , -11.5 , and $+31.0\text{ cm}^{-1}$ are all pyrazine- d_4 dimer origins (0 , 15.4 , and 57.9 cm^{-1} relative to the scale in Fig. 2) for each vibronic transition. Table I presents the energies of and assignments for these features.

TABLE I. Pyrazine- d_4 dimer.

Energy (vac. cm^{-1})	Energy relative to corresponding pyrazine- d_4 feature (cm^{-1})	Energy relative to corresponding pyrazine- d_4 dimer feature (cm^{-1})	Assignment ^{a,b}
31 003.5	-26.9	0	II base 0_0^0
31 018.9	-11.5	0	I 0_0^0
31 024.0	-6.4	20.5	
31 041.9	11.5	23.0	
31 055.9	25.5	37.0	
31 061.4	31.0	0	II stem 0_0^0
31 076.3	45.9	14.9	
31 081.4	51.0	20.0	
31 094.5	64.1	33.1	
31 296.6	-26.4	0	II base $10a_0^1$
31 310.5	-12.5	0	I $10a_0^1$
31 356.6	33.6	0	II stem $10a_0^1$
31 566.4	-28.9	0	II base $6a_0^1$
31 572.2	-23.1	5.8	
31 582.9	-12.4	0	I $6a_0^1$
31 632.5	37.2	0	II stem $6a_0^1$
31 646.0	50.7	13.5	

^a See Fig. 3.^b Peaks at shifts of -11.5, 11.5, 25.5, and 64.1 cm^{-1} vanish at the lower ionization energy (42 300 cm^{-1}).

Potential energy calculations utilizing a LJ function with hydrogen bonding terms give three configurations for the pyrazine dimer. Two of these configurations are depicted in Fig. 3 with their calculated binding energies. One configuration is planar and the other is perpendicular. The third configuration, not shown in Fig. 3, is parallel stacked with the two pyrazines rotated 90° with respect to each other. This third configuration does not apparently contribute to the observed dimer spectrum probably due to excimer formation.

B. Pyrazine- h_4 -pyrazine- d_4 dimer

The energy difference between the monomer origins of pyrazine- h_4 (30 876.0 cm^{-1}) and pyrazine- d_4 (31 030.4 cm^{-1}) is 154.4 cm^{-1} . Such a large separation between monomer origins allows the excitation of either the protonated or deuterated pyrazine moieties to be accessed and identified individually: spectra of one excitation do not interfere with or congest the spectra of the other excitation. The top part of Fig. 4 shows the spectrum associated with excitation of the deuterated pyrazine of the isotopic mixed dimer, while the lower part of the figure displays the spectrum associated with excitation of the protonated pyrazine of the mixed dimer. The spectra of the two different isotopes in the dimer are nearly identical. Table II lists the energies and assignments for these features. The origins for the different dimer configurations are found shifted from their respective monomer transitions by -38, -12, and +23 cm^{-1} . These features are also nearly identical to those of the two homo dimers, with the exception of an 11 cm^{-1} red shift for the low and high energy pair of features.

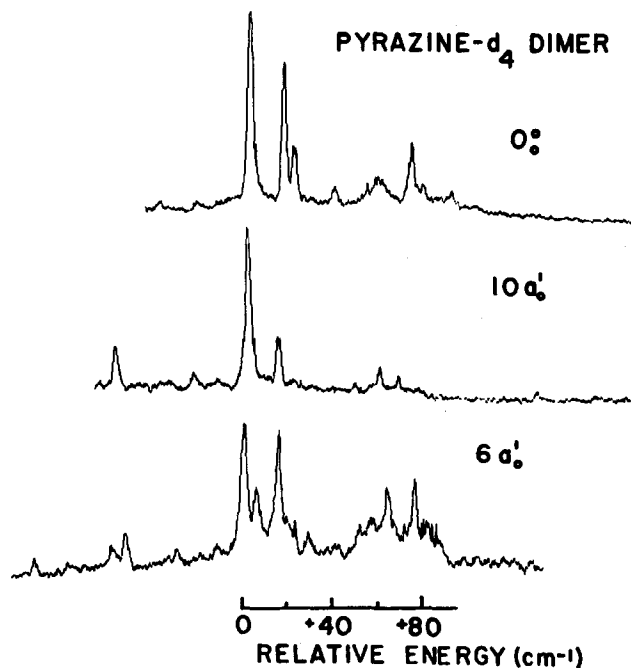


FIG. 2. Two-color TOFMS of the pyrazine- d_4 dimer in the 0_0^0 , $10a_0^1$, and $6a_0^1$ regions. See Table I for absolute energies. The high ionization energy of Fig. 1 is employed.

