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Local Rovibrational Instability in a Water Molecule[*]

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Using the stability matrix method, the occurrence of locally unstable states in the water molecule has been shown. Detailed analysis of this problem reveals a dependence of the state stability on the rotational quantum numbers *J* and *k*, as well as on the rotation about the *z* axis perpendicular to the molecular plane, *i.e.* on the rotation at which the Coriolis coupling reaches a maximum.

Key words: internal stability, rovibrational states, water molecule

Dynamics of quantum states is governed by the time-dependent Schroedinger equation [1], whose solution gives the probability of finding a state described by the wave function $\Psi_n(r)$ after time *t* at the nth energy level. This probability depends on the matrix elements of Hamiltonian, which describes the external or internal force field imposed on the molecule considered. The main conclusion following from this approach is that the decay of excited states is ruled by the matrix element of the perturbation operator.

The above described mechanism does not lead to any anomalies in the stability of the excited states as long as the matrix elements of the perturbation operators, expressed in the base of electronic states or rovibrational states, do not show any anomalies. The problem of changes in population of excited states is of key importance to understand the photochemical processes taking place in a molecule [2–5], dynamics of chemical reactions, and the emission spectra of atoms and molecules.

According to recent literature, deactivation of excited states does not always run according to the above scheme, and can show many deviations and anomalies [6–10]. The deviations are mainly related to an extension or shortening of a lifetime at a given energy level, relative to the lifetimes of the neighbouring levels. As indicated in [8–11], the most convenient way to analyse the problem is based on the use of the stability matrix [12–14], which provides the information if a given state is stable in the vicinity of a given point and gives a quantitative characteristics of this stability. The analysis of the method performed by Cejran and Reinhardt [11] has proved the applicability of this approach for description of internal motions in polyatomic molecules. The same authors have proposed calculation schemes for such analyses.

This paper presents the applications of the schemes to study the stability of rovibrational states of the water molecule.

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

THE METHOD

The stability matrix is defined [11,12] as the matrix of gradients of forces acting at the singular points of a problem studied, assumed as the points at which all forces acting in a given system are in equilibrium. Consequently

$$\frac{\partial V(q_1,...,q_f)}{\partial q_i} = 0 \Rightarrow (q_1^0,...,q_f^0) \tag{1}$$

where: V(q_i) is the potential of forces acting in a given system, q_i (i = 1,…,f) are the coordinates describing independent motions (f – the number of degrees of freedom), q_i^0(i = 1,…,f) to the singular points at which the forces cease to act.

The stability matrix is built of the elements (l = 1,…,2f)

$$A_{kl} = \frac{\partial F_k}{\partial q_l} \tag{2}$$

where $F_n = \frac{-\partial V}{\partial q_n}, \quad n = 1,...,f \quad F_m = \frac{\partial H}{\partial p_m}, \quad m = f+1,...,2f$

Analysis of the matrix [11,12] shows that if its eigenvalues at a given point q_i^0 are either imaginary or negative, the motion in the vicinity of this point is stable, and if they are positive, the motion is unstable. The above method is applied to analyse the stability of the rotational states of the water molecule H_2O, described by the quantum numbers J, k, and for the vibrational state described by the quantum number v.

The rotational states of the water molecule are the solutions to the eigenproblem of water described by the Hamiltonian [15–17], where

$$V = \sum_{i=1}^{2} \frac{D_i}{2}(1 - l_i^0 / l_i)^2 + \frac{D_3}{2}(\theta^0 - \theta)^2 \tag{3}$$

is the Simons-Parr-Finlan (SPF) potential [18–20], describing the stretching vibrations with an additional term describing bending vibrations. D_i are the constants related to the dissociation energy of the molecule, and μ is the reduced mass. An important element of the Hamiltonian, describing the intramolecular energy flow, and thus nonlinear effects, is the term corresponding to the Coriolis force, so the term including the expression $J_z p_\theta$. In order to simplify its form the Augustin-Miller transformation [21] is used, that relates this term to the Euler angle χ [22]. The transformation introduces new components of the rotational moments of momentum expressed by the formulae

