

## Supporting Informations

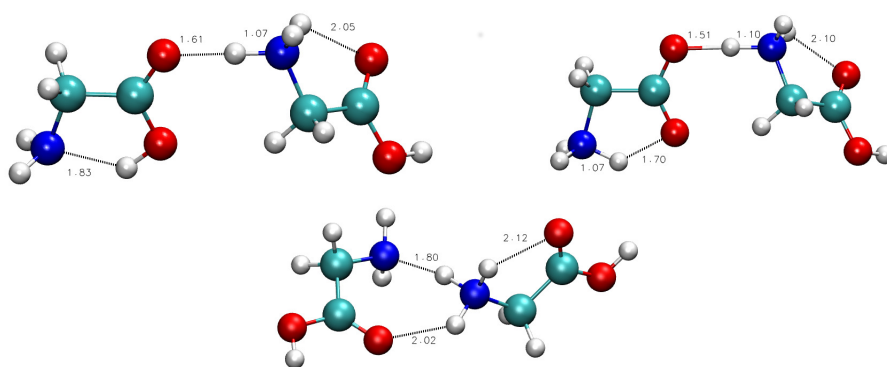
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### CS01, CS02, and ZW01 isomers

Figure (S1) shows the optimized structures of CS01, CS02, and ZW01 calculated at the DFT-B3LYP level of theory with 6-311+G\*\* basis set by means of the NWChem package.<sup>1</sup> CS01 is the global minimum, while CS02 and ZW01 are isomers respectively 650 cm<sup>-1</sup> and 950 cm<sup>-1</sup> above in energy.

Figure S1: Structures of the CS01, ZW01, and CS02 isomers of the protonated glycine dimer. The left side of the panel shows the CS01 structure, the right one its zwitterionic version (ZW01), while the CS02 local minimum is reported below.



Tables (S1), (S2), and (S3) report instead the computed harmonic frequencies in the 1000-4000 cm<sup>-1</sup> energy range, obtained via diagonalization of the Hessian matrix at the equilibrium geometry.

Table S1: Harmonic vibrational frequencies of the CS01 isomer reported in  $\text{cm}^{-1}$ . Values are presented in ascending order.

Mode	HO	Mode	HO	Mode	HO
26	1020	37	1435	48	3059
27	1075	38	1443	49	3084
28	1133	39	1461	50	3101
29	1159	40	1485	51	3142
30	1178	41	1570	52	3191
31	1192	42	1669	53	3309
32	1246	43	1675	54	3499
33	1315	44	1686	55	3537
34	1338	45	1756	56	3610
35	1339	46	1811	57	3730
36	1351	47	2707		

Table S2: Harmonic vibrational frequencies of CS02 isomer reported in  $\text{cm}^{-1}$ . Values are presented in ascending order.

Mode	HO	Mode	HO	Mode	HO
25	1036	36	1362	47	2707
26	1054	37	1438	48	3048
27	1091	38	1447	49	3086
28	1117	39	1479	50	3087
29	1156	40	1485	51	3138
30	1186	41	1593	52	3359
31	1194	42	1662	53	3431
32	1202	43	1665	54	3481
33	1305	44	1700	55	3546
34	1319	45	1784	56	3727
35	1334	46	1817	57	3734

Table S3: Harmonic Vibrational frequencies of the ZW01 isomer reported in  $\text{cm}^{-1}$ . Values are presented in ascending order.

Mode	HO	Mode	HO	Mode	HO
25	1032	36	1416	47	2253
26	1089	37	1442	48	2814
27	1098	38	1483	49	3058
28	1141	39	1488	50	3107
29	1165	40	1594	51	3133
30	1192	41	1638	52	3166
31	1295	42	1661	53	3350
32	1309	43	1674	54	3471
33	1321	44	1685	55	3509
34	1345	45	1696	56	3534
35	1385	46	1812	57	3735

Values well agree with the ones reported in the literature for CS01 and CS02 at the same level of theory, as reported in Table (S4).

Table S4: Harmonic frequencies of CS01 and CS02 compared with the corresponding ones reported in the literature, calculated at the same level of theory. Values labeled by <sup>(a)</sup> are taken from Ref ( 2).

