

Microwave Structure Measurements on the Furan-Argon Complex

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Abstract: Rotational transitions were measured for furan-argon and [2-D]furan-argon using a pulsed nozzle Fourier transform spectrometer. Analysis of the data indicates that the argon atom is above the plane of furan, a distance of 3.54 Å from the furan center of mass. The line between the argon and furan center of mass makes an angle of 11° with the furan *c* axis with the displacement toward the oxygen atom of furan. Measured rotational constants for argon-furan are $A = 4802.340$ (3), $B = 1362.612$ (2), and $C = 1360.289$ (2) MHz. For argon-[2-D]furan, $A = 4591.442$ (18), $B = 1358.191$ (4), and $C = 1338.736$ (2) MHz. An analysis of the centrifugal distortion and interaction potential is given for this complex. The stretching force constant is $k_s = 0.27$ mdyne/Å and the approximate well depth is $\epsilon = 236$ cm⁻¹.

Introduction

Rotational transitions have been measured and assigned for the argon-furan complex. The first brief report¹ on this complex, using only the common isotopic form of furan, gave two possible structures. In the present work all spectroscopic data are given, more transitions have been measured for the common form, and measurements have been made on the argon-[2-D]furan complex. The data on the two isotopic species allow an unambiguous determination of the structure. Further data on the ordinary form allow a centrifugal distortion analysis which yields force constants and information on the potential between argon and furan. The present structure indicates that the argon atom is most closely associated with the α -carbon atoms of furan. This appears to be correlated with the higher reactivity of the α -carbon atoms. The slight tilt toward the oxygen atom is more surprising since oxygen or other electronegative atoms tend to be avoided in other complexes involving argon.

A large number of weakly bound molecular complexes containing a rare gas atom have been studied by molecular beam, optical, and microwave spectroscopy. This appears to be the first microwave structure of a complex between a rare gas atom and aromatic molecule. Complexes of tetrazine with helium and argon were studied by Smalley, Wharton, and Levy² using laser induced fluorescence with a supersonic jet. There are a number of examples of other complexes with argon bound to a carbon atom. ArClCN,³ ArOCS,⁴ and ArCO₂⁵ are T-shaped structures with the argon-carbon distance ranging from 3.49 Å for ArCO₂ to 3.62 Å for ArClCN. A hydrogen-bonded complex between furan and HCl was recently reported.⁶

Experimental Section

A very sensitive, high-resolution Fourier transform microwave spectrometer has been developed by Balle and Flygare.^{7,8} The rapid expansion of gas through the pulsed nozzle beam source provides effective cooling of translational and rotational degrees of freedom of the emerging gas mixture. Cooling the translational degrees of freedom allows the formation of large numbers of van der Waals complexes with binding energy on the order of 50 cm⁻¹ or greater. The expansion cools the rotational distribution to an effective temperature of 2-10 K and this accounts, in part, for the high sensitivity of this spectrometer. The complex was formed by expanding a 4% mixture of furan in argon at 2 atm pressure through a 0.4-mm nozzle into a high *Q* evacuated Fabry-Perot cavity. The gas supply to the nozzle was pulsed with a solenoid valve. Microwave pulses of 2.5 μ s duration were used to produce the coherent, "free induction decay" molecular emission signal.

The coherent free induction decay from all transition frequencies within the 1-MHz bandwidth of the cavity is then detected and amplified with a gated superheterodyne receiver. Coherent second detection with a balanced mixer is used on the receiver. The time domain signal is digitized, averaged, and Fourier transformed to give the frequency spectrum.

The [2-D]furan was made by decarboxylating furoic acid-*d*; 30 g furoic acid in 100 mL of quinoline was refluxed with 15 g of copper powder as described earlier⁷ for 3-methylfuran. A 6-in. Vigreux column was placed over the heated quinoline mixture and the furan was collected with a condenser and receiver at 0 °C. The furoic acid-*d* was made by hydrolyzing furoyl chloride in D₂O and also by exchanging furoic acid in D₂O and distilling off the water. The samples of [2-D]furan were analyzed by NMR, mass spectrometry, and microwave spectroscopy and shown to contain about 50% or greater [2-D]furan with most of the remaining component being furan. No deuterium substitution at the β position was detectable (<3%).

