

# Supplementary Material for Conformer-selection by matter-wave interference

Christian Brand,<sup>1</sup> Benjamin A. Stickler,<sup>2</sup> Christian Knobloch,<sup>1</sup> Armin Shayeghi,<sup>1</sup> Klaus Hornberger,<sup>2</sup> and Markus Arndt<sup>1</sup>

<sup>1</sup>University of Vienna, Faculty of Physics, Boltzmannngasse 5, A-1090 Vienna, Austria

<sup>2</sup>Faculty of Physics, University of Duisburg-Essen, Lotharstraße 1, 47048 Duisburg, Germany

(Dated: June 8, 2018)

## OPTICAL POLARIZABILITY AND ROTATIONAL AVERAGE FOR 2-PHENYLETHYLAMINE (PEA)

For each conformer of PEA, the complex optical polarizability at laser wavelength  $\lambda_L = 2\pi c/\omega_L$  is calculated using the Lorentz-Drude formula for a single electronic transition [1–3],

$$\alpha(\omega_L) = \alpha_0 + \frac{e_0^2 f}{m_e} \frac{1}{\omega_0^2 - \omega_L^2 - i\omega_L/\tau}. \quad (1)$$

We assumed a common excited state lifetime  $\tau$  of 70 ns based on experimental data [4]. The static polarizabilities were calculated using density functional theory with the PBE0 functional employing the Def2-TZVP basis set and are compiled in Table I. The oscillator strength  $f$  and the electronic transition wavelength  $\lambda_0 = 2\pi c/\omega_0$  are also compiled in Table I for each conformer of PEA.

In order to take the rotational structure of the transition from the electronic ground to the excited state ( $g, r$ )  $\rightarrow$  ( $e, r'$ ) into account, we note that the final measurement traces over all rotation states. Thus, any coherences between rotational levels can be neglected and we determine the interference pattern for each transition, replacing  $\omega_0$  by  $\omega_{rr'} = (E_{er'} - E_{gr})/\hbar$  in (1), and sum over the resulting interference patterns, weighted by their respective spectroscopic relative intensity. Several hundred transitions relevant for PEA are collected in a histogram. We use the mean frequency and spectroscopic weight of each bin to perform the calculation. Only in the case of rotation-state resolved detection, the coherences between rotational levels need to be considered.

## SELECTION EFFICIENCY

The selectivity of the proposed method depends on both the wavelength  $\lambda_L$  of the grating laser and the surface energy density. The wavelength stability of current pulsed dye lasers

TABLE I. Calculated oscillator strength  $f$  [5], electronic transition energy  $\lambda_0$ , static polarizability  $\alpha_0/(4\pi\epsilon_0)$ , and relative population  $P$  [6] in molecular beams of the four experimentally observed [4, 6] conformers of PEA.

Conformer	$f \times 10^3$	$\lambda_0$ (nm)	$\alpha_0$ ( $\text{\AA}^3$ )	$P$ (%)
Gauche(out)	0.56	265.89	14.5	52
Gauche(up)	0.92	266.25	14.5	25
Anti(out)	0.64	266.34	14.6	12
Anti(up)	1.94	265.70	14.7	11

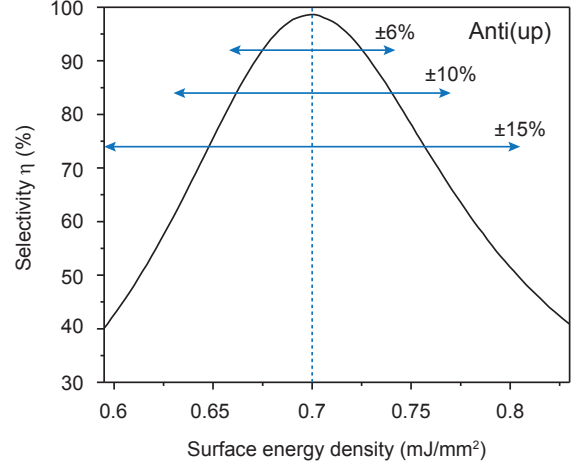


FIG. 1. Mean selectivity  $\eta$  for the Anti(out) conformer at a laser wavelength of  $\lambda_L = 265.55$  nm depending on the surface energy density. At  $0.7$  mJ/mm<sup>2</sup> (dashed line) a maximum selectivity of 99% is reached. The integrated selectivity due to power variations between 6 and 15% is indicated by horizontal lines. It ranges between 92 and 74%.

