VIBRATIONAL ENERGIES OF H_3^+ AND Li_3^+ BASED ON THE "DIATOMICS-IN-MOLECULES" POTENTIALS

Jan VOJTÍK[a], Vladimír ŠPIRKO[a] and Per JENSEN[b]

[a] *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2, Czechoslovakia and*
[b] *Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

Received January 21st, 1986

The present publication reports variational calculations of the vibrational energy levels for H_3^+, D_3^+, $^6Li_3^+$, and $^7Li_3^+$, starting from potential energy surfaces generated by the DIM scheme. The vibrational energies obtained agree semiquantitatively with those based on the best *ab initio* potentials available. The results seem to indicate that an analogous approach might be useful in describing the vibrational motion of heavier alkali cluster cations A_3^+.

In recent publications[1,2], the rotation-vibration Hamiltonians for equilateral X_3 and X_2Y molecules have been derived in terms of the three stretching vibrational coordinates Δr_i $(\Delta r_i = r_i - r_e)$ and expanded as power series in the variables $y_i = 1 - \exp\{-a(\Delta r_i)\}$, where a is a molecular parameter, r_i is an actual $(X—X)_i$ bond length and r_e is its equilibrium value. By using the y_i variables a rapidly converging parametrization of the stretching potentials has been obtained as well as Hamiltonians which are eminently suited for diagonalization in a basis of Morse oscillator eigenfunctions.

Using these Hamiltonians, the rotation-vibration energies of H_3^+, D_3^+, H_2D^+, and D_2H^+ have been calculated variationally from published *ab initio* potential energy surfaces. Despite a very large anharmonicity of the H_3^+ molecules, satisfactorily converged energies were obtained with relatively small basis sets.

From a numerical point of view, the application of the Hamiltonians does not pose any particular problem. Hence, it appears tempting to use them to predict the rotation-vibration energies of other equilateral X_3 molecules for which no experimental spectra are presently known. The case of the alkali cluster cations A_3^+ (A = Li, Na, K, ...; see, *e.g.* ref.[3]) appears especially interesting. However, as these systems contain a much greater number of electrons than H_3^+, a sufficient amount of a high quality *ab initio* information about the potential energy surfaces is not available at present, and presumably such high precision calculations will not be carried out in the near future.

Fortunately, the molecules mentioned above represent a class of systems for which physically reasonable information about the relevant portions of the potential energy surfaces can be generated using the semiempirical VB technique of "diatomics-in-molecules" (DIM)[4-7] which has turned out to be quite successful in calculation of potential energy surfaces for use in the theoretical interpretation of gas-phase reactions[7-9], the simplest molecular Penning ionization processes[10-12] and adsorbate-cluster interactions[13-15]. It is to be emphasized that if the necessary diatomic fragment input data are available, the DIM models of potential energy surfaces for triatomic collision systems are very simple; in many cases they are so simple that they can be used directly in the dynamical calculations. An example of a successful application of DIM in this fashion is the classical trajectory study of the collision systems $H^+ + H_2 \rightarrow H + H_2^+$ and their isotopic variants[16-18] in which the potentials, gradients and nondiabatic coupling between the Born–Oppenheimer electronic states were all calculated by DIM.

This successful application, together with previous experience with the DIM method[8,9] suggests that analogous DIM models could be adequate for the description of the collision systems corresponding to the positively charged triatomics A_3^+ mentioned above and, hopefully, for a reasonable description of the vibrational motion in these molecules.

Nevertheless the region of the configuration space near the most stable molecular geometries need not be the most important for the theoretical description of collision processes. Further, as already noted, the experimental spectra of these systems are not known. Therefore, it appears desirable to gain first some indirect information about the performance one can expect from the DIM model for the A_3^+ systems in the region of the configuration space essential for a theoretical prediction of their lowest vibrational levels.

The present communication serves this purpose. Starting from the DIM models for H_3^+ and Li_3^+, we calculate vibrational energies for H_3^+, D_3^+, $^6Li_3^+$, and $^7Li_3^+$ and compare them with those based on the potential surfaces corresponding to *ab initio* wavefunctions.

CALCULATIONS AND CONCLUSIONS

The DIM models used for both H_3^+ and Li_3^+ are based on the minimum basis which arises by including the ^2S ground state and the ionized $A^+(^1S)$ state on each nucleus[20,21]. The resulting VB structures lead to three spin adapted singlet polyatomic basis functions. For the evaluation of the diatomic fragment contributions to the polyatomic Hamiltonian matrix, the $^1\Sigma_g^+$ potential energy function of A_2 ($A = H, Li$) and the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ potential curves of A_2^+ were needed. These were taken from the work of Pedersen and Porter[21] for $A = H$. In the $A = Li$ case, the analytic functions of Pickup[22] were employed. The DIM approximation to the true potential energy surface for the A_3^+ system was obtained as the lowest eigenvalue of the resulting 3×3 DIM polyatomic Hamiltonian matrix.