The first set of transitions observed was a *Q*-branch series with $K_P = 1 \rightarrow 2$ near 10 GHz. The spectrum for this series was shown earlier.¹ The 2-7 MHz spacing of lines indicated that the complex was a near-symmetric rotor. For argon-furan a total of 38 transitions were observed in the 2722 to 17070-MHz frequency range. These included 19 *c*-dipole, *Q*-branch ($\Delta J = 0$) transitions, 12 *c*-dipole *R*-branch ($\Delta J = 1$) transitions, and 7 *a*-dipole *R*-branch transitions.

Four rotational transitions were observed for argon-[2-D]furan. These were all the stronger *c*-dipole, *R*-branch transitions. The $0_{00} \rightarrow 1_{01}$, $2_{12} \rightarrow 2_{11}$, $3_{22} \rightarrow 3_{21}$, and $4_{32} \rightarrow 4_{31}$ transitions of the [2-D]furan molecule could be observed using 0.4 atm pressure behind the pulsed nozzle source. No lines were found for the [2,5-D]furan molecule, however, indicating that the sample was indeed [2-D]furan. The possibility of [3-D]furan or [3,4-D]furan was eliminated by NMR evidence.

Results and Analysis

The measured transitions for argon-furan were analyzed by carrying out least-squares fits to the observed frequencies. In the first fit (fit I) the adjustable parameters used were the rotational constants A , B , and C and the symmetric-top distortion parameters D_J , D_{JK} , and D_K . The measured and calculated transition frequencies are given in Table I for fit I and fit II. For fit II the parameters A' , B' , C' , τ_{aaaa} , τ_{bbbb} , τ_{cccc} , τ_1 , and τ_2 as described by Kirchhoff¹⁰ were used. Values for the parameters used in these fits are given in Table II. It was expected that since the rotational constant for this complex indicate that it is nearly a prolate

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Table I. Measured and Calculated Transition Frequencies (in MHz) for the Argon-Furan Complex. Fit I Uses the Parameters A, B, C, D_J, D_{JK} , and D_K While Fit II Uses $A', B', C', \tau_{aaaa}, \tau_{bbbb}, \tau_{cccc}, \tau_1$, and τ_2

transition $J(K_P, K_O) \rightarrow J'$ (K_P', K_O')	measd frequency	calcd fit I	δ_I	calcd fit II	δ_{II}	exptl std dev
0(0,0)-1(0,1)	2 722.894	2 722.880	0.014	2 722.881	0.013	0.009
4(2,3)-5(1,5)	3 272.891	3 272.880	0.011	3 272.886	0.005	0.004
4(2,2)-5(1,4)	3 307.685	3 307.704	-0.019	3 307.694	-0.008	0.003
7(0,7)-7(1,7)	3 406.835	3 406.866	-0.031	3 406.835	0.000	0.003
6(0,6)-6(1,6)	3 415.359	3 415.356	0.003	3 415.359	0.000	0.003
5(0,5)-5(1,5)	3 422.663	3 422.645	0.018	3 422.664	-0.001	0.003
4(0,4)-4(1,4)	3 428.750	3 428.727	0.022	3 428.751	-0.001	0.002
3(0,3)-3(1,3)	3 433.621	3 433.598	0.022	3 433.618	0.003	0.002
2(0,2)-2(1,2)	3 437.268	3 437.255	0.014	3 437.272	-0.004	0.003
1(0,1)-1(1,1)	3 439.702	3 439.694	0.009	3 439.704	-0.002	0.001
0(0,0)-1(1,0)	6 164.898	6 164.896	0.002	6 164.901	-0.003	0.001
3(1,2)-4(0,4)	7 442.717	7 442.708	0.009	7 442.717	0.000	0.003
1(0,1)-2(1,1)	8 889.852	8 889.855	-0.003	8 889.855	-0.003	0.003
4(1,3)-5(0,5)	10 159.902	10 159.891	-0.012	10 159.901	0.001	0.003
7(1,6)-7(2,6)	10 285.561	10 285.593	-0.032	10 285.538	0.023	0.005
6(1,5)-6(2,5)	10 294.950	10 294.950	0.000	10 294.939	0.011	0.002
5(1,4)-5(2,4)	10 302.987	10 302.971	0.016	10 302.981	0.005	0.003
4(1,3)-4(2,3)	10 309.674	10 309.656	0.019	10 309.674	0.000	0.003
3(1,2)-3(2,2)	10 315.014	10 315.005	0.009	10 315.023	-0.009	0.002
2(1,1)-2(2,1)	10 319.022	10 319.016	0.006	10 319.030	-0.008	0.004
2(1,2)-2(2,0)	10 325.973	10 325.986	-0.013	10 325.983	-0.010	0.006
3(1,3)-3(2,1)	10 328.930	10 328.947	-0.018	10 328.936	-0.007	0.002
4(1,4)-4(2,2)	10 332.884	10 332.901	-0.018	10 332.886	-0.002	0.003
5(1,5)-5(2,3)	10 337.935	10 337.854	-0.018	10 337.840	-0.005	0.006
6(1,6)-6(2,4)	10 343.811	10 343.810	0.001	10 343.809	0.002	0.005
7(1,7)-7(2,5)	10 350.817	10 350.779	0.038	10 350.805	0.013	0.005
3(1,3)-4(1,4)	10 885.375	10 885.372	0.003	10 885.375	0.000	0.002
3(3,1)-4(3,2)	10 888.148	10 888.143	0.005	10 888.137	0.011	0.004
3(2,1)-4(2,2)	10 889.326	10 889.314	0.011	10 889.324	0.002	0.004
3(0,3)-4(0,4)	10 890.243	10 890.243	0.000	10 890.243	0.000	0.003
3(1,2)-4(1,3)	10 894.661	10 894.663	-0.003	10 894.660	0.001	0.003
2(0,2)-3(1,2)	11 615.657	11 615.664	-0.007	11 615.657	0.000	0.003
5(1,4)-6(0,6)	12 875.328	12 875.324	0.004	12 875.327	0.001	0.002
4(1,3)-5(1,4)	13 617.375	13 617.378	-0.003	13 617.378	-0.003	0.005
3(0,3)-4(1,3)	14 342.185	14 342.198	-0.013	14 342.186	-0.001	0.003
1(1,0)-2(2,0)	15 766.860	15 766.856	-0.004	15 766.867	-0.007	0.003
1(1,1)-2(2,1)	15 769.175	15 769.178	-0.003	15 769.182	-0.007	0.004
4(0,4)-5(1,4)	17 069.324	17 069.333	-0.009	17 069.321	0.003	0.003