Calculated geometries of the isotopic hetero dimers are of course identical to those of the homo dimers. The potential energy employed to obtain geometries and binding energies does not depend on isotopic substitution.

C. Pyrazine- d_4 -pyrimidine dimer

The 0_0^0 transition of the pyrimidine monomer at 31 072.7 cm^{-1} is only about 42 cm^{-1} to the blue of the pyra-

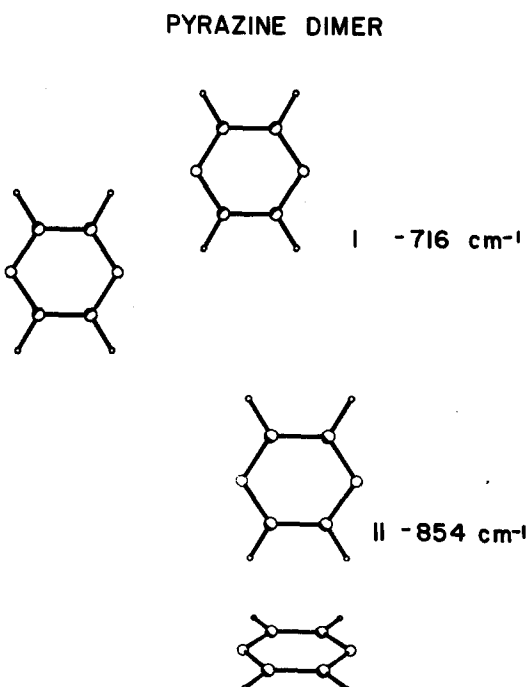


FIG. 3. Minimum energy configurations and binding energies for the spectroscopically observed pyrazine dimers as obtained with the LJ-HB potential calculation.

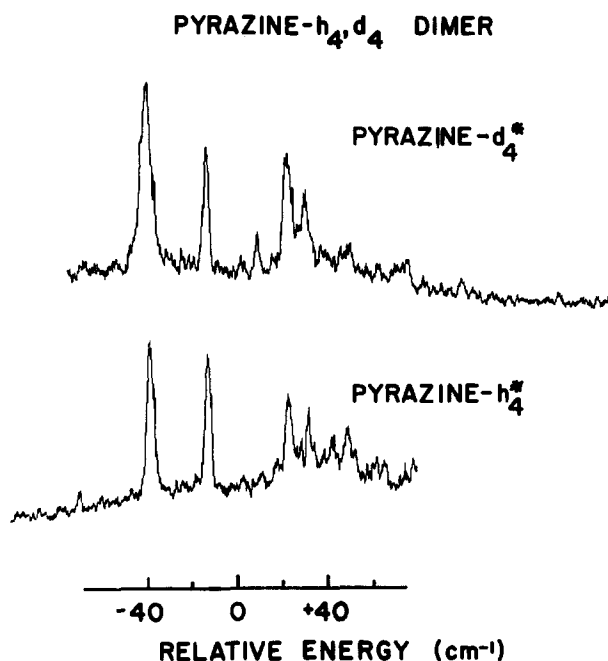


FIG. 4. Top: Two-color TOFMS of pyrazine- h_4 -pyrazine- d_4 dimer exciting pyrazine- d_4 moiety. Bottom: Two-color TOFMS of pyrazine- h_4 -pyrazine- d_4 dimers exciting pyrazine- h_4 moiety. Scale relative to either monomer origin located at 0 cm^{-1} ($d_4 0_0^0$ at $31\,030.4 \text{ cm}^{-1}$ and $h_4 0_0^0$ at $30\,876.0 \text{ cm}^{-1}$). Ionization energy employed to obtain these spectra is $43\,598 \text{ cm}^{-1}$.