$$J_x = -(j^2 - k^2)^{1/2} \sin\chi; \; J_y = -(j^2 - k^2)^{1/2} \cos\chi; \; J_z = k \tag{4}$$

where the angle χ and the moment of momentum component along the **z** axis make a new pair of canonical variables. After this transformation the Hamiltonian describing the internal states of a three-atomic molecule becomes

$$H = \frac{p_{l_1}^2}{2\mu_1} + \frac{p_{l_2}^2}{2\mu_2} + \frac{p_\theta^2}{2\mu_2 l_2^2} + \frac{(k - p_\theta)^2}{2\mu_1 l_1^2} - \frac{(j^2 - k^2)\sin^2(\theta - \chi)}{2\mu_1 l_1^2 \sin^2\theta} - \frac{(j^2 - k^2)^{1/2}\sin\chi}{2\mu_2 l_2^2 \sin^2\theta} + V \tag{5}$$

The critical points are found from the condition of equilibrium of all forces acting at a given point, that is from the condition (1). Then we get a system of equations of the form

$$F_{l_1} = \frac{(k - p_\theta)^2}{\mu_1 l_1^3} - \frac{(j^2 - k^2)\sin^2(\theta - \chi)}{\mu_1 l_1^3 \sin^2\theta} - \frac{2D_1}{l_1^2}\left(1 - \frac{l_1^0}{l_1}\right) l_1^0 \tag{6a}$$

$$F_{l_2} = \frac{p_\theta^2}{\mu_2 l_2^3} - \frac{(j^2 - k^2)^{1/2} \sin\chi}{\mu_2 l_2^3 \sin^2\theta} - \frac{2D_2}{l_2^2}\left(1 - \frac{l_2^0}{l_2}\right) l_2^0 \tag{6b}$$

$$F_\theta = \frac{(j^2 - k^2)\sin(\theta+\chi)\cos(\theta+\chi)}{\mu_1 l_1^2 \sin^2\theta} - \frac{(j^2 - k^2)\sin^2(\theta+\chi)\cos\theta}{\mu_1 l_1^2 \sin^3\theta} - \frac{(j^2 - k^2)^{1/2}\sin\chi\cos\theta}{\mu_2 l_2^2 \sin^3\theta} + D_3(\theta^0 - \theta) \tag{6c}$$

The equation system with the parameters of the potential describing the rovibrational states of the water molecule given in [23,24] is solved, and the critical points obtained l_1, l_2, θ_0 are substituted into the matrix elements of the stability matrix given by (2). Analysis of the eigenvalues of the stability matrix gives information on the character of motions about these points.

RESULTS AND DISCUSSION

Data in Table 1 illustrate changes in the eigenvalues of the stability matrix A for the electronic and vibrational states (0,0,0) and (0,1,0), for different rotational states *J*, *k*. The calculations have been preformed for $\chi = \theta$, when the horizontal angle of rotation about the *z* axis is equal to the valence angle H–O–H. The results for $J < 15$ are not given, as for such values of *J* all normal vibrations of the water molecule are stable and the motions are regular.

Table 2 presents calculations illustrating the dependence of the stability matrix eigenvalues on the angle of rotation about the new *z* axis, *i.e.* on the angle χ. A comparison of the data given in Tables 1 and 2 leads to the following conclusions:

1. An increase in the projection of the total angular momentum onto the *z* axis, leading to an increase in the Coriolis coupling energy (5), increases the stability of the water molecule structure. It means, that rotation makes the molecule more rigid, which is consistent with the gyroscopic effect.
2. Excitation of the bending vibration decreases the stability of normal vibrations, which leads to the appearance of local vibrations, instead of the normal vibrations typical of the motions in the rovibrational ground states [25,26].
3. A change in the angle χ, corresponding to the onset of the molecule rotation about the *z* axis, changes the situation. The effect of varying this angle on the eigenvalues of the stability matrix is shown in Table 2. The results imply that during the rotation about the *z* axis the character of the bending vibration H–O–H changes from the stable for any set of quantum numbers (v, J, k) to unstable for certain rotational states at the angle $\chi = 0$. The regions of instability increase with increasing the angle of rotation (Figs. 1–5). An increase in the quantum number *k* results in a return to the stable state. This effect is in agreement with the results of our earlier studies of the internal dynamics of water molecule atoms [9], showing on the basis of Poincaré cross-sections, Lyapunov coefficients, and the power spectrum analyses that the rotational excitation of the bending vibration of the water molecule transforms normal vibrations into local ones. The transformation occurs through an unstable state appearing at some rotational quantum numbers.