is in the pm regime which is sufficient to maintain stable diffraction pattern over time. The effect of power fluctuations is illustrated in Fig. 1 for the Anti(out) conformer at a wavelength of 265.55 nm. The selectivity peaks at a surface energy density of  $0.7$  mJ/mm<sup>2</sup>. Power fluctuations of  $\pm 6\%$  would reduce the integrated selectivity to 92%. Even under strong energy fluctuations, for instance, at  $0.7$  mJ/mm<sup>2</sup>  $\pm 15\%$  the selectivity still reaches 74%. The power-dependent selectivities of all four conformers are compiled in Table II.

## EXPECTED MOLECULAR FLUX BEHIND THE SELECTION SLITS

The particle flux  $j = nv = pv/k_B T$  is determined by the partial pressure  $p$  of 2-phenylethylamine, the temperature  $T$ , and the velocity  $v$  of the molecules. Taking the velocity of an adiabatic expansion of Argon ( $v = 650$  m/s) and the partial pressure of 2-phenylethylamine at  $T = 410$  K [7], this yields a flux of  $j = 2.4 \times 10^{27}$  m<sup>-2</sup>s<sup>-1</sup>.

We consider the example of a supersonic expansion from an Even-Lavie valve [8] with a nozzle diameter of  $50$   $\mu\text{m}$ , emitting a molecular current of  $4.6 \times 10^{18}$  s<sup>-1</sup>. The spatial distribution of the expansion can be described by a gaussian with a full width at half maximum of  $12^\circ$  [9]. At the second collimation slit  $S_2$ ,  $0.1$  m behind the nozzle, the molecular beam

TABLE II. Influence of power variations on the selection efficiency  $\eta$  for PEA. For each conformer the selectivity is stated at the center surface power density and averaging over region of  $\pm 10\%$  and  $\pm 15\%$ .

Conformer	Wavelength (nm)	Surface power density (mJ/mm <sup>2</sup> )	Mean selectivity
Gauche(out)	265.84	0.72	100
		$0.72 \pm 10\%$	97
		$0.72 \pm 15\%$	95
Gauche(up)	266.17	0.63	83
		$0.63 \pm 10\%$	79
		$0.63 \pm 15\%$	75
Anti(out)	266.26	0.61	88
		$0.61 \pm 10\%$	77
		$0.61 \pm 15\%$	70
Anti(up)	265.55	0.70	99
		$0.70 \pm 10\%$	84
		$0.70 \pm 15\%$	74

has a half width at half maximum of 10 mm. The fraction of molecules transmitted through the slit of 1 mm height and 10  $\mu\text{m}$  width is calculated from the two-dimensional integral over the size of the detector slit. This yields a reduction factor of  $2.2 \times 10^{-5}$ , leading to a particle current  $I = 1.0 \times 10^{14} \text{ s}^{-1}$  for a continuous flow of molecules. Here we consider that the skimmer  $S_1$  does not play a significant role as  $S_2$  leads to a more stringent collimation. The collimated beam propagates 1 m until it reaches the skimmer  $S_3$  (1 mm  $\times$  10  $\mu\text{m}$ ), where the number of particles is reduced by another factor of  $1.4 \times 10^{-3}$ . This yields an overall reduction factor of  $3.0 \times 10^{-8}$ . For a spot size of  $\ell^2 = 1 \times 1 \text{ mm}^2$ , the number of molecules illuminated by the laser is  $I\ell/v = 215\,500$  molecules per pulse. The number of isolated molecules also depends on the relative population of the targeted conformer, the population of the vibrational ground state, the number of molecules ionized by the grating laser, and the percentage of molecules diffracted into the first order.