Table II. Best Fit Parameters Obtained from Fit I

parameter	value
A	4802.340 \pm 0.003 MHz
B	1362.612 \pm 0.002 MHz
C	1360.289 \pm 0.002 MHz
D_J	5.27 \pm 0.03 kHz
D_{JK}	29.40 \pm 0.08 kHz
D_K	-24.0 \pm 0.6 kHz

Table III. Best Fit Parameters Obtained from Fit II

parameter	value, MHz
A'	4802.349 \pm 0.017
B'	1362.558 \pm 0.016
C'	1360.344 \pm 0.017
τ_{aaaa}	-0.048 \pm 0.015
τ_{bbbb}	-0.0208 \pm 0.0014
τ_{cccc}	-0.0215 \pm 0.0014
τ_1	-0.181 \pm 0.004
τ_2	-0.0425 \pm 0.0014

symmetric rotor ($B - C = 2$ MHz), the D_J, D_{JK} , and D_K distortion parameters would give a very good fit to the data. The fit obtained using D_J, D_{JK} , and D_K was not as good as expected but the fit using the τ 's was somewhat better. The standard deviation for fit I was 0.016 MHz and for fit II it was 0.007 MHz. The spectroscopic parameters from fit I are given in Table II and those from fit II are given in Table III. The indicated errors in Table II are the statistical errors for the fit, whereas the errors in Table III include the contribution to the error from the experimental standard deviation for the measured lines. The A, B , and C and A', B' , and C' rotational constants are in reasonably good agreement,

Table IV. Measured and Calculated Transition Frequencies for [2-D]Furan-Argon. DATA' Is the Measured Frequency, Corrected for Centrifugal Distortion Effects. All Frequencies in MHz with $A = 4591.442$ (18), $B = 1358.190$ (4), and $C = 1338.736$ (2) MHz

$J(K_P, K_O) \rightarrow J'$ (K_P', K_O')	measd frequency	DATA'	calcd	δ
3(1,2)-4(0,4)	7484.069 (6)	7485.101	7485.107	-0.006
1(0,1)-2(1,1)	8665.639 (2)			
	8665.688 (3)	8666.007	8666.014	-0.007
	8665.729 (7)			
4(1,3)-5(0,5)	10139.465 (3)	10141.556	10141.551	0.005
2(0,2)-3(1,2)	11391.262 (4)	11392.160	11392.155	0.005

indicating that contributions to the primed rotational constants from $\tau_{\alpha\beta\alpha\beta}$ terms are relatively small.