Table 1. Eigenvalues ($\times 10^{-4}$) of the stability matrix for the ground electronic and for two vibrational states (0,0,0) and (0,1,0) as a function of rotational states (J, k) for the rotational angle equal to the valence angle.

	$v = 0$ $J = 50$ $\chi = \theta$						$v = 1$ $J = 50$ $\chi = \theta$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.8961	0.8903	122.2	–6.9175	–6.3495	–2.3274	0.8990	0.8932	122.2	–6.7930	–6.2874	–2.3356
5	0.8977	0.8903	122.1	–6.8767	–6.3493	–2.3520	0.9006	0.8932	122.0	–6.7532	–6.2872	–2.3600
10	0.9024	0.8903	121.7	–6.7588	–6.3487	–2.4225	0.9053	0.8932	121.7	–6.6384	–6.2867	–2.4295
20	0.9198	0.8904	120.5	–6.3473	–6.3428	–2.6626	0.9226	0.8933	120.4	–6.2846	–6.2335	–2.6671
30	0.9455	0.8906	118.8	–6.3427	–5.7935	–2.9623	0.9482	0.8935	118.8	–6.2808	–5.6959	–2.9645
40	0.9770	0.8909	117.1	–6.3367	–5.2079	–3.2589	0.9798	0.8938	117.1	–6.2749	–5.1225	–3.2597
50	1.0131	0.8916	115.4	–6.3199	–4.6505	–3.5189	1.0158	0.8946	115.4	–6.2582	–4.5762	–3.5189
	$v = 0$ $J = 55$ $\chi = \theta$						$v = 1$ $J = 55$ $\chi = \theta$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.8705	0.8901	125.2	–7.6653	–6.3536	–1.7017	0.8737	0.8930	125.0	–7.5170	–6.2915	–1.7214
5	0.8726	0.8901	125.0	–7.6025	–6.3534	–1.7455	0.8758	0.8930	124.9	–7.4564	–6.2912	–1.7641
10	0.8787	0.8901	124.4	–7.4255	–6.3527	–1.8668	0.8819	0.8930	124.3	–7.2853	–6.2906	–1.8827
20	0.9004	0.8902	122.6	–6.8426	–6.3503	–2.2467	0.9034	0.8931	122.5	–6.7198	–6.2883	–2.2558
30	0.9304	0.8904	120.4	–6.3466	–6.1352	–2.6712	0.9332	0.8933	120.4	–6.2846	–6.0304	–2.6754
40	0.9654	0.8906	118.3	–6.3413	–5.4315	–3.0581	0.9681	0.8936	118.3	–6.2794	–5.3421	–3.0595
50	1.0041	0.8910	116.3	–6.3326	–4.7857	–3.3826	1.0068	0.8940	116.3	–6.2708	–4.7090	–3.3830
55	1.0246	0.8916	115.4	–6.3199	–4.4955	–3.5189	1.0273	0.8946	115.4	–6.2582	–4.4245	–3.5189
	$v = 0$ $J = 60$ $\chi = \theta$						$v = 1$ $J = 60$ $\chi = \theta$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.7816	0.8895	138.5	–11.1860	–6.3653	2.1705	0.8163	0.8926	132.7	–9.5418	–6.2986	0.2395
1	0.7813	0.8895	138.6	–11.2039	–6.3654	2.1994	0.8166	0.8927	132.6	–9.5294	–6.2986	0.2262
2	0.7803	0.8895	138.8	–11.2549	–6.3656	2.2828	0.8175	0.8927	132.5	–9.4933	–6.2985	0.1879
3	0.8124	0.8897	133.0	–9.7690	–6.3610	0.3259	0.8189	0.8927	132.3	–9.4363	–6.2983	0.1281
4	0.8147	0.8897	132.6	–9.6752	–6.3607	0.2263	0.8208	0.8927	132.0	–9.3625	–6.2981	0.0515
5	0.8173	0.8897	132.3	–9.5688	–6.3604	0.1156	0.8230	0.8927	131.7	–9.2754	–6.2979	–0.0371
6	0.8201	0.8898	131.9	–9.4541	–6.3601	–0.0008	0.8255	0.8927	131.4	–9.1785	–6.2976	–1.3390
10	0.8331	0.8898	130.2	–8.9590	–6.3587	–0.4740	0.8375	0.8928	129.8	–8.7376	–6.2964	–0.5520
15	0.8510	0.8899	128.1	–8.3321	–6.3569	–1.0148	0.8547	0.8928	127.9	–8.1521	–6.2946	–1.0579
20	0.8698	0.8900	126.1	–7.7349	–6.3550	–1.4809	0.8731	0.8929	126.0	–7.5820	–6.2928	–1.5061
30	0.9091	0.8902	122.7	–6.6634	–6.3508	–2.2225	0.9121	0.8931	122.6	–6.5452	–6.2887	–2.2317
40	0.9501	0.8904	119.8	–6.3457	–5.7517	–2.7765	0.9529	0.8934	119.8	–6.2837	–5.6559	–2.7795
50	0.9927	0.8908	117.4	–6.3386	–4.9790	–3.1989	0.9954	0.8937	117.4	–6.2767	–4.8992	–3.1996
60	1.0372	0.8916	115.4	–6.3199	–4.3336	–3.5189	1.0399	0.8946	115.4	–6.2582	–4.2659	–3.5189