zine- d_4 monomer 0_0^0 transition at $31\,030.4 \text{ cm}^{-1}$. This spectrum is shown in two segments in Fig. 5. The first section depicts the spectrum close to the monomer origins and the second section depicts the spectrum $\sim 300 \text{ cm}^{-1}$ to blue of the pyrazine- d_4 monomer origin. If one compares the spectrum near the origin of the pyrazine- d_4 -pyrimidine hetero dimer (first section of Fig. 5) to that of the pyrazine- h_4 -

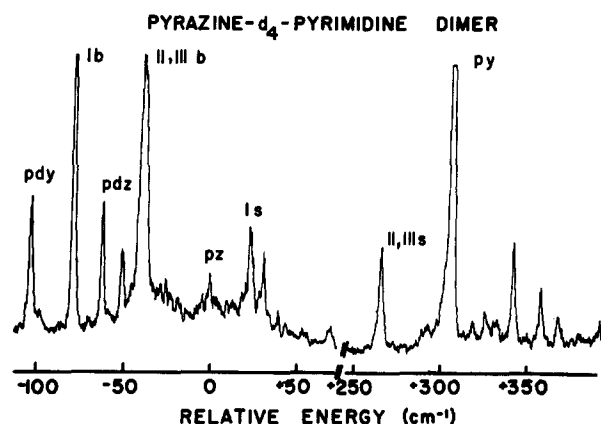


FIG. 5. Two-color TOFMS of pyrazine- d_4 -pyrimidine dimer shown in two segments. Scale relative to the pyrazine- d_4 monomer origin ($31\,030.4 \text{ cm}^{-1}$) located at 0 cm^{-1} in the figure. The assignment codes refer to dimer configuration and a particular member of the dimer: pdy stands for parallel displaced pyrimidine, pdz for parallel displaced pyrazine, py for planar pyrimidine, pz for planar pyrazine, Ib and Is for configuration I base and stem, respectively, II, IIIb and II, IIIs for either configuration II or III base and stem, respectively. These calculated geometries are displayed in Figs. 7 and 8.

pyrazine- d_4 hetero dimer (Fig. 4), one concludes that some of the features are apparently the same in both spectra. The supposed common features occur at shifts of -39.6 , 23.2 , and 31.4 cm^{-1} in the pyrazine- d_4 -pyrimidine spectrum (see Fig. 5 and Table III). Another set of features are found at shifts of -104.3 , -79.8 , -62.7 , and -51.2 cm^{-1} with respect to the pyrazine- $d_4 0_0^0$ transition; these latter features are not observed in the pyrazine- h_4 -pyrazine- d_4 hetero-dimer spectrum. A final set of features for the pyrazine- d_4 -pyrimidine hetero dimer is displayed in the second segment of Fig. 5, 300 cm^{-1} to the blue of the monomer origins. The two intense features in this latter region are shifted 219.5 and

TABLE II. Pyrazine- d_4^* -pyrazine- h_4 .

Energy (vac. cm^{-1})	Energy relative to corresponding 0_0^0 of the excited molecule of the dimer (cm^{-1})	Energy relative to corresponding dimer feature (cm^{-1})	Assignment ^a
30 991.8	-38.4	0	II base 0_0^0
31 018.0	-12.2	0	I 0_0^0
31 040.4	10.0	22.4	
31 054.2	24.0	0	II stem 0_0^0
31 061.8	31.4	7.6	
31 081.5	51.1		
31 108.0	77.6		
31 230.7	200.3		
Pyrazine- d_4 -pyrazine- h_4^*			
30 838.1	-37.9	0	II base 0_0^0
30 863.8	-12.2	0	I 0_0^0
30 899.0	23.0	0	II stem 0_0^0
30 908.3	32.3	9.3	
30 918.9	42.9		
30 925.6	49.6		

^a See Fig. 3.

TABLE III. Pyrazine- d_4 -pyrimidine dimer origins only.

Energy (vac. cm^{-1})	Energy relative to pyrazine- d_4 0_0^0 (cm^{-1})	Energy relative to pyrimidine 0_0^0 (cm^{-1})	Assignment ^a
30 926.1		-146.6	pdy pyrimidine parallel displaced
30 950.6		-122.1	Ib pyrimidine base
30 967.7	-62.7		pdz pyrazine parallel displaced
30 979.2		-93.5	
30 990.8	-39.6		II and IIIb pyra- zine base
31 030.2	-0.2		pz pyrazine planar
31 053.6	23.2		Is pyrazine stem
31 061.8	31.4		
31 292.2		219.5	II and IIIs pyrimi- dine stem
31 334.4		261.7	py pyrimidine planar

^a See Figs. 5, 7, and 8.