The $3_{12} \rightarrow 4_{04}, 1_{01} \rightarrow 2_{11}, 4_{13} \rightarrow 5_{05}$, and $2_{02} \rightarrow 3_{12}$ transitions in the [2-D]furan-argon complex were measured and the frequencies are given in Table IV. The DATA' frequencies which were fit to obtain rotational constants were obtained by adding a centrifugal distortion correction to the measured frequencies. The centrifugal distortion correction used is the shift which would be obtained for this molecule if D_J, D_{JK} , and D_K were the same as for argon-furan. Rotational constants obtained from this fit are $A = 4591.442$ (18), $B = 1358.190$ (4), and $C = 1338.736$ (2) MHz.

Structure of the Complex

In order to determine the structure of the complex, the position of the argon atom was moved relative to the argon molecule, and rotational constants were calculated as a function of the distance R_0 between argon and the furan center of mass and the angle θ

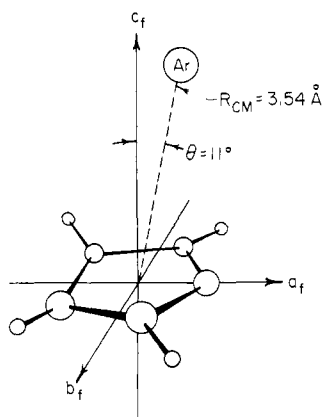


Figure 1. Structure and coordinate system for the argon-furan complex. The a_f , b_f , and c_f axes are the a , b , and c principal axes of furan. R_{CM} is indicated by the dashed line. $R_{CM} = 3.54 \text{ \AA}$; $\theta = 11^\circ$.

Table V. Results of Adjusting R_0 and θ To Obtain the Best Fit to Pairs of Rotational Constants (A,B), (B,C), and (A,C) and the Average Coordinates Are Given Below. The Rotational Constants A , B , and C Calculated with These Coordinates Are Also Given. The R_0 and θ Values Listed Are "Best Fit" Values

	(A,B)	(B,C)	(A,C)	av
R_0 , Å	3.54456	3.54456	3.54227	3.54380
θ , deg	11.3002	10.3218	11.2984	10.9735
A , MHz	4802.34	4783.79	4802.34	4795.97
B , MHz	1362.61	1362.61	1364.12	1363.11
C , MHz	1358.79	1360.28	1360.29	1359.80

between R_0 and the c axis of furan. It was assumed that argon would be in a plane defined by the a and c axes of furan. It was further assumed the structure of furan remained unchanged on formation of the complex.

The model used to analyze the structure involves calculating moments of inertia of the complex from moments of inertia of furan and coordinates of argon relative to the center of mass of furan.¹¹ It was noted¹² that this approach is nearly equivalent to using the Kraitchman equations¹³ to calculate the structure, treating argon as the substituted atom. The equations for the moments of the complex (given below) follow from the parallel axis theorem of classical mechanics

$$\begin{aligned}
 I_{xx} &= I_{bb}(\text{furan}) + \mu R_0^2 \\
 I_{yy} &= I_{aa}(\text{furan}) + \mu R_0^2 \cos^2 \theta \\
 I_{zz} &= I_{cc}(\text{furan}) + \mu R_0^2 \sin^2 \theta \\
 I_{yz} &= -\mu R_0^2 \sin \theta \cos \theta
 \end{aligned}$$

where x , y , and z are respectively the b_f , a_f , and c_f axes shown in Figure 1, $\mu = m(\text{furan})m(\text{argon})/(m(\text{furan}) + m(\text{argon}))$, and R_0 = the distance between argon and the furan center of mass. The above inertia tensor is diagonalized to get moments for the complex. The moments for furan were obtained from rotational constants obtained from earlier work.¹⁴

The results of varying R_0 and θ to obtain the best fit to the pairs of rotational constants (A,B), (B,C), and (A,C) are shown in Table VI. The results given in Table V are independent of the sign of θ since the inertia tensor for furan is symmetric with respect to reflections in planes containing two principal axes. We note that the different sets of rotational constants give somewhat different structures and this is interpreted as due to large vibrational amplitudes of argon relative to furan. With the results obtained we

Table VI. Experimental and Calculated Values of Changes in Rotational Constants δA , δB , and δC on Deuterium Substitution at the Furan 2 Position for the Furan-Argon Complex. Frequencies in MHz. Results for the Average Structure and for Structures Determined from (A,B), (B,C), and (A,C) Pairs of Rotational Constants and for Positive and Negative Values of θ