In Fig. 4a of the main text we consider the diffraction of the Gauche(out) conformer of PEA. Its relative population is 52% [6], 78% of all molecules are expected to be in the vibrational ground state, and 35% of the conformers are diffracted into the first order. The ionization probability at this wavelength is computed to be below  $10^{-4}$  and can be neglected. This yields about 30 800 molecules per laser shot and a mean current of  $1.3 \times 10^9 \text{ s}^{-1} \text{ cm}^{-2}$ , assuming a laser repetition rate of 100 Hz and a detection area of 2 mm  $\times$  115  $\mu\text{m}$ . The width of the area is given by separation of the first diffraction orders. The peak density corresponds to  $1.3 \times 10^8 \text{ cm}^{-3}$  which compares well to the beam density used in XUV diffraction experiments at free electron lasers ( $8.0 \times 10^7 \text{ cm}^{-3}$ ) [10]. As shown in Fig. 4b of the main text, also less abundant conformers can be isolated with high selectivity. Fig. 2a shows the molecular diffraction patterns for all conformers at  $\lambda_L = 266.1 \text{ nm}$  and a surface power density of  $0.57 \text{ mJ/mm}^2$ . At these parameters the Gauche(up) conformer

is selected and 51% of all molecules in the Gauche(up) conformation are in the first diffraction orders, leading to a peak density of  $9.4 \times 10^7 \text{ cm}^{-3}$ . The diffraction patterns at points of high selectivity for the two Anti-conformers are shown in the lower panels. The extracted peak density is  $4.6 \times 10^7 \text{ cm}^{-3}$  for Anti(up) and  $3.3 \times 10^7 \text{ cm}^{-3}$  for Anti(out).