Table 2. Eigenvalues ($\times 10^{-4}$) of the stability matrix for ground electronic and for two vibrational states (0,0,0) and (0,1,0) as a function of rotational states (J, k) for different rotational angle.

$v = 0$ $J = 15$ $\chi = 0.5\,\pi$							$v = 1$ $J = 15$ $\chi = 0.5\,\pi$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.8600	0.8843	167.4	–86.1317	–64.8133	409.9212	0.8624	0.8872	167.4	–84.7700	–64.1817	410.9537
1	0.9573	0.8912	115.7	–63.2907	–55.1475	–34.6058	0.9600	0.8941	115.7	–62.6731	–54.2156	–34.6090
5	0.9579	0.8912	115.6	–63.2855	–55.0343	–34.6681	0.9606	0.8942	115.6	–62.6680	–54.1049	–34.6710
10	0.9599	0.8913	115.6	–63.2672	–54.6838	–34.8608	0.9626	0.8942	115.5	–62.6500	–53.7621	–34.8627
15	0.9633	0.8916	115.4	–63.1986	–54.1108	–35.1893	0.9660	0.8946	115.4	–62.5823	–53.2018	–35.1893
$v = 0$ $J = 20$ $\chi = 0.3\,\pi$							$v = 1$ $J = 20$ $\chi = 0.3\,\pi$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.8746	0.8834	167.6	–81.3783	–65.0023	445.4737	0.8770	0.8863	167.6	–80.1007	–64.3681	446.4537
1	0.8747	0.8834	167.6	–81.3580	–65.0032	445.9368	0.8770	0.8863	167.6	–80.0807	–64.3689	446.9177
2	0.8749	0.8834	167.6	–81.2971	–65.0057	447.3352	0.8772	0.8863	167.7	–80.0205	–64.3714	448.3189
3	0.8751	0.8834	167.7	–81.1946	–65.0099	449.6975	0.8775	0.8863	167.7	–79.9193	–64.3755	450.6858
4	0.8755	0.8834	167.8	–81.0492	–65.0159	453.0726	0.8779	0.8862	167.8	–79.7757	–64.3815	454.0676
5	0.8760	0.8833	167.9	–80.8589	–65.0237	457.5338	0.8784	0.8862	167.9	–79.5877	–64.3892	458.5375
6	0.8767	0.8833	168.0	–80.6209	–65.0336	463.1825	0.8790	0.8862	168.0	–79.3527	–64.3990	464.1974
7	0.8775	0.8832	168.1	–80.3315	–65.0458	470.1567	0.8798	0.8861	168.2	–79.0669	–64.4110	471.1854