TABLE I

The potential function parameters[a] of the H_3^+ and Li_3^+ molecules

	F_{11}	F_{12}	F_{111}	F_{112}	F_{123}	F_{1111}	F_{1122}	F_{1112}	F_{1123}	r_e[b]/Å	a/Å^{-1}	E_{lim}[c]/cm^{-1}
H_3^+	66 825	2 270	−48 478	−1 576	9 876	9 224	−11 170	1 354	5 760	0·9187 (0·8724)	0·95	40 000
Li_3^+	13 859	403	−5 276	−381	857	3 229	0[d]	−57	0[d]	2·9446 (3·0842)	0·56	10 000

[a] The units of the force constants are chosen such that the resulting energy is in cm^{-1} (1 Å ≙ 10^{-10} m, 1 cm^{-1} ≙ 1·196256 . 10^{-2} kJ mol^{-1}); [b] the values given in parentheses were derived in refs[1,25] for H_3^+ and Li_3^+, respectively; [c] points exceeding E_{lim} have been excluded from the fitting; [d] held fixed.

For each of the cations about 250 points on the ground electronic state potential energy surface have been computed by the DIM approach over a wide range of values for the vibrational coordinates. In accordance with the previous nonempirical calculations (see, *e.g.*, refs[23–25]), the surfaces exhibit D_{3h} symmetry and possess relatively deep minima. Consequently, the corresponding low lying rotation-vibration energies can be calculated by means of the rotation-vibration Hamiltonians[1,2] mentioned above. As a first step in this calculation it is necessary to determine the appropriate potential energy functions in the following form

$$V = \sum_{i\leq j} F_{ij}y_iy_j + \sum_{i\leq j\leq k} F_{ijk}y_iy_jy_k + \sum_{i\leq j\leq k\leq l} F_{ijkl}y_iy_jy_ky_l\,, \qquad (1)$$

where the force constants F_{ij}, F_{ijk}, ... *etc.* are free parameters and the variables y_i are those introduced above. In this study we have obtained V in the desired form by a least squares adjustment of the force constants and parameters r_e and a to the regions of the DIM surfaces with energies lower than a chosen limit (see Table I). The results of the fitting are shown in Table I. The selected DIM points are reproduced very well by the analytical expression of Eq. (*1*), the deviations are typically of the order of magnitude of 0.2% of the fitted values. This means that the expansion to quartic terms in the y_i is adequate for representing the potential energy function. However, if we compare the potential energy function obtained from the DIM points with function determined with *ab initio* methods that are more costly and therefore more precise, we find the agreement to be less satisfactory. In order to illustrate this

TABLE II

The calculated[a] vibrational energies for the H_3^+ and Li_3^+ molecules (in cm^{-1})

Symmetry	$^1H_3^+$		D_3^+		$^6Li_3^+$	$^7Li_3^+$		
	Ref.[1]	DIM	Ref.[1]	DIM	DIM	Ref.[25]	Ref.[26]	DIM
A_1'	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
E'	2 525·5	2 272·7	1 834·7	1 641·6	263·8	253	240	244·5
A_1'	3 191·3	3 313·4	2 310·0	2 391·3	380·5	316	307	352·8
A_1'	4 811·2	4 319·5	3 541·1	3 163·5	522·4	—	—	484·7
E'	5 006·7	4 554·2	3 650·7	3 291·9	527·8	—	—	489·3
E'	5 573·1	5 452·6	4 070·3	3 965·8	639·9	—	—	593·6
A_2'	7 494·2	6 903·2	5 466·0	4 971·1	792·3	—	—	734·5

[a] Calculated using 120 basis functions: for details see end of Section IV of ref.[1].

we compare in Table I the DIM r_e values for H_3^+ and Li_3^+ with the H_3^+ value determined in ref.[1] from the *ab initio* potential energy surface by Carney and Porter[24] and the Li_3^+ obtained by Gole and coworkers[25]. We see that there is a considerable discrepancy. In view of this, we have not found it worthwhile to calculate the corresponding rotational energies.