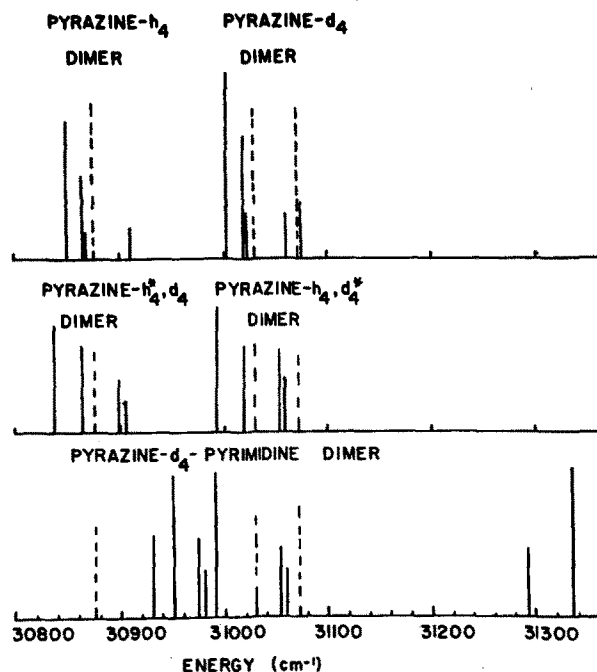


FIG. 6. Stick diagram showing features associated with the different dimers. The top diagram represents pyrazine- h_4 dimer and pyrazine- d_4 dimer. Dashed lines identify the three origins of the monomers involved: pyrazine- h_4 at $30\,876\text{ cm}^{-1}$, pyrazine- d_4 at $31\,030.4\text{ cm}^{-1}$, and pyrimidine at $31\,072.7\text{ cm}^{-1}$. The middle diagram represents the dimer pyrazine- h_4 -pyrazine- d_4 : first part exciting pyrazine- h_4 and second part exciting pyrazine- d_4 . The bottom diagram represents the pyrazine- d_4 -pyrimidine dimer.

261.7 cm^{-1} from the pyrimidine 0_0^0 transition. For simplicity, we present in Fig. 6 a stick diagram representing the spectra of the four possible homo and hetero dimers. Given these comparisons, one concludes that the features at -39.6 , 23.3 , and 31.4 cm^{-1} with respect to the pyrazine- d_4 origin are associated with (two) dimer origins of a nature similar to those assigned for the pyrazine dimer. The intense features to the red and blue of this group have no counterparts in the homo or hetero dimers of pyrazine itself, and must therefore be associated with the pyrimidine moiety.

To assign the remainder of the pyrazine- d_4 -pyrimidine hetero dimer spectrum, more information is quite helpful. The pyrazine- h_4 -pyrimidine- h_4 hetero dimer spectra are studied by two-color TOFMS to provide this additional input; however, in this instance, all three h_4 dimers of pyrazine and pyrimidine are observed without mass discrimination. Since the homo dimers have been studied and their spectra reported, one may uniquely identify the pyrazine- h_4 -pyrimidine- h_4 spectrum and compare it to that of the pyrazine- d_4 -pyrimidine spectra. Hence, those features common to both pyrazine- h_4 and pyrazine- d_4 -pyrimidine hetero dimer spectra with roughly constant shifts from the pyrimidine 0_0^0 transition can be confidently assigned to the pyrimidine moiety. These specific assignments will be made in the discussion section to follow.