8	0.9595	0.8912	115.3	–63.2892	–54.7647	–34.8448	0.9622	0.8941	115.3	–62.6717	–53.8412	–34.8467
9	0.8795	0.8831	168.5	–79.5782	–65.0779	488.8826	0.8819	0.8860	168.5	–78.3232	–64.4427	489.9483
10	0.9603	0.8912	115.3	–63.2843	–54.6237	–34.8800	0.9630	0.8942	115.3	–62.6668	–53.7033	–34.8818
15	0.9631	0.8913	115.3	–63.2641	–54.1382	–35.0029	0.9659	0.8943	115.3	–62.6469	–53.2287	–35.0039
20	0.9671	0.8916	115.4	–63.1986	–53.4692	–35.1893	0.9698	0.8946	115.4	–62.5823	–52.5746	–35.1893
v = 0 $J = 20$ $\chi = 0.5\,\pi$							$v = 1$ $J = 20$ $\chi = 0.5\,\pi$					
k	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$	l_1	l_2	θ	$\lambda_{l1}\times 10^{-4}$	$\lambda_{l2}\times 10^{-4}$	$\lambda_{\theta}\times 10^{-4}$
0	0.9563	0.8911	115.9	–63.3221	–55.3231	–34.1456	0.9590	0.8940	115.9	–62.7041	–54.3877	–34.1512
9	0.9585	0.8911	115.8	–63.3087	–54.9360	–34.3620	0.9612	0.8940	115.8	–62.6909	–54.0091	–34.3665
10	0.8553	0.8847	166.0	–88.3115	–64.7089	356.5625	0.8576	0.8876	166.0	–86.9312	–64.0784	357.4923
11	0.8573	0.8846	166.4	–87.5078	–64.7370	369.8945	0.8596	0.8875	166.4	–86.1374	–64.1061	370.8487
12	0.8598	0.8845	166.8	–86.5665	–64.7705	386.1000	0.8621	0.8873	166.8	–85.2078	–64.1393	387.0842
13	0.8626	0.8843	167.3	–85.4598	–64.8109	406.0400	0.8649	0.8872	167.3	–84.1149	–64.1792	407.0614
14	0.9616	0.8912	115.6	–63.2864	–54.3967	–34.6616	0.9643	0.8942	115.6	–62.6689	–53.4816	–34.6645
20	0.9671	0.8916	115.4	–63.1986	–53.4692	–35.1893	0.9698	0.8946	115.4	–62.5823	–52.5746	–35.1893

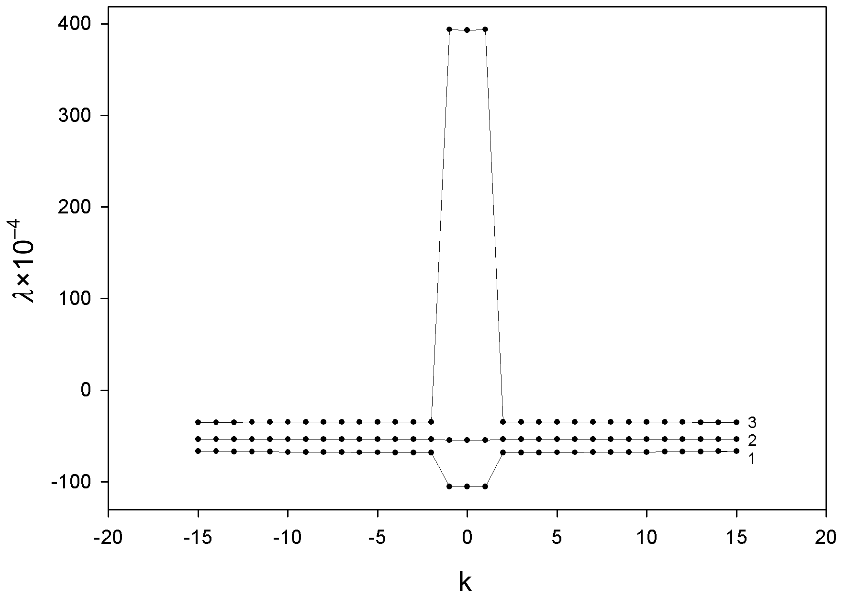

Figure 1. Eingenvalues of the stability matrix as a function of rotational quantum number k for symmetric stretching vibrations (1), antisymmetric stretching (2) and bending one (3) for $\chi = 0.5\pi$ and $J = 15$.

