Ab initio CALCULATIONS OF THE ROTATION-VIBRATION SPECTRUM OF Na_3^+

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Dedicated to Professor Václav Horák on the occasion of his 70th birthday.

SCF, 6C-SCF, MP4 and valence-electron full CI calculations were performed in order to determine the potential surface of Na_3^+. A power series in the variables $y_i = 1 - \exp(-a\Delta r_i)$, where Δr_i are bond length displacements from equilibrium, has been fitted through the surface obtained and used in a variational rotation-vibration calculation with a basis set of products of Morse-oscillator eigenfunctions and symmetric top rotational wave functions. In contrast to H_3^+, Na_3^+ behaves as a very rigid molecule and does not exhibit any anomalous anharmonicity. With our best potential surface, MP4, the predicted E' and A_1' fundamental frequencies are 105.1 and 146.7 cm^{-1}, and the harmonic E' and A_1' frequencies are 106.5 and 148.3 cm^{-1}.

The objective of this paper is twofold. Primarily it represents a continuation of the long-term project on alkali metal clusters pursued in Berlin[1,2]. Secondly, Na_3^+ is also of spectroscopic interest on its own right. The archetype of equilateral triangular molecules, H_3^+, exhibits an unusually high anharmonicity of stretching vibrations and if accurate rotation-vibration energies of H_3^+ are to be obtained, the standard polynomial expansion of the potential energy function must be abandoned and a power series of the Morse-oscillator-like functions must be used instead[3,4]. We treat here Na_3^+ in order to investigate whether these problems also occur for other equilateral X_3 molecules.

CALCULATIONS

We have employed several different methods of calculation to investigate the effect of the basis set and the electron correlation, and also a possible near-degeneracy effect on the potential surface. We have used two basis sets, 3-21G and [6*s*4*p*1*d*] basis set[5], and

SCF, six-configuration SCF, MP4 and full valence-electron CI methods. Five-component *d*-functions were assumed throughout. The published low vibrational frequencies of Na_3^+ suggest that, unlike in H_3^+, the gap between the frontier MO's (constructed mainly from the 3*s* AO's) may be rather small and the single-determinant approach need not be adequate in this case. To check this effect we performed the six-configuration SCF (6C-SCF) calculations, in which all singly and doubly excited configurations for the three frontier MO's were assumed.

Two sets of vibrational coordinates were used: the usual curvilinear stretching coordinates

$$\Delta r_i = r_i - r_e , \qquad i = 1, 2, 3 \tag{1}$$

where r_e is the equilibrium bond length, and

$$y_i = 1 - \exp(-a\Delta r_i) , \tag{2}$$

where a is a molecular adjustable parameter. About 50 data points were calculated for each potential surface. An expansion of the following form was fitted through them:

$$V = \tfrac{1}{2}\sum_{i,j} f_{ij}\, y_i\, y_j + \tfrac{1}{6}\sum_{i,j,k} f_{ijk}\, y_i\, y_j\, y_k . \tag{3}$$

For comparison the calculated energies were also fitted to the expansion in the Δr_i coordinates. For the 3-21G surface the optimum fit was obtained for $a = 0.71$ Å^{-1}. Since the change in a up to 10% had only a marginal effect on the standard errors of the adjusted f parameters, a was fixed at 0.71 and this value was also used for the other surfaces. The potential surfaces obtained in this fashion were used in the variational rotation-vibration calculations, following closely the procedure developed previously[4] for H_3^+.

RESULTS AND DISCUSSION

The calculated optimum geometries, energies, and basic spectroscopic constants are summarized in Table I. The geometry and spectroscopic constants obtained with the MP4 and full 2 electrons CI procedures are in a fair agreement. The optimized parameters used in the potential function of Eq. (*3*) and for the analogous expansion in the Δr_i coordinates are summarized in Table II. The theoretical model assumed is justifiable only when the energy of the linear structure with respect to the optimum $\mathcal{D}_{3h}$ geometry is considerably higher than the vibrational quanta. To check it we calculated also the linear structures assuming the r_e values from Table I. In the SCF/3-21G, 6C-SCF/3-21G, SCF/[6*s*4p1*d*], MP4/[6*s*4*p*1*d*] and 2e full CI/[6*s*4*p*1*d*] approaches, respectively, the linear structures were higher in energy by 6 506.6, 2 634.1, 6 652.1, 4 908.7,

and 4 136.0 cm^{-1}, which is more than an order of magnitude higher than harmonic frequencies of about 100 and 140 cm^{-1}.

In our literature search for the *ab initio* calculations of vibrational energies of Na_3^+ we have found only two calculations in the harmonic approximation and one study taking into account anharmonicity. Eades et al.[6] obtained 92 and 138 cm^{-1} from the SCF/[6*s*4*p*] calculations. Martins et al.[7] used the pseudopotential and the local-spin-density approximations and arrived at harmonic frequencies of 107 and 147 cm^{-1}.

TABLE I
Calculated molecular parameters for the equilibrium ($\mathcal{D}_{3h}$) geometries of Na_3^+

Quantity[a]	Method				
	SCF/3-21G	6C-SCF/3-21G	SCF/[6*s*4*p*1*d*]	MP4/[6*s*4*p*1*d*]	2e-CI/[6*s*4*p*1*d*]
Energy, a.u.	−482.438702	−482.456300	−485.335211	−485.737767	−485.365827
r_e, a.u.	6.781	6.886	6.720	6.652	6.658
$\omega(A_1')$, cm^{-1}	142.3	135.0	144.0	148.3	147.7
$\omega(E')$, cm^{-1}	105.6	97.2	108.0	106.5	105.8

[a] The observed A_1' and E' fundamental wavenumbers are 139.6 ± 0.5 and 101.5 ± 0.5 cm^{-1} (ref.[9]).