A LJ potential energy calculation with a hydrogen bonding term produces six possible configurations for the mixed dimer. Two of these configurations are displayed in Fig. 7 with their calculated binding energies. The largest binding energy configuration for the hetero dimer is parallel

PYRAZINE-PYRIMIDINE DIMER

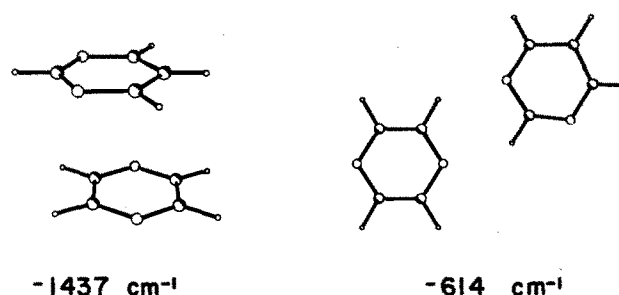


FIG. 7. Two minimum energy configurations and binding energies for pyrazine-pyrimidine dimer as obtained with LJ-HB potential calculation.

stacked with the pyrimidine center of mass displaced 0.61 Å from the pyrazine center-of-mass and the two-ring planes separated by 3.3 Å . The two metaposition carbons of the pyrimidine ring are situated nearly above the nitrogens of the pyrazine ring. The other configuration depicted in Fig. 7 is a planar hydrogen bonded geometry with the most "acidic" or electropositive hydrogen on pyrimidine and one hydrogen on pyrazine forming two $\text{N}\cdots\text{H}$ hydrogen bonds. The center-to-center molecular distance in this configuration is 5.7 Å and the $\text{H}\cdots\text{N}$ distance is $\sim 2.3\text{ Å}$. An additional parallel stacked undisplaced configuration is not shown: it has the *para*-position carbons of pyrimidine above the nitrogens of pyrazine. This configuration is not assigned in the spectrum.

In addition to these configurations the LJ calculations produce three distinct perpendicular geometries for the pyrazine-pyrimidine dimer. These are shown in Fig. 8. Configuration I has pyrimidine at the base and pyrazine at the stem of the structure with a center-to-center distance of 4.5 Å . The second and third configurations (Fig. 8, II and III) both have pyrazine at the base and pyrimidine at the stem. The center-to-center distance for these geometries is 4.9 Å and the $\text{N}\cdots\text{H}$ hydrogen bonding distance varies from 2.8 to 3.0 Å in both dimers. Configurations II and III of Fig. 8 are nearly identical except for a rotation of pyrimidine about an axis perpendicular to the pyrazine plane.

PYRAZINE-PYRIMIDINE DIMER

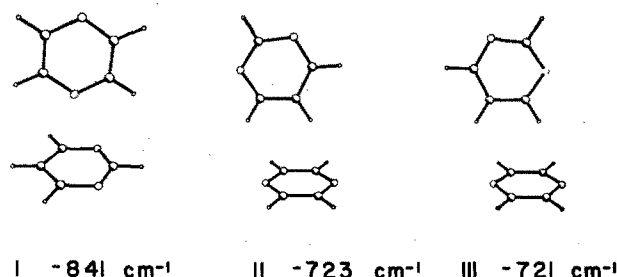


FIG. 8. Three perpendicular minimum energy configurations and binding energies for pyrazine-pyrimidine dimer as obtained with a LJ-HB potential calculation.

These calculations can thus produce pyrazine or pyrimidine molecules in either the stem or base position of a perpendicular hetero pyrazine-pyrimidine dimer.

IV. DISCUSSION

In this section we attempt the sometimes difficult task of assigning observed spectroscopic features of the various dimers to the calculated configurations. In all instances such a unique correspondence is possible. The specific assignments are summarized in Tables I, II, and III and the configurations to which the assignments refer are found in Figs. 3, 7, and 8. For added assistance, the pyrazine- d_4 -pyrimidine dimer spectrum (Fig. 5) has assignments written on it directly.

A. Pyrazine- d_4 dimer

Spectra of the pyrazine- d_4 and pyrazine- h_4 ³ dimers are quite similar in terms of ionization energy dependence and spectroscopic feature position and intensity. The features that vanish at low ionization energy (Fig. 1) are assigned to a single dimer origin with its associated vdW vibronic modes. The spectra are summarized for easy comparison in Fig. 6. The dimer configuration with the higher ionization energy is most likely a symmetrical one because only one clear origin is associated with it. We have previously argued^{1(a),2,3} that different dimer geometries should possess different ionization energies depending on the involvement of the π -electron cloud in the ion "solvation" process.

Therefore, based on the above reasoning and comparisons, the features associated with the high ionization energy cluster (-11.5 cm^{-1} cluster 0_0^0) are attributed to the dimer with the planar configuration (I in Fig. 3). The planar dimer can be argued to have the higher ionization because the π system is not involved in the bonding. Note that the planar hydrogen bonded configuration is composed of two symmetry equivalent molecules and thus only one spectroscopic origin is expected for this dimer.