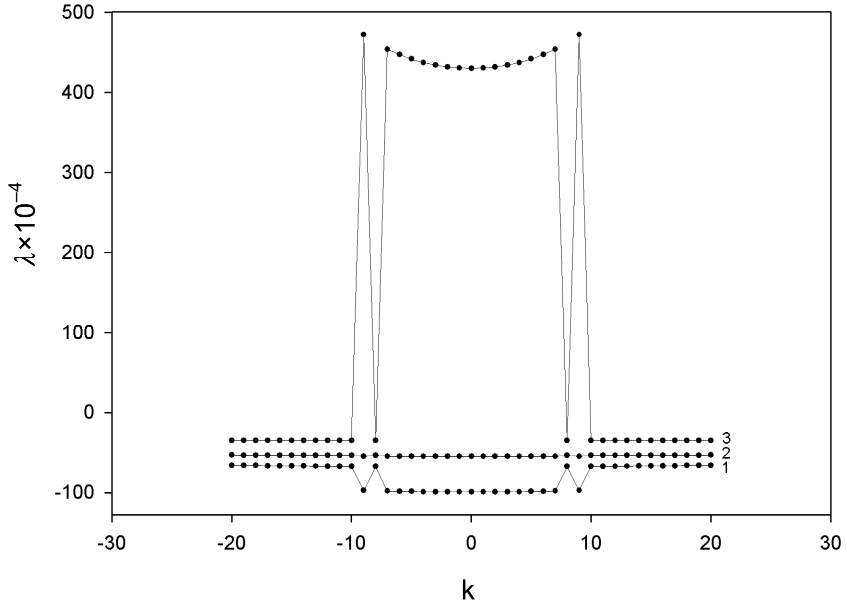

Figure 2. Eigenvalues of the stability matrix for $\chi = 0.3\,\pi$ and $J = 20$.

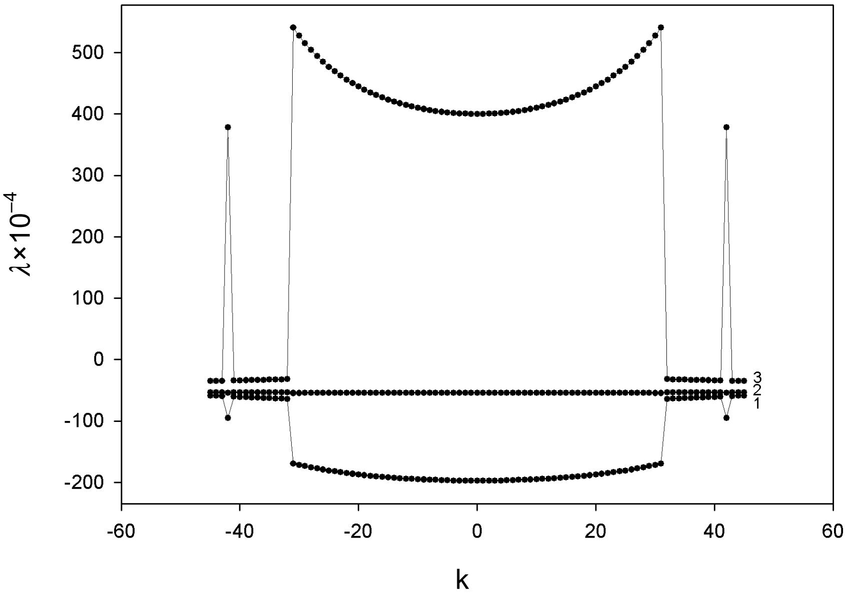

Figure 3. Eigenvalues of the stability matrix for $\chi = 0.5\,\pi$ and $J = 45$.