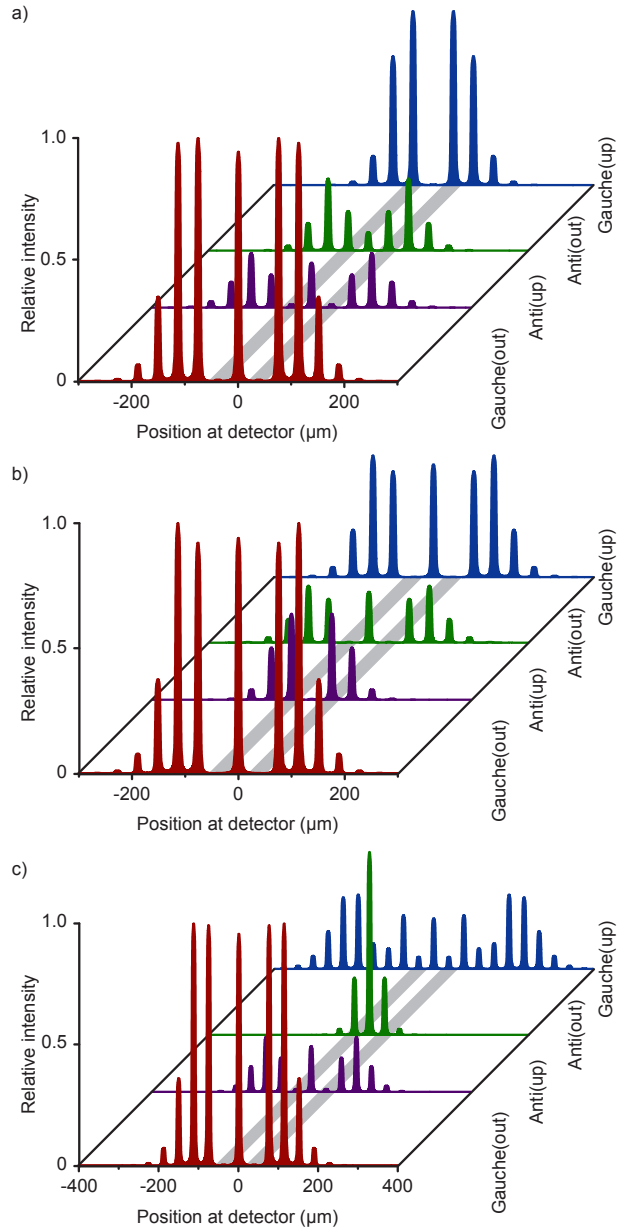


FIG. 2. Molecular diffraction patterns of the four conformers of 2-phenylethylamine at parameters of high selectivity for one specific conformer according to Fig. 4b in the main text. At  $\lambda_L = 266.1 \text{ nm}$  and  $0.57 \text{ mJ/mm}^2$  the Gauche(up) conformer is selected with high selectivity (a). The diffraction patterns in (b) and (c) show the points of high selectivity for the Anti(up) conformer ( $\lambda_L = 265.5 \text{ nm}$  and  $0.7 \text{ mJ/mm}^2$ ) and the Anti(out) conformer ( $\lambda_L = 266.3 \text{ nm}$  and  $0.61 \text{ mJ/mm}^2$ ).

In Fig. 3 the diffraction patterns of PEA and Argon at a phase grating with period 266 nm are compared. As the

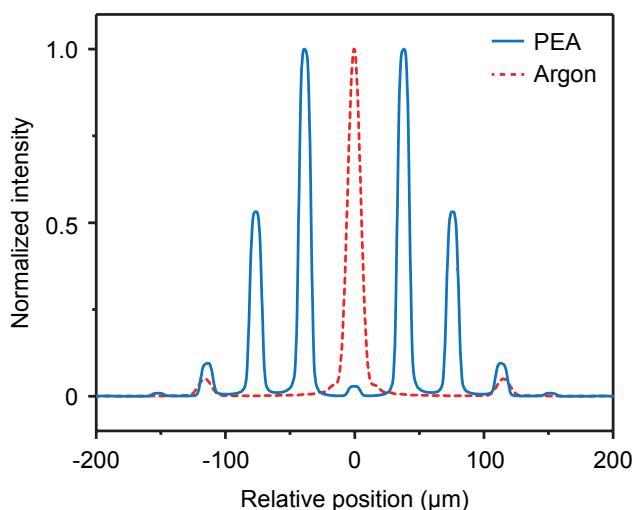


FIG. 3. Comparison of the diffraction pattern of 2-Phenylethylamine (PEA) and Argon at a phase grating with  $\lambda_L = 266$  nm. The first diffraction order of Ar overlaps with the third of PEA due to their mismatch in mass.

spacing of the diffraction orders scales inversely with mass, the backing gas is diffracted to larger angles. Hence, the diffraction orders do not overlap, preventing the gas from reaching the detection area.

### SUITABLE MOLECULAR SYSTEMS

In Table III-V we list a number of molecules which can be addressed with the proposed selection method. It contains a set of systems systems which are of importance for several fields of physics and chemistry and is by no means exhaustive. The chosen particles molecules have sufficiently high vapor pressure and are light enough to be compatible with fast molecular beams. We have compiled all conformers even though not all of them might be isolated, either because their relative population is too small or they are spectrally overlapping with other conformers. This list can easily be extended to clusters with noble gas atoms, and small molecules like  $O_2$ ,  $N_2$ , and  $CH_4$ . Often these can be prepared in high abundance by co-expanding them with the desired molecule. As the clusters do not absorb a photon and remain in their electronic ground state during the diffraction, fragmentation can be neglected.

- 
- [1] W. M. Hayes, *CRC Handbook of Chemistry and Physics*, 97th ed. (Taylor & Francis, 2016).  
 [2] C. H. Townes and L. Schawlow, *Microwave Spectroscopy* (Dover, 1975).  
 [3] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley-VCH Verlag GmbH, 2007).  
 [4] S. J. Martinez, J. C. Alfano, and D. H. Levy, *J. Mol. Spectrosc.* **158**, 82 (1993).