The other two features previously identified as origins (-26.9 and $+31.0 \text{ cm}^{-1}$) are assigned to the perpendicular configuration (II in Fig. 3). The red shifted feature is suggested to be due to the base pyrazine and the blue shifted feature is associated with the stem pyrazine. These latter detailed assignments are made under the assumption that red shifts are caused by π -cloud interactions and blue shifts are caused by hydrogen bonding interactions. Table I lists these and other assignments for the pyrazine- d_4 homo dimer. The cause of cluster shifts are discussed in previous publications from this laboratory.^{1(a),2-5}

From Fig. 2 and Table I one can also see that strong vibronic coupling exists between the pyrazine $6a^1$ and $10a^1$ modes and the vdW modes even though the cluster vibronic origins at the pyrazine vibronic levels do not vary significantly in position and relative intensity. The nature of these vibronic interactions is presently under investigation.

Finally we note that the intermolecular interactions in the h_4 - and d_4 -homo dimers are nearly identical.

B. Pyrazine- h_4 -pyrazine- d_4 dimer

The spectra that arise from the isotopic pyrazine hetero dimer are nearly identical to those of the homo dimers, inde-

pendent of which moiety of the dimer is excited. Thus the assignments of the hetero dimer spectra to particular calculated configurations should follow exactly from the homo-dimer analysis (see Figs. 4 and 6). The features at -12.2 cm^{-1} from their respective origins are due to excitation of the planar configuration of the dimer, the features at an average shift of $-38.2 \pm 0.4 \text{ cm}^{-1}$ are due to excitation of the base molecules in the perpendicular dimer, and the features at an average shift of $23.5 \pm 0.5 \text{ cm}^{-1}$ are due to excitation of the stem molecules of the perpendicular dimer. The assignments are summarized in Table II and all the pyrazine dimer spectra are compared schematically in Fig. 6.

All three pyrazine dimers have, within experimental error, the same shift for the planar configuration feature, $-11.5 \pm 0.5 \text{ cm}^{-1}$. Thus deuteration has no effect on the shift or the exciton splitting in the planar hydrogen bonded dimer (Fig. 3, I); exciton interaction in this geometry is essentially zero.

As can be seen from Tables I and II, some isotopic shift differences are found for the perpendicular configuration of the pyrazine dimers even though the base-stem splitting remains constant at $59.5 \pm 1.5 \text{ cm}^{-1}$. The spectrum of the perpendicular hetero dimer is red shifted by roughly 11 cm^{-1} with respect to that of the homo dimers. Little or no exciton splitting exists for this configuration: the total hetero dimer splitting is slightly larger than, but within experimental uncertainty of, the homo dimer splittings.

C. Pyrazine- d_4 -pyrimidine- h_4 dimer

As pointed out in the Results section, the spectrum of the pyrazine- d_4 -pyrimidine hetero dimer (Figs. 5 and 6) is quite complicated. Additional information would be useful in assigning features to the calculated configurations. We thus employ the pyrazine, pyrimidine, and pyrazine- h_4 -pyrimidine dimer spectra to assist with the task.

Examining the stick diagram representation of Fig. 6, we can now assign the two features at -39.6 and $+23.2 \text{ cm}^{-1}$ from the pyrazine- d_4 origin: in accordance with the discussion for the pyrazine dimers these features must be, respectively, the pyrazine- d_4 moiety in the perpendicular geometry at the base and stem of the pyrazine- d_4 -pyrimidine hetero dimer. The configurations responsible for these transitions are depicted in Fig. 8 and assigned to the spectra in Fig. 5 and Table III.

One can properly expect that two such comparable features will arise from the pyrimidine moiety in the perpendicular geometries depicted in Fig. 8. In addition, features associated with both pyrazine- d_4 and pyrimidine in the planar (pl) and parallel stacked displaced (pd) configurations are also to be expected.