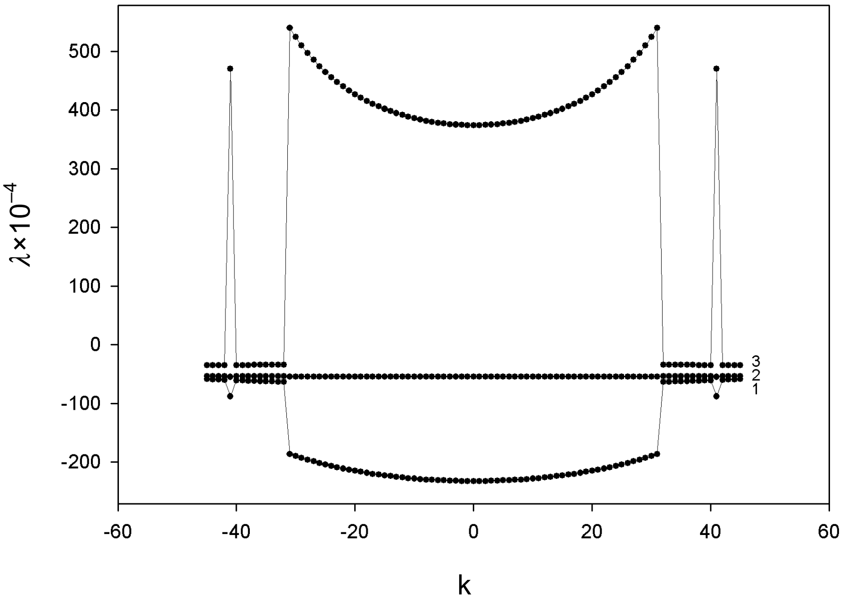

Figure 4. Eigenvalues of the stability matrix for $\chi = 0.3\,\pi$ and $J = 45$.

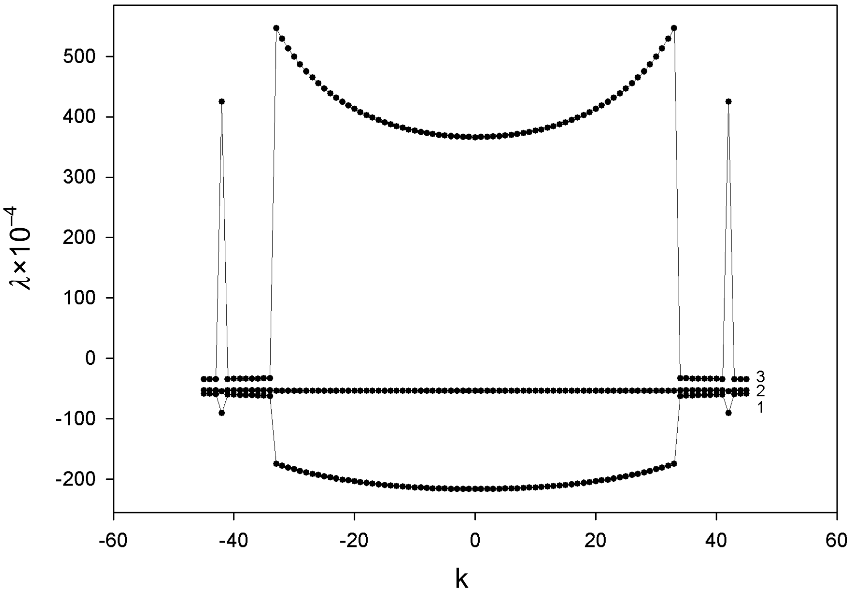

Figure 5. Eigenvalues of the stability matrix for $\chi = 0.4\,\pi$ and $J = 45$.

The following important effect has been observed: The instability of the water molecule in the range of the bending vibration is compensated by an enhanced stability of the stretching vibrations changing their character from normal to local. This fact has been indicated by the Poincaré cross-sections [9], in which the chaotic movement within the bending vibration (in the region of the bending vibration) does not eliminate islands of stability of the stretching vibrations in the range of the local vibrations. This implies a change of the axis about which the rotation takes place. The approach presented in this paper permits investigation of locally unstable motions of polyatomic systems, which is important in analysis of the molecule stability after its rovibrational excitation. Consequence of the calculated instability will be manifested as a dependence of life time of excited states on rotation quantum number. This effect has been detected by Aldener *et al.* for two atomic molecules [10].

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