Nevertheless, the quality of the DIM potentials appears to be adequate for a realistic estimation of the vibrational energies. To get these, we have diagonalized the following vibrational Hamiltonian

$$\mathbf{H} = \tfrac{1}{2} \sum_{ij} \mathbf{P}_i G_{ij} \mathbf{P}_j + \tfrac{1}{2} \mathbf{p}_z \mu_{zz} \mathbf{p}_z + V \tag{2}$$

using as a basis symmetry adapted combinations of products of three Morse oscillator functions (one for each X—X bond). In (2), $\mathbf{P}_i = -i\hbar\, \partial/\partial \Delta r_i$ and the vibrational angular momentum $\mathbf{p}_z$ is given by

$$\mathbf{p}_z = \tfrac{1}{2} \sum_{ij} \{\mathbf{P}_i G_{ij} X_j + G_{ij} X_j \mathbf{P}_i\}\,, \tag{3}$$

where μ_{zz}, G_{ij} and X_j are known power series in the coordinate Δr_i (see the appendix of ref.[1]). As in refs[1,2] the Watson pseudopotential U was neglected.

The resulting vibrational energy leves are collected in Table II together with the energies based on the previously published potentials. It is seen from this table that for the H_3^+ molecule, the present energies are in reasonable agreement with those calculated from a highly precise *ab initio* potential, the magnitude of the relevant differences practically not exceeding 10%.

A similar degree of accuracy seems to have been achieved for the Li_3^+ molecule. A bigger disagreement for the excited A_1' energies appears to be due to the approximate character of the potentials used in refs[25,26] and the fact that their calculations of the lowest vibrational energies were performed within the harmonic approximation.

Summarizing, the DIM models for alkali cluster cations do not seem to be capable of providing potentials which could lead to straightforward spectral identifications. On the other hand, the models appear to lead to semiquantitatively correct predictions which could be helpful in the experimental search for these cations as well as in organizing more sophisticated *ab initio* calculations.

REFERENCES

1. Špirko V., Jensen P., Bunker P. R., Čejchan A.: J. Mol. Spectrosc. *112*, 183 (1985).
2. Jensen P., Špirko V., Bunker P. R.: J. Mol. Spectrosc., *115*, 269 (1986).
3. Eades R. A., Hendework M. L., Frey R., Dixon D. A.: J. Chem. Phys. *76*, 3075 (1982).
4. Ellison F. O.: J. Amer. Chem. Soc. *85*, 3540 (1963).
5. Tully J. C.: J. Chem. Phys. *58*, 1396 (1973).
6. Steiner E., Certain P. R., Kuntz P. J.: J. Chem. Phys. *59*, 47 (1973).

7. Tully J. C., Truesdale C. M.: J. Chem. Phys. *65*, 1002 (1976).
8. Kuntz P. J. in the book: *Atom-Molecule Collision Theory. A Guide for the Experimentalist* (R. B. Bernstein, Ed.) p. 79. Plenum Press, New York 1979.
9. Tully J. C.: Advan. Chem. Phys. *42*, 63 (1980).
10. Vojtík J., Paidarová I.: Chem. Phys. Lett. *99*, 93 (1983).
11. Vojtík J., Paidarová I.: Chem. Phys. Lett. *103*, 305 (1984).
12. Paidarová I., Vojtík J.: Chem. Phys. *84*, 225 (1984).
13. Vojtík J., Fišer J., Polák R.: Chem. Phys. Lett. *80*, 569 (1981).
14. Vojtík J., Fišer J.: Surface Sci. *121*, 111 (1982).
15. Vojtík J., Šavrda J., Fišer J.: Chem. Phys. Lett. *97*, 397 (1983).
16. Tully J. C., Preston R. .K: J. Chem. Phys. *55*, 562 (1971).
17. Preston R. K., Cross R. J. jr: J. Chem. Phys. *59*, 3616 (1973).
18. Krenos J. R., Preston R. K., Wolfgang R., Tully J. C.: J. Chem. Phys.: *60*, 1634 (1974).
19. Preston R. K., Tully J. C.: J. Chem. Phys. *54*, 4297 (1971).
20. Vojtík J., Krtková A., Polák R.: Theor. Chim. Acta *63*, 235 (1983).
21. Pedersen L., Porter R. N.: J. Chem. Phys. *47*, 4751 (1967).
22. Pickup B. T.: Proc. Roy. Soc. A*333*, 47 (1973).
23. Carney G. D., Porter R. N.: J. Chem. Phys. *64*, 2783 (1976).
24. Carney G. D., Porter R. N.: J. Chem. Phys. *60*, 4251 (1974).
25. Gole J. L., Childs R. H., Dixon D. A., Eades R. A.: J. Chem. Phys. *72*, 6368 (1980).
26. Martins J. L., Car R., Buttet J.: J. Chem. Phys. *78*, 5646 (1983).