Many features in the pyrazine- d_4 -pyrimidine spectrum are at shifts (with respect to the pyrimidine monomer 0_0^0 transition) that are nearly identical to those found in the pyrazine- h_4 -pyrimidine spectrum. These transitions are of course associated with the pyrimidine moiety in the various dimer configurations. Similarly, features are found in the two spectra that are at similar positions relative to the pyrazine- h_4 or $-d_4$ monomer origins. The pyrazine- h_4 -pyrimi-

dine spectrum is very congested (even in the two-color TOFMS because of the identical masses of pyrazine- h_4 and pyrimidine- h_4) and would be of little pictorial assistance to the reader.

Features that have comparable shifts with respect to the pyrimidine monomer 0_0^0 transition in both hetero dimers are found at shifts of -146.6 , -122.1 , $+219.5$, and $+261.7$ cm^{-1} in the pyrazine- d_4 hetero dimer (Figs. 5 and 6 and Table III) and at -155.8 , -123.7 , $+219.6$, and $+255.7$ cm^{-1} in the pyrazine- h_4 hetero dimer (not shown). Once transitions can be associated with a particular molecular component of the dimers the task of assigning the features to a calculated configuration is a relatively straightforward one.

The feature at -146.6 cm^{-1} with respect to the pyrimidine monomer origin in the pyrazine- d_4 -pyrimidine hetero-dimer spectrum, the lowest energy feature belonging to the dimer, must be due to the pyrimidine molecule in the parallel displaced geometry. Exciting the pyrazine- d_4 partner in this parallel displaced geometry (Fig. 7) yields a feature at -62.7 cm^{-1} with respect to the pyrazine- d_4 origin. This latter feature is the most red shifted transition that can be associated with pyrazine in the hetero dimer and is consequently a reasonable assignment. Comparable features are found at -155.8 and -70.4 cm^{-1} (with respect to the two monomer origins) in the pyrazine- h_4 -pyrimidine hetero dimer spectrum and are also assigned to the parallel stacked displaced configuration.

The features at ~ -122 cm^{-1} in both hetero dimers must be associated with the pyrimidine moiety. Since these are also highly red shifted peaks, they must involve pyrimidine molecules with their π systems well "solvated" in the dimers. The only such remaining unassigned calculated geometry is configuration I in Fig. 8 with pyrimidine at the base of a perpendicular configuration. These assignments are summarized in Fig. 5 and Table III.

Since no perpendicular configurations for the pyrimidine dimer itself are identified,³ comparisons must be made to the pyrazine dimers for some guidance in assigning the stem features for the perpendicular configurations. The stem molecule of the perpendicular pyrazine dimers is assigned to a blue shifted transition (see Tables I and II). Thus the feature to be associated with pyrimidine at the stem of the perpendicular configurations will likely have a blue shift because its π -electron system is not directly involved in the dimer bonding while its hydrogen atoms are (Fig. 8). A blue shifted transition should then occur in both the pyrazine- h_4 and pyrazine- d_4 -pyrimidine dimers at equal shifts with respect to the pyrimidine monomer 0_0^0 transition. The only unique candidate for such an assignment is the feature at $+219.5$ cm^{-1} in both dimers. While this shift is at first glance rather larger than expected, the assignment is both unique and compelling.

The final calculated configuration that must be assigned to the remaining spectroscopic features is the planar configuration shown in Fig. 7. The feature at $+261.7$ cm^{-1} with respect to the pyrimidine monomer 0_0^0 transition in the pyrazine- d_4 -pyrimidine dimer and at $+255.7$ cm^{-1} with respect to the pyrimidine monomer 0_0^0 transition in the pyra-

zine- h_4 -pyrimidine dimer is very similar to that found in the pyrimidine dimer $+296$ cm^{-1} . Moreover, this transition apparently has associated van der Waals vibrational modes at relative energies of 38.5 and 54.5 cm^{-1} , just as the pyrimidine dimer feature does.³ In the pyrimidine dimer the 296 cm^{-1} transition is assigned to the planar hydrogen bonded geometry involving the hydrogen atom between the two nitrogens on both pyrimidine molecules (see Fig. 7 of Ref. 3). Since this is comparable to the planar structure shown in Fig. 7, the $\sim +260$ cm^{-1} feature of the pyrazine-pyrimidine hetero dimer is assigned to the pyrimidine moiety of the planar hydrogen bonded hetero dimer.