CS01	HO	HO <sup>(a)</sup>	CS02	HO	HO <sup>(a)</sup>
	1192	1194		3431	3438
	1756	1763		3546	3546
	1811	1816		3734	3738
	3499	3501			
	3610	3610			
	3730	3731			

Below are reported the computed DC SCIVR fundamental frequencies of CS01 and CS02, compared with the experimental ones. Table (S5) shows the fundamental excitations of CS01 in the 1000-4000  $\text{cm}^{-1}$  energy range, while Table (S6) the fundamental excitations of CS02.

Table S5: Vibrational frequencies of the CS01 isomer reported in  $\text{cm}^{-1}$ . Values are compared with their harmonic and experimental counterparts. The Mean Absolute Error (MAE) is computed with respect to the experimental vibrational excitations.

Mode	DC-SCIIVR	HO	Exp[ 2]	Mode	DC-SCIIVR	HO	Exp[ 2]
26	1003	1020		43	1633	1675	
27	1074	1075		44	1641	1686	
28	1108	1133		45	1750	1756	1757
29	1109	1159		46	1804	1811	1808
30	1174	1178		47	2658	2707	
31	1172	1192	1191	48	2959	3059	
32	1188	1246		49	2987	3084	
33	1267	1315		50	2966	3101	
34	1340	1338		51	3051	3142	
35	1320	1339		52	3197	3191	
36	1320	1351		53	3243	3309	
37	1386	1435		54	3375	3499	3372
38	1344	1443		55	3415	3537	
39	1450	1461	1439	56	3435	3610	
40	1434	1485		57	3628	3730	3585
41	1511	1570	1523				
42	1629	1669		MAE	14		

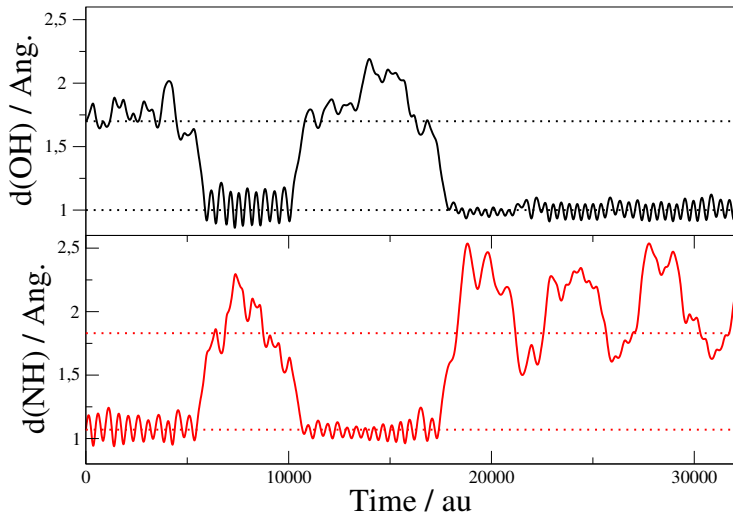
Table S6: Vibrational frequencies of the CS02 isomer reported in  $\text{cm}^{-1}$ . Values are compared with their harmonic and experimental counterparts. The Mean Absolute Error (MAE) is computed with respect to the experimental vibrational excitations.

Mode	DC-SCIIVR	HO	Exp[ 2]	Mode	DC-SCIIVR	HO	Exp[ 2]
25	1033	1036		42	1617	1662	
26	1015	1054		43	1598	1665	1523
27	1050	1091		44	1610	1700	
28	1095	1117		45	1771	1784	1757
29	1106	1156		46	1761	1817	1808
30	1138	1186		47	2714	2707	
31	1106	1194		48	2979	3048	
32	1155	1202	1191	49	2975	3086	
33	1255	1305		50	2988	3087	
34	1295	1319		51	3007	3138	
35	1362	1334		52	3171	3359	
36	1341	1362		53	3185	3431	
37	1382	1438		54	3316	3481	
38	1421	1447		55	3362	3546	3372
39	1463	1479		56	3615	3727	3585
40	1452	1485		57	3640	3734	
41	1466	1593	1439	MAE	32		

The zwitterionic isomer very quickly interconverts into the global minimum CS01, in agreement with the literature consensus about its negligible contribution to the vibrational

spectrum. Figure (S2) shows the OH (black line) and NH (red line) distances during the dynamics of ZW01. We observe that the OH distance starts oscillating from the equilibrium one for ZW01, but after very short time it drops into the CS01 basin and the distance oscillates around the equilibrium one of CS01 reported with a black horizontal dashed line. A similar behavior is followed by NH distance.