- [5] C. Brand, W. L. Meerts, and M. Schmitt, *J. Phys. Chem. A* **115**, 9612 (2011).  
 [6] J. A. Dickinson, M. R. Hockridge, R. T. Kroemer, E. G. Robertson, J. P. Simons, J. McCombie, and M. Walker, *J. Am. Chem. Soc.* **120**, 2622 (1998).  
 [7] I. Mokbel, A. Razzouk, T. Sawaya, and J. Jose, *J. Chem. Eng. Data* **54**, 819 (2009).  
 [8] U. Even, *EPJ Tech. Instrum.* **2**, 17 (2015).  
 [9] M. Hillenkamp, S. Keinan, and U. Even, *J. Chem. Phys.* **118**, 8699 (2003).  
 [10] J. Küpper, S. Stern, L. Holmegaard, F. Filsinger, A. Rouzée, A. Rudenko, P. Johnsson, A. V. Martin, M. Adolph, A. Aquila, S. Bajt, A. Barty, C. Bostedt, J. Bozek, C. Caleman, R. Coffee, N. Coppola, T. Delmas, S. Epp, B. Erk, L. Foucar, T. Gorkhover, L. Gumprecht, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, N. Kimmel, F. Krasniqi, K.-U. Kühnel, J. Maurer, M. Messerschmidt, R. Moshhammer, C. Reich, B. Rudek, R. Santra, I. Schlichting, C. Schmidt, S. Schorb, J. Schulz, H. Soltau, J. C. H. Spence, D. Starodub, L. Strüder, J. Thøgersen, M. J. J. Vrakking, G. Weidenspointner, T. A. White, C. Wunderer, G. Meijer, J. Ullrich, H. Stapelfeldt, D. Rolles, and H. N. Chapman, *Phys. Rev. Lett.* **112**, 083002 (2014).  
 [11] J. Sipior, C. K. Teh, and M. Sulkes, *J. Fluorescence* **1**, 41 (1991).  
 [12] T. A. LeGreve, E. E. Baquero, and T. S. Zwier, *J. Am. Chem. Soc.* **129**, 4028 (2007).  
 [13] T. A. LeGreve, W. H. James III, and T. S. Zwier, *J. Phys. Chem. A* **113**, 399 (2009).  
 [14] G. M. Florio, R. A. Christie, K. D. Jordan, and T. S. Zwier, *J. Am. Chem. Soc.* **124**, 10236 (2002).  
 [15] G. M. Florio and T. S. Zwier, *J. Phys. Chem. A* **107**, 974 (2003).  
 [16] Y. D. Park, T. R. Rizzo, L. A. Peteanu, and D. H. Levy, *J. Chem. Phys.* **84**, 6539 (1986).  
 [17] J. R. Carney and T. S. Zwier, *Chem. Phys. Lett.* **341**, 77 (2001).  
 [18] T. V. Nguyen, T. M. Korter, and D. W. Pratt, *Mol. Phys.* **103**, 1603 (2005).  
 [19] J. Sipior and M. Sulkes, *J. Chem. Phys.* **88**, 6146 (1988).  
 [20] T. B. C. Vu, I. Kalkman, W. L. Meerts, C. Brand, Y. N. Svartsov, S. Wiedemann, R. Weinkauff, and M. Schmitt, *Phys. Chem. Chem. Phys.* **11**, 2433 (2009).  
 [21] R. Brause, H. Fricke, M. Gerhards, R. Weinkauff, and K. Kleinermanns, *Chem. Phys.* **327**, 43 (2006).  
 [22] J. Yao, H. S. Im, M. Foltin, and E. R. Bernstein, *J. Phys. Chem. A* **104**, 6197 (2000).  
 [23] M. Gerhards, C. Unterberg, A. Gerlach, and A. Jansen, *Phys. Chem. Chem. Phys.* **6**, 2682 (2004).  
 [24] B. C. Dian, A. Longarte, S. Mercier, D. A. Evans, D. J. Wales, and T. S. Zwier, *J. Chem. Phys.* **117**, 10688 (2002).  
 [25] M. R. Nimlos, D. F. Kelley, and E. R. Bernstein, *J. Phys. Chem.* **93**, 643 (1989).  
 [26] A. Held and D. W. Pratt, *J. Am. Chem. Soc.* **115**, 9708 (1993).  
 [27] F. O. Talbot and J. P. Simons, *Phys. Chem. Chem. Phys.* **4**, 3562 (2002).  
 [28] R. A. Jockusch, R. T. Kroemer, F. O. Talbot, and J. P. Simons, *J. Phys. Chem. A* **107**, 10725 (2003).  
 [29] R. A. Jockusch, F. O. Talbot, and J. P. Simons, *Phys. Chem. Chem. Phys.* **5**, 1502 (2003).  
 [30] J. A. Korn, D. P. Tabor, E. L. Sibert, and T. S. Zwier, *J. Chem. Phys.* **145**, 124314 (2016).  
 [31] J. A. Dickinson, P. W. Joireman, R. T. Kroemer, E. G. Robertson, and J. P. Simons, *J. Chem. Soc. Faraday Trans.* **93**, 1467 (1997).