The remaining transition to locate for the pyrazine-pyrimidine hetero dimer is that associated with the pyrazine excitation of the planar hydrogen bonded dimer. Excitation of pyrazine- h_4 or - d_4 in the planar configuration of the pyrazine homo and hetero (isotopic) dimers gives a transition with a shift of -11.5 ± 0.5 cm^{-1} with respect to the pyrazine monomer 0_0^0 transition. Pyrazine in any of the perpendicular hetero dimers has shifts of -38.5 ± 1.0 and 23.0 ± 1.0 cm^{-1} for the base and stem molecules, respectively. One concludes therefore that pyrazine transitions are not much affected by the other molecular component of the dimer and specifically, that the pyrazine- d_4 planar hydrogen bonded transition of the pyrazine- d_4 -pyrimidine hetero dimer should be found near the pyrazine- d_4 monomer 0_0^0 . The only feature in this region occurs at a shift of -0.2 cm^{-1} and we assign this transition to the pyrazine- d_4 moiety in the pyrazine- d_4 -pyrimidine planar hydrogen bonded dimer. In the pyrazine- h_4 -pyrimidine spectrum the region near the pyrazine- h_4 monomer origin is very congested and a clear assignment is difficult to make for a comparable feature.

The remaining unassigned transitions in the pyrazine- d_4 -pyrimidine spectrum can readily be identified as van der Waals mode vibrations. For example, the weak feature at -51.0 cm^{-1} in Fig. 5 is at -93.5 cm^{-1} with respect to the pyrimidine monomer origin. A comparable feature is found in the pyrazine- h_4 -pyrimidine dimer at -94.2 cm^{-1} . The transition can be assigned as a van der Waals mode built on the pyrimidine perpendicular base (Ib in Fig. 5 and Table III) origin at ~ -122 cm^{-1} . The six features following the pyrimidine planar transition at ~ 300 cm^{-1} in Fig. 5 (261.7 cm^{-1} from the pyrimidine monomer 0_0^0 transitions) can also be assigned as van der Waals modes of the planar hydrogen bonded pyrazine-pyrimidine hetero dimer.

In general, substituting pyrazine- h_4 for pyrazine- d_4 in the pyrazine-pyrimidine dimer affects some spectral features more than others. For example, in the parallel displaced configuration the two features are shifted $+8.5 \pm 0.5$ cm^{-1} in the d_4 dimer (-146.6 and -62.5 cm^{-1}) with respect to the h_4 dimer (-155.8 and -70.4 cm^{-1}) even though the overall dimer splitting is nearly constant at 84.8 ± 0.6 cm^{-1} . A comparable effect ($+6$ cm^{-1} shift) exists for the h_4 and d_4 dimers of the planar configuration (255.7 cm^{-1} for h_4 and 261.7 cm^{-1} for d_4). Transitions of the perpendicular configurations, however, have nearly identical positions (-122.9 ± 0.8 , $+219.5$, -39.5 , and -23.7 ± 0.3 cm^{-1}).

V. CONCLUSIONS

The pyrazine homo and hetero isotopic dimers form a set of dimers whose spectra and structure now seem to be quite well understood. Two configurations are calculated and assigned from the spectra: a planar hydrogen bonded geometry and a perpendicular geometry. A third configuration, parallel stacked, rotated 90°, is also calculated for pyrazine dimers but not observed spectroscopically. The interaction strengths (that is, splittings for the perpendicular dimer and energy of the single feature for the planar dimer with respect to the appropriate monomer origin) do not seem to depend on the isotopic composition of the dimer. This strongly implies that the exciton or exchange interactions for this system are vanishingly small (less than 1 cm^{-1}). The general red and blue shifts of the dimer features with respect to the monomer origins are consistent with the π -system coordination and electron donor-acceptor (hydrogen bonding) behavior found for solute/solvent complexes.

The pyrazine-pyrimidine hetero dimer falls into this general pattern as well, and its spectra can be assigned with some certainty. Parallel stacked displaced, perpendicular, and planar hydrogen bonded configurations can be calculated

and identified experimentally for this dimer. In all five distinct configurations can be assigned for the pyrazine-pyrimidine dimer.

The pyrimidine dimer itself has been previously found to have six configurations: a parallel stacked head-to-tail displaced dimer, a parallel stacked rotated 90° dimer, and four planar hydrogen bonded dimers. Apparently heterocyclic dimer geometry is very rich and a number of different configurations are stable for each system.

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