Figure S2: Plot of NH and OH distances during the dynamics of ZW01. The black line reports the OH distance, while the red line the NH one. Horizontal dashed lines are centered at equilibrium distances for CS01 and ZW01.



## $(\text{GlyH}+\text{H}_2)^+$ and $(\text{GlyH}+3\text{H}_2)^+$

In figure S3 the optimized structures of protonated glycine tagged with a single hydrogen molecule in front of the NH and of the OH bond are displayed. In Figure S4 is instead represented the protonated glycine tagged with three hydrogen molecules, with all NH bonds tagged. For all the calculations we employed the DFT-B3LYP level of theory with aug-cc-pvdz basis set, as implemented in the NWChem software package.

The four highest harmonic frequencies of each structure, together with semiclassical DC-SCIVR and classical estimates through the Fourier transform of the velocity autocorrelation function are reported in Table S7.

Figure S3: Minimum geometry of the protonated glycine tagged with hydrogen. On the left side the NH tagged structure is reported, while on the right side the hydrogen tag is on the OH.

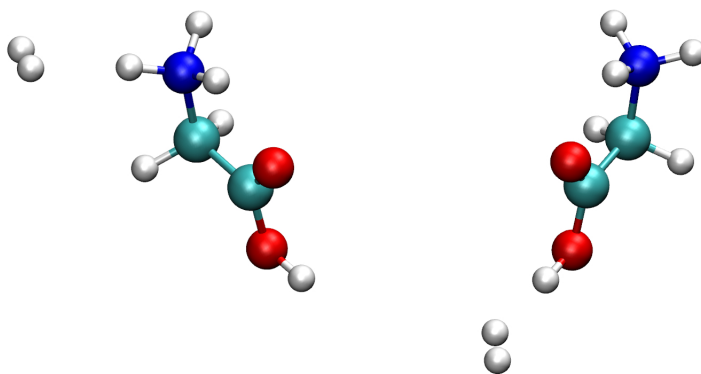


Figure S4: Minimum structure of protonated glycine tagged with three hydrogen molecules.

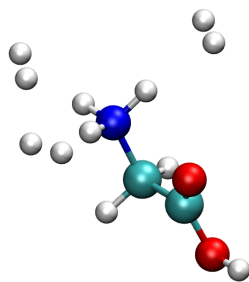


Table S7: Semiclassical (DC-SCIVR) vibrational frequencies of tagged glycine systems reported in  $\text{cm}^{-1}$ . Values are compared with their harmonic (HO) and classical counterparts.

$(\text{GlyH}+\text{H}_2)^+$ (NH tagged)				$(\text{GlyH}+\text{H}_2)^+$ (OH tagged)			
Mode	DC-SCIVR	HO	Classical	Mode	DC-SCIVR	HO	Classical
NHa	2920	3139	3030	NHa	2950	3095	3035
NHb	3310	3377	3310	NHb	3340	3446	3340
NHc	3370	3485	3370	NHc	3370	3507	3350
OHb	3610	3696	3600	OHr	3480	3561	3485
$(\text{GlyH}+3\text{H}_2)^+$				$(\text{Deuterated GlyH}+3\text{H}_2)^+$			
Mode	DC-SCIVR	HO	Classical	Mode	DC-SCIVR	HO	Classical
NHa	3000	3312	3185	NDa	2376	2517	2370
NHb	3240	3367	3260	NDb		3099	
NHc	3260	3410	3250	NDc		3159	
OHb	3600	3701	3600	OHb		3701	

## Quantum Anharmonicity

In Fig.(S5) one can appreciate the amount of delocalization induced by the potential anharmonicity.