TABLE III. Molecular systems and their water clusters suitable for conformer selection.

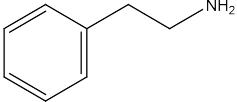
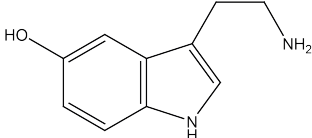
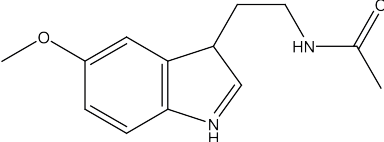
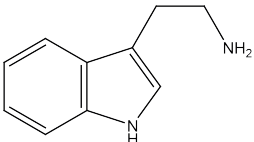
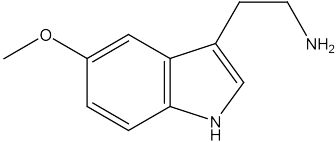
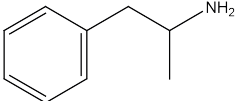
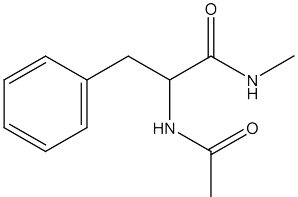
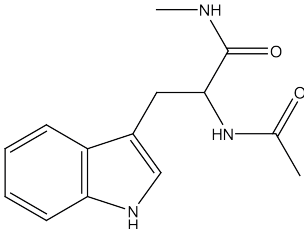
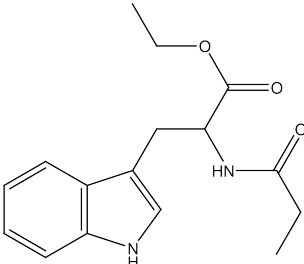
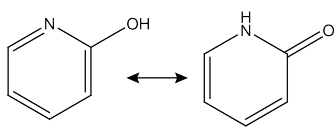
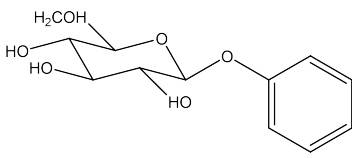
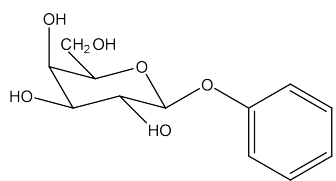
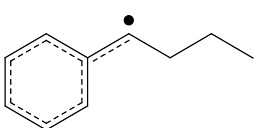
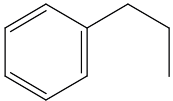
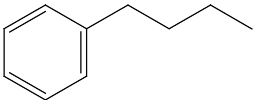
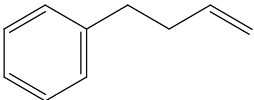
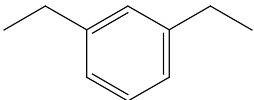
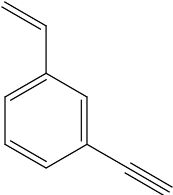
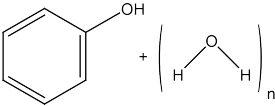
Substance	Structure		Electronic origin ( $\text{cm}^{-1}$ )						
<u>Neurotransmitter and hormones</u>									
2-Phenylethylamine		4 conformers [6, 11]	37 546 37 558 37 610 37 636						
Serotonin		( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [6]	37 630						
		8 conformers [12]	32 282 32 313 32 353 32 537 32 545 32 548 32 560 32 584						
		( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [13]	32 183 32 449 32 666						
		Melatonin		5 conformers [14]	32 432 32 483 32 614 32 621 32 795				
				( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [15]	32 442 32 673 32 842 32 956				
				Tryptamine		7 conformers [16–18]	34 832 34 868 34 879 34 880 34 884 34 896 34 916		
						( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [19]	34 957		
						Mexamin		3 conformers [20]	32 734 32 764 32 808
( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [20]	32 528								
Amphetamine								3 conformers [21]	37 549 37 558 37 592
								( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [21, 22]	37 574 37 578 37 617