	δA	δB	δC	θ
experimental	210.90	4.42	21.55	
average	211.41	5.12	21.72	10.97
(A,B)	211.97	5.13	21.59	11.30
(B,C)	210.31	5.10	21.92	10.32
(A,C)	211.97	5.13	21.63	11.30
average	204.11	8.62	24.66	-10.97
(A,B)	204.46	8.71	24.63	-11.30
(B,C)	203.43	8.42	24.68	-10.32
(A,C)	204.46	8.72	24.68	-11.30

give the structure parameters $\theta = 11 (1)^\circ$ and $R_0 = 3.54 (1) \text{ \AA}$, with reasonable estimates of the accuracy of the parameters.

The rotational constants for the argon-[2-D]furan substituted complex, however, provide additional information since the principal axis system for [2-D]furan is rotated and displaced with respect to the furan principal axis system. On substitution of deuterium at the 2 position of furan, the rotational constants for the complex change by amounts $\delta A = 210.90$, $\delta B = 3.32$, and $\delta C = 21.55$ MHz. We can calculate these changes in rotational constants for positive and negative values of θ . The results of the calculation are shown in Table VI. We note that the shifts for positive values of θ are much more consistent with the experimental shifts. For the calculation using average values of R_0 and θ , positive θ gives a standard deviation for shifts of 0.44 MHz whereas negative θ gives a standard deviation of 4.95 MHz. This factor of 10 difference in the quality of the fit is interpreted as strong evidence for a positive value of θ , that is, a displacement toward the oxygen atom.

Additional evidence for the structure with positive θ is obtained from the Kraitchman equations.¹³ The distance (r) of a substituted atom from the center of mass of the parent molecule is given by $2\mu r^2 = \Delta I_x + \Delta I_y + \Delta I_z$, where $\mu = \Delta m M / (\Delta m + M)$ with Δm the change in mass of the substituted atom, M the mass of the parent molecule, and the ΔI 's being changes in principal moments of inertia on substitution. For the hydrogen atom at position 2 on furan in the complex we get $r = 2.456 \text{ \AA}$. When this distance is calculated for the positive θ structure, we get $r = 2.483 \text{ \AA}$, but when r is calculated for the negative θ structure, $r = 2.641 \text{ \AA}$. Again a displacement argon atom toward the oxygen atom in furan is strongly favored.

Centrifugal Distortion Constants and the Argon-Furan Potential

Information on the intermolecular potential between argon and furan can be obtained from the centrifugal distortion constants. An estimate of the stretching force constant k_s for the argon-furan bond and for the well depth may be obtained from the distortion constant D_J as described earlier.¹⁴ The argon and furan are treated as localized, structureless masses held together by a spring with force constant k_s . We use experimental values of D_J to obtain the force constant k_s from the relation

$$k_s = 8\pi^3(\mu R_0)^2[(B^2 + C^2)^2 + 2(B^4 + C^4)]/\hbar D_J$$

This is a reasonably good approximation for argon-furan since the angle between R_0 and the a axis is only about 2° . We obtain a stretching force constant for 0.0269 millidyne/Å. If we use a Lennard-Jones 6-12 potential⁸ to describe the argon furan interaction we find that the equilibrium, pseudo-diatomic rotation constant B_0^* is given by $2B_0^* = \nu_s/18 - ((\nu_s/18)^2 - 4(\nu_s/18)B_0^*)^{1/2}$. ν_s is the stretching frequency. This leads to an equilibrium bond length r_e from which we obtain the well depth using $\epsilon = k_s r_e^2/72$ to get $\epsilon \approx 236 \text{ cm}^{-1}$. This is a strong bond in comparison with other argon complexes as we see from data in Table VII.¹⁵ We

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Table VII. Comparison of Force Constants from the Pseudo-Diatomic Model, k_s (P.D.), from a Two-Component Force Field Model, k_s (F.F.); Well Depths, ϵ , and Bending Force Constants, k_θ , for Argon-Furan and Related Complexes

	k_s (P.D.), mdyn/Å	ϵ , cm ⁻¹	k_s (F.F.), mdyn/Å	k_θ , mdyn/Å	bond length, Å
argon-furan	0.0269	236	0.0272	0.0354	3.54
argon-ClCN ^a		172	0.0185	0.0333	3.65
argon-BF ₃ ^b	0.0211	163			3.33
argon-CO ₂ ^c		148	0.0174	0.0165	3.49
argon-HCl ^{d,e}	0.0117	128	0.0164	0.0015	
argon-HBr ^d	0.0076	89	0.0166	0.0014	