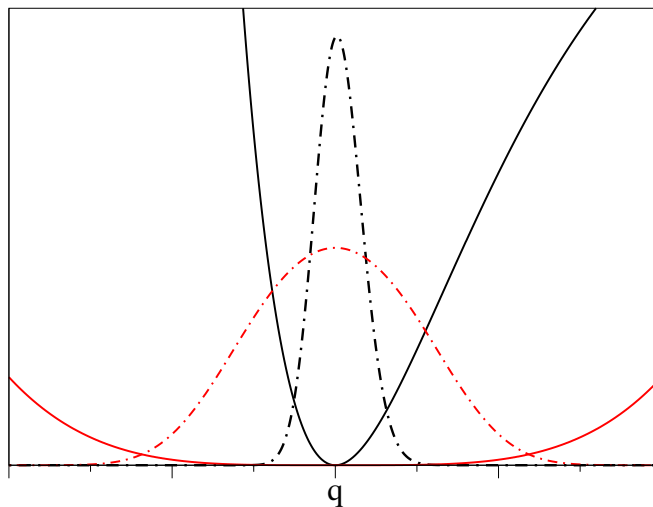


Figure S5: Continuous black line and red lines show potential energy profiles of a stiff and a mild oscillators, while black and red dashed lines their respective ground state wavefunctions.

# Theoretical methods employed for the calculation of vibrational frequencies

## Computational details

All preliminary optimization and harmonic frequency calculations, as well as the molecular dynamics simulations, have been performed employing the NWChem package,<sup>1</sup> and evaluating the electronic energy at the DFT-B3LYP level of theory.<sup>3</sup> Each classical trajectory was propagated for about 600 fs, which is a standard length for semiclassical simulations.<sup>4-10</sup> The same 6-311+G(d,p) basis set of Ref. ( 2) was used for the protonated glycine dimer, while the aug-cc-pvDZ basis set was employed for hydrogen-tagged protonated glycine molecules. This latter basis set has already been demonstrated to be reliable in previous semiclassical calculations, including neutral glycine.<sup>6,11,12</sup>

## Semiclassical approximation to the spectral density

The power spectrum of a molecular system described by the Hamiltonian  $\hat{H}$  can be written as  $I(E) \equiv \sum_i |\langle \chi | \psi_i \rangle|^2 \delta(E - E_i)$ .  $E_i$  is a generic eigenenergy we want to calculate and  $|\psi_i\rangle$  is the associated eigenfunction. By representing the Dirac-delta in terms of a Fourier integral, the spectrum becomes<sup>13</sup>

$$I(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{iEt/\hbar} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle \quad (1)$$

where  $|\chi\rangle$  is an arbitrary quantum mechanical reference state. The semiclassical theory approximates the quantum time evolution operator  $e^{-i\hat{H}t/\hbar}$  by means of a stationary-phase approximation to the Feynman Path Integral representation.<sup>14</sup> The semiclassical propagator thus obtained is equal to the one proposed by van Vleck,<sup>15</sup> and it relies on the calculation of



all possible classical paths connecting the initial  $\mathbf{q}(0)$  and final  $\mathbf{q}(t)$  points. Thus, one needs to solve a nonlinear boundary value problem and to find all possible trajectories knowing the starting and ending positions. Finding these trajectories is a formidable task. In the seventies,<sup>16-19</sup> Miller introduced the Semiclassical Initial Value Representation (SC-IVR), by replacing the boundary condition summation with an initial phase space integration, which is amenable to Monte Carlo (MC) implementation. Later, Heller-Herman-Kluk-Kay pioneered a more suitable representation of the propagator for molecular systems, based on coherent states.<sup>13,20-22</sup> Coherent states have the advantage to feature a Gaussian-type shape centered at classical momenta and positions  $(\mathbf{p}(t), \mathbf{q}(t))$  in the coordinate representation, and they can be expressed for a F-dimensional system as

$$\langle \mathbf{x} | \mathbf{p}(t), \mathbf{q}(t) \rangle = \left( \frac{\det(\Gamma)}{\pi^F} \right)^{1/4} e^{-(\mathbf{x}-\mathbf{q}(t))^T \Gamma (\mathbf{x}-\mathbf{q}(t))/2 + i \mathbf{p}^T(t) (\mathbf{x}-\mathbf{q}(t))/\hbar}, \quad (2)$$

where  $\Gamma$  is a matrix describing the width of the wavepacket. Then, the semiclassical propagator becomes in this representation