TABLE IV. Molecular systems and their water clusters suitable for conformer selection - *continued*.

Substance	Structure		Electronic origin ( $\text{cm}^{-1}$ )
<u>Protected amino acids</u>			
N-acetyl phenylalanine methyl amide		3 conformers [23]	37 414 37 518 37 593
N-acetyltryptophan methyl amide		3 conformers [24]	34 881 34 913 -
N-acetyl tryptophan ethyl ester		4 conformers [16]	34 694 34 832 34 855 34 999
<u>Tautomers</u>			
2-Hydroxypyridine		2 tautomers [25, 26]	29 831 36 136
		( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [25, 26]	35 468
<u>Sugars</u>			
Phenyl $\beta$ - D-glucopyranoside		3 conformers [27]	36 868 36 903 36 906
		( $\text{H}_2\text{O}$ ) <sub>1</sub> -cluster [28]	36 767 36 870
Phenyl $\beta$ - D-galactopyranoside		2 conformers [29]	36 839 36 854
<u>Aromatic radicals</u>			
$\alpha$ -Propyl benzyl radical		2 conformers [30]	21 922 <sup>a</sup> 21 929

<sup>a</sup> The electronic origin is not known. This wavenumber corresponds to a strong vibrational band from the IR-UV hole-burning spectrum.

TABLE V. Molecular systems and their water clusters suitable for conformer selection - *continued*.

Substance	Structure		Electronic origin ( $\text{cm}^{-1}$ )
<u>Aromatic hydrocarbons</u>			
Propylbenzene		2 conformers [31]	37 533 37 583
Butylbenzene		4 conformers [31]	37 514 37 516 37 573 37 576
4-phenyl-1-butene		3 conformers [32]	37 525 37 528 37 580
1,3-Diethylbenzene		2 conformers [33]	37 134 37 151
Meta-Ethynylstyrene		2 conformers [34]	32 672 32 926
<u>Size-selected water cluster</u>			
Phenol( $\text{H}_2\text{O}$ ) <sub>n</sub>		n=1 [35] n=3 [35] n=4 [35] n=5 [35] n=8 [36]	35 996 36 258 36 170 36 297 35 923

[32] J. A. Sebree, V. V. Kislov, A. M. Mebel, and T. S. Zwier, *Farad. Discuss.* **147**, 231 (2010).

[33] P. J. Breen, E. R. Bernstein, and J. I. Seeman, *J. Chem. Phys.* **87**, 3269 (1987).

[34] T. M. Selby, J. R. Clarkson, D. Mitchell, J. A. J. Fitzpatrick, H. D. Lee, D. W. Pratt, and T. S. Zwier, *J. Phys. Chem. A* **109**,

4484 (2005).

[35] C. Jacoby, W. Roth, M. Schmitt, C. Janzen, D. Spangenberg, and K. Kleiner-manns, *J. Phys. Chem. A* **102**, 4471 (1998).

[36] W. Roth, M. Schmitt, C. Jacoby, D. Spangenberg, C. Janzen, and K. Kleiner-manns, *Chem. Phys.* **239**, 1 (1998).