^a See ref 3; ϵ calculated from data in ref 3. ^b Values calculated using data in ref 15. ^c See ref 5; ϵ from data in ref 5. ^d See M. R. Keenan, E. J. Campbell, T. J. Balle, L. W. Buxton, T. K. Minton, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, 72, 3070 (1980). ^e See M. R. Keenan, L. W. Buxton, E. J. Campbell, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.*, 73, 3523 (1980).

Table VIII. Derivatives of Rotational Constants for Argon-Furan with Respect to Changes in R_0 and θ

$\partial A/\partial R_0 = 12.64$ MHz/Å	$\partial A/\partial \theta = 1133$ MHz
$\partial B/\partial R_0 = 656.2$ MHz/Å	$\partial B/\partial \theta = 87.4$ MHz
$\partial C/\partial R_0 = 651.5$ MHz/Å	$\partial C/\partial \theta = 90.8$ MHz

note that the bending constant k_θ is similar to that obtained for Ar-ClCN.

The τ centrifugal distortion constants may also be used to obtain information on the force constants holding the complex together. We consider a simple force field represented by k_s and k_θ where

k_s is associated with changes in the bond length R_0 and k_θ with changes in θ . There will also be a force constant for motion of the argon in the direction of the b axis of the complex but since first derivatives of moments of inertia with respect to this coordinate vanish, it will not contribute to the τ 's. We will neglect τ 's of the form $\tau_{\alpha\beta\alpha\beta}$ with $\alpha \neq \beta$. In this case we can write

$$\tau_{\alpha\beta\alpha\beta} = -2\hbar \sum_i \frac{\partial G_\alpha}{\partial R_i} \frac{\partial G_\beta}{\partial R_i} \left(\frac{1}{k_i} \right)$$

where $\tau_{\alpha\beta\alpha\beta}$ is in Hz, G_α are rotational constants, and k_i are the force constants k_s and k_θ . The derivatives $\partial G/\partial R_i$ were calculated numerically and values are given in Table VIII. Using the experimental results for τ_{aaaa} , τ_{bbbb} , and τ_{cccc} with the above model gives $k_s = 0.0272(8)$ mdyn/Å and $k_\theta = 0.0354$ mdyn Å.

The discovery and characterization of the furan-argon complex and the benzene-HCl complex¹¹ indicates the aromatic π -electron system in ring compounds can act either as a Lewis acid or a Lewis base. This suggests that interactions between π -electron systems of two aromatic ring compounds should be important in the formation of stacked complexes.

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pH Jump: Kinetic Analysis and Determination of the Diffusion-Controlled Rate Constants

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Abstract: Excitation of proton-emitter compounds such as 8-hydroxypyrene-1,3,6-trisulfonate or sulfonated β -naphthol derivatives by short, intensive laser pulses discharges protons into the solution. These protons are readily detected by their reaction with pH indicators. The kinetics are followed by transient light absorption techniques with a time resolution of 100 ns. The observed proton cycle, protonation and relaxation of the indicator, is a sum of simultaneous first- and second-order reactions between the various reactants. This dynamic is a complex function of all rate constants and reactant concentrations. In the present study, we employed a numerical solution of nonlinear differential rate equations to simulate the dynamics of the observed proton cycle. This analysis permits a direct determination of the diffusion-controlled rate constants of all participating reactions with an accuracy better than 20%.

The laser-induced pH jump^{2,3} employs the pH shift of electronically excited aromatic alcohols⁴ for rapid acidification of aqueous solutions. Excitation of a proton emitter, such as hydroxypyrenetrisulfonate⁵ in dilute solution by a short laser pulse,

lowers the pH by 3-4 log units within a few nanoseconds.³ The protons dissociate from the excited molecules and are detected by their reaction with pH indicator present in the solution.

The proton cycle consists of two sets of temporally resolved reactions: the reactions between the excited molecules and the reactions between the ground-state compounds.

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(5) Abbreviations: PhOH and PhO⁻ are the neutral and anionic forms of the proton emitter; HIn and In⁻, the protonated and deprotonated forms of the indicator; HPTS, 8-hydroxypyrene-1,3,6-trisulfonate; BCG, bromocresol green.