$$\begin{aligned} & \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle \approx \\ & \left( \frac{1}{2\pi\hbar} \right)^F \iint d\mathbf{p}(0) d\mathbf{q}(0) C_t(\mathbf{p}(0), \mathbf{q}(0)) e^{\frac{i}{\hbar} S_t(\mathbf{p}(0), \mathbf{q}(0))} \langle \chi | \mathbf{p}(t) \mathbf{q}(t) \rangle \langle \mathbf{p}(0) \mathbf{q}(0) | \chi \rangle \end{aligned} \quad (3)$$

where  $(\mathbf{p}(0), \mathbf{q}(0))$  are the initial conditions of the classical trajectories that are evolved to  $(\mathbf{p}(t), \mathbf{q}(t))$ .  $S_t$  is the classical action computed at time  $t$ , while  $\langle \chi | \mathbf{p}(t) \mathbf{q}(t) \rangle \langle \mathbf{p}(0) \mathbf{q}(0) | \chi \rangle$  is the product of two coherent-state overlaps, which is analytical. Finally,  $C_t$  is the pre-exponential factor arising from the quantum fluctuations around the classical paths,<sup>4</sup> that is calculated from the monodromy (stability) matrix elements as

$$C_t(\mathbf{p}(0), \mathbf{q}(0)) = \sqrt{\det \left| \frac{1}{2} \left( \frac{\partial \mathbf{q}(t)}{\partial \mathbf{q}(0)} + \frac{\partial \mathbf{p}(t)}{\partial \mathbf{p}(0)} - i\hbar \Gamma \frac{\partial \mathbf{q}(t)}{\partial \mathbf{p}(0)} + \frac{i}{\Gamma \hbar} \frac{\partial \mathbf{p}(t)}{\partial \mathbf{q}(0)} \right) \right|}. \quad (4)$$

The convergence of Eq. (3) with the number of phase space trajectories can be tamed by

applying the Time-Averaging filtering technique developed by Kaledin and Miller<sup>23,24</sup> and, by approximating  $C_t(\mathbf{p}(0), \mathbf{q}(0)) \approx e^{i\phi_t/\hbar}$ , to obtain the following semiclassical power spectrum expression

$$I(E) = \left(\frac{1}{2\pi\hbar}\right)^F \iint d\mathbf{p}(0) d\mathbf{q}(0) \frac{1}{2\pi\hbar T} \left| \int_0^T e^{\frac{i}{\hbar}[S_t(\mathbf{p}(0), \mathbf{q}(0)) + Et + \phi_t]} \langle \chi | \mathbf{p}(t), \mathbf{q}(t) \rangle dt \right|^2. \quad (5)$$

This formulation requires roughly 1000 trajectories per degree of freedom, which makes any on-the-fly ab initio molecular dynamics approach unaffordable. In the recent years, one of us developed a formulation of Eq. (5) able to recover accurate spectra by means of few or even a single trajectory by properly selecting the initial conditions and tailoring the reference state  $|\chi\rangle$ <sup>9,12</sup>. More specifically, we choose the initial conditions  $(\mathbf{p}(0), \mathbf{q}(0))$  at the molecular equilibrium configuration  $\mathbf{q}_{eq}$ , while the momentum of each degree of freedom is such that  $p_{eq}^i = \sqrt{\hbar\omega_i(n_i + 1/2)}$  according to its harmonic frequency  $\omega_i$ . For the ground state trajectory  $n_i = 0$  for each degree of freedom. Also, we enforce the reference state to be of the type  $|\chi\rangle = |\mathbf{p}_{eq}, \mathbf{q}_{eq}\rangle + \varepsilon |-\mathbf{p}_{eq}, \mathbf{q}_{eq}\rangle$ . With a proper choice of the  $\varepsilon$  vector elements, we can filter the signal and selectively enhance the signal of the ZPE or of any given fundamental excitation<sup>11,25</sup>. For instance, if we select each element to be equal to one, i.e.  $\varepsilon = +\mathbf{1}$ , the ZPE will be recovered. By selecting  $\varepsilon_i = -1$  with all the other values equal to +1, the fundamental excitation of mode  $i$  will be mainly reproduced with respect to the other vibrational peaks. By combining these strategies, one can employ just a few or even a single classical trajectory to obtain accurate spectroscopic signals for systems as complex as glycine.<sup>6</sup> Unfortunately, this approach runs out of steam when the system dimensionality increases to 25-30 degrees of freedom, because of the curse of dimensionality. To overcome this issue, we have recently developed the divide-and-conquer SC-IVR (DC-SCIVR) method which was shown to be able to recover spectra of high-dimensional molecular systems.<sup>5,7</sup>