TABLE II
Potential function parameters obtained by fitting to the calculated energies

Polynomial terms	Coefficients in different approaches				
	SCF/3-21G	6C-SCF/3-21G	SCF/[6*s*4*p*1*d*]	MP4/[6*s*4*p*1*d*]	2e-CI/[6*s*4*p*1*d*]
Δr_i^2, cm^{-1} Å^{-2}	5 048.2	4 419.3	5 251.9	5 249.3	5 235.8
$\Delta r_i \Delta r_j$, cm^{-1} Å^{-2}	−151.11	−28.283	−200.67	−56.582	−45.890
Δr_i^3, cm^{-1} Å^{-3}	−7 276.5	−7 197.6	−7 581.9	−7 882.0	−8 350.2
$\Delta r_i^2 \Delta r_j$, cm^{-1} Å^{-3}	−164.22	−252.29	−274.67	−195.41	−239.65
$\Delta r_i \Delta r_j \Delta r_k$, cm^{-1} Å^{-3}	405.39	188.38	469.44	334.12	345.51
σ^a, cm^{-1}	8.90	18.55	13.80	15.27	22.24
y_i^2, cm^{-1}	9 813.7	8 364.2	10 128	10 092	9 986.2
$y_i y_j$, cm^{-1}	−329.80	−57.174	−418.06	−92.447	−74.272
y_i^3, cm^{-1}	7 095.4	1 607.3	6 683.9	4 838.6	1 868.3
$y_i^2 y_j$, cm^{-1}	−724.06	−443.81	−894.17	−308.53	−308.76
$y_i y_j y_k$, cm^{-1}	1 497.4	970.56	1 597.7	1 267.3	1 424.9
σ^a, cm^{-1}	4.34	7.32	4.34	2.47	2.27

[a] Standard deviation.

Carter and Meyer[8] performed valence-shell CI calculation with a pseudopotential for the Na cores. By means of vibrational variational calculations applied to this surface they arrived at the following lowest vibrational levels (in cm^{-1}): A_1' 0.00; E' 99.95; A_1' 140.45; A_1' 198.90; E' 199.72.

Our calculated vibrational energies are listed in Table III. The effect of anharmonicity is surprisingly small. Surprising is also the almost uniform prediction by different

TABLE III
The calculated[a] vibrational energies for Na_3^+ (in cm^{-1})

Symmetry	SCF/3-21G	6C-SCF/3-21G	SCF/[6*s*4*p*1*d*]	MP4/[6*s*4*p*1*d*]	2e-CI/[6*s*4*p*1*d*]
A_1'	0.0	0.0	0.0	0.0	0.0
E'	104.94	95.37	107.00	105.14	104.36
A_1'	141.06	133.42	142.10	146.71	145.96
A_1'	208.88	189.69	212.97	209.23	207.63
E'	209.71	190.55	213.80	210.15	208.53
E'	245.17	227.68	248.24	250.93	249.26
A_1'	281.56	266.13	283.62	292.84	291.28
E'	312.65	283.84	318.65	313.19	310.73
A_1'	314.26	285.49	320.38	315.00	312.49
A_2'	314.32	285.58	320.44	315.07	312.58
z.p.e.[b]	176.61	163.58	179.25	179.74	178.81

[a] Calculated using 165 Morse-oscillator basis functions; the observed A_1' and E' fundamental wavenumbers are 139.6 ± 0.5 and 101.5 ± 0.5 cm^{-1} (ref.[9]). [b] Zero point energy.

TABLE IV
The calculated[a] rotational and centrifugal distortion constants for Na_3^+ (in cm^{-1})

Constant	Ground state	$\nu_1 = 1$ state	$\nu_2 = 1$ state[b]
B_v	0.118229	0.117935	0.118083
C_v	0.058915	0.058765	0.058741
$D_v^{JJ} . 10^7$	−4.504	−4.489	
$D_v^{JK} . 10^7$	7.546	7.500	
$D_v^{KK} . 10^7$	−3.426	−3.387	
$\eta_2^J . 10^5$			−1.188
$q_2 . 10^3$			−1.128
σ^c	$1 . 10^{-5}$	$1 . 10^{-5}$	$1 . 10^{-3}$

[a] Calculated using the MP4 potential energy function. [b] Data processed using the Watson's theory (ref.[10]). [c] Standard deviation.

methods, except for the six-configuration SCF calculations that give somewhat lower energies. As the comparison of SCF/3-21G and 6C-SCF/3-21G vibrational energies suggests, this energy lowering may be assigned to non-dynamical correlation effects. This explains why also single-reference MP4 and 2e-CISD treatments give vibrational energies that are by several wavenumbers higher than experiment[9]. Rotational energy levels, evaluated up to $J = 10$, have been fitted quantitatively using the standard spectroscopic rotational and centrifugal distortion constants[10]. The fitted constants, illustrated here by the MP4 results for the lowest vibrational states (see Table IV), indicate a rather strong rigidity of the Na_3^+ cluster.

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