## Divide-and-Conquer semiclassical molecular dynamics<sup>7</sup>

Our Divide-and-Conquer method reproduces the full-dimensional molecular spectrum as a combination of reduced dimensionality spectra, each one composed of a reduced number of vibrational degrees of freedom. The power spectrum for a reduced  $M$ -dimensional vibrational space, extracted from the full  $N_{vib}$ -dimensional vibrational space ( $M < N_{vib}$ ), is given in analogy to Eq. (5) by

$$\tilde{I}(E) = \left(\frac{1}{2\pi\hbar}\right)^F \iint d\tilde{\mathbf{p}}(0) d\tilde{\mathbf{q}}(0) \frac{1}{2\pi\hbar T} \left| \int_0^T e^{\frac{i}{\hbar}[\tilde{S}_t(\tilde{\mathbf{p}}(0), \tilde{\mathbf{q}}(0)) + Et + \tilde{\phi}_t]} \langle \tilde{\chi} | \tilde{\mathbf{p}}(t), \tilde{\mathbf{q}}(t) \rangle dt \right|^2, \quad (6)$$

where the  $\sim$  indicates the reduced dimensionality quantities. These quantities are obtained by projection via singular value decomposition of the corresponding full dimensional ones.<sup>5,7,26</sup> The criterion that we employed to partition the  $N_{vib}$  degrees of freedom into groups of subspaces is by inspection of the magnitude of the off-diagonal terms of the time-averaged Hessian matrix elements  $H_{ij}$  along the trajectory started at equilibrium  $(\mathbf{p}_{eq}, \mathbf{q}_{eq})$ . After choosing a certain threshold value  $\varepsilon$ , if a generic Hessian element  $H_{ij} \geq \varepsilon$ , then modes  $i$  and  $j$  are collected in the same subspace. The  $\varepsilon$  parameter is chosen in order to have a maximum subspace dimensionality not exceeding 15-20, which is a good compromise between accuracy and feasibility of the power spectrum calculations. Specifically, for the CS01 isomer of the protonated glycine, the maximum subspace dimensionality was equal to 16, while for CS02 it was 18. In the case of hydrogen tagged protonated glycine the maximum subspace dimensionality was selected to be equal to 19. More details on the method have been provided elsewhere.<sup>5</sup> In conclusion, all semiclassical vibrational spectra have been calculated employing the DC-SCIVR approach, which has already been demonstrated to be able to reproduce spectra of variously sized molecules, up to 60 atoms, either under strong or weak interactions, such as hydrogen bonds in water clusters or in the protonated water dimer (Zundel cation).<sup>5,7,27</sup> Each excitation was selected by properly tailoring the reference

state  $|\chi\rangle$  according to the Multiple Coherent state approach mentioned above.

## Classical evaluation of the vibrational frequencies

To appreciate the relevance of quantum effects better, we have reported in the article some classical estimates for the vibrational frequencies of the hydrogen tagged systems. A standard classical simulation would require a preliminary thermalization of the system at the temperature of the experiment followed by the computation of the Fourier transform of the velocity-velocity autocorrelation function. However, the reference experiments were performed at very low temperature (10K and 21K) and such a classical simulation would have basically returned harmonic estimates. We decided to work instead in analogy to the divide-and-conquer formula for semiclassical calculations by adopting its classical analog

$$I_{cl}(E) = \lim_{T \rightarrow \infty} \int \int d\tilde{q}_0 d\tilde{p}_0 \tilde{\rho}(\tilde{q}_0, \tilde{p}_0) \frac{1}{2T} \left| \int_0^T dt e^{iE(t)} \tilde{v}(t) \right|^2, \quad (7)$$

where  $\tilde{\rho}(\tilde{q}_0, \tilde{p}_0)$  is the same sampling phase-space distribution function in reduced dimensionality employed in the semiclassical simulations, i.e. the set of classical trajectories are the same. The details about the derivation of the formula can be found in Ref. 27.

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