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Calculated ro-vibrational spectrum of $^7Li_3^+$ and $^7Li_2{}^6Li^+$

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Abstract—Calculated ro-vibrational energy levels ($J \leqslant 4$) and transition intensities are presented for the two most abundant isotopomers of Li_3^+. The calculations use the recent *ab initio* potential energy surface of SEARLES *et al.* (*Spectrochim. Acta* **43A**, 699 (1987); **44A**, 505 (1988); **44A**, 985 (1988)). The rotational levels of the ground state and vibrational fundamentals are given in terms of parameterised Hamiltonians due to WATSON retaining terms to fourth-order. The small splitting of the degenerate ν_2 mode in the mixed isotopomer leads to strong Coriolis coupling between the ν_2 and ν_3 in $^7Li_2{}^6Li^+$.

INTRODUCTION

Understanding simple alkali metal clusters, such as Li_3^+, gives important insight into the nucleation process from free atom to metallic state. The spectrum of Li_3^+ has yet to be observed, but SEARLES, DUNNE and VON NAGY-FELSOBUKI (SDF) [1–3] have recently performed a series of *ab initio* studies aimed at elucidating its vibrational spectrum to facilitate laboratory observation of this species. The object of this paper is to corroborate their findings and to extend their work in two important aspects.

Firstly, SDF mainly considered vibrational motion in their studies, rotations being only considered through the vibrational averaging of certain matrix elements. A knowledge of the rotational constants of the systems is important for any observational study. Secondly, SDF studied only the symmetric isotopomers $^7Li_3^+$ and $^6Li_3^+$. As experience with H_3^+ has shown [4], the study of the asymmetric species is at least as important as the purely symmetric isotopomers. In particular the symmetric ions studied by SDF do not have any dipole allowed pure rotational transitions. We estimate that $^7Li_3^+$ has a natural abundance of about 80% and $^7Li_2{}^6Li^+$ of about 18% in any sample of Li_3^+. We therefore present a spectroscopic analysis of both these isotopomers to aid the observation of Li_3^+.

In this work, ro-vibrational energy levels and wave functions are calculated using the two-step variational method described previously [5] and the analytic 5th-order exponential Dunham expansion potential energy surface used by SDF [2] to represent their Configuration Interaction (CISD) data. Dipole transition intensities are also calculated using the dipole surface given by SDF [3].

This method is the same as has been employed by us for a series of studies on the H_3^+ system [6–10] which has led to a thorough theoretical understanding of the spectroscopy of the low-lying states of this sytem and its deuterated isotopomers. In particular, the rotational constants obtained for the ground state and fundamentals of H_3^+, H_2D^+, D_2H^+ and D_3^+ are competitive in accuracy with those obtained experimentally.

COMPUTATIONAL DETAILS

The vibration-only ($J = 0$) problem was solved in body-fixed scattering coordinates using a basis set expansion. These coordinates represent the interaction between an atom at distance R and angle θ from the centre of a diatom whose bondlength is r. The body-fixed z-axis was taken parallel to the R coordinate. Associated Legendre functions were used to carry the angular coordinate and Morse oscillator-like functions to carry the two radial coordinates [11].

As the method is variational, the parameters in the Morse oscillator-like functions (r_e, D_e, ω_e) can be adjusted to give the best basis for a particular system, without influencing the potential. Optimised parameters for the calculations presented here are given in Table 1. These parameters were found to give a good representation for both ions considered.

In test calculations, basis functions were selected for the calculation according to a number of criteria [12]. For this system the most efficient method proved to be selection by weighted quantum numbers. This meant that all products of the one-dimensional basis functions were included that satisfied the condition

$$N \geqslant m + n + \frac{j}{6}, \tag{1}$$

for a given value of N. In Eqn (1) m, n and j are the number of quanta in the basis function representing the r, R and θ coordinates respectively. Note that in each expansion the first function has quantum number zero. Tables 1 and 2 demonstrate the convergence of the $^7Li_3^+$ and $^7Li_2{}^6Li^+$ band origins as a function of N. In both cases the fundamentals were converged to 0.01 cm^{-1} for $N = 9$, an accuracy very much higher than one can expect for the potential.

The first step of the rotationally excited calculations involves diagonalising a series of vibrational calculations in which it is assumed that the projection of the total angular momentum onto the body-fixed z-axis, k,

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Table 1. Calculated* vibrational band origins for $^7Li_3^+$ in cm^{-1}

v_1v_2l	Symmetry	Parity†	$N=6$	$N=7$	$N=8$	$N=9$	SDF [2]
011	E	e	226.27	226.04	226.01	225.99	225.98
		o	225.94	225.89	225.77	225.98	
100	A_1	e	298.92	298.79	298.78	298.77	298.76
020	A_1	e	449.01	448.35	447.93	447.80	447.76
022	E	e	453.86	451.83	451.32	451.10	451.05
		o	451.95	451.15	450.97	451.07	
111	E	e	522.58	521.00	520.66	520.57	520.54
		o	521.16	520.52	520.37	520.55	
200	A_1	e	596.80	595.67	595.53	595.48	595.47

*Parameters used for Morse oscillator-like functions—r coordinate: $r_e=3.96$ Å, $D_e=10\,100\ cm^{-1}$, $\omega_e=285\ cm^{-1}$; R coordinate: $r_e=2.65$ Å, $D_e=8800\ cm^{-1}$, $\omega_e=285\ cm^{-1}$.

†Parity of Legendre functions used in the basis—e = even; o = odd.

Table 2. Calculated vibrational band origins for $^7Li_2{}^6Li^+$ in cm^{-1}

$v_1v_2v_3$	Symmetry	$N=7$	$N=8$	$N=9$
010	A_1	231.44	231.41	231.40
001	B_2	231.93	231.93	231.93
100	A_1	307.31	307.30	307.30
020	A_1	459.16	458.88	458.80
002	A_1	462.35	462.11	462.06
011	B_2	462.92	462.83	462.81
101	B_2	534.34	534.28	534.28
110	A_1	535.17	534.92	534.86
200	A_1	612.50	612.36	612.34

is a good quantum number. These results are then energy ordered and the lowest I eigenvectors used as a basis for the fully-coupled problem [5]. It was found that the rotational calculations converged rapidly with I. For all the results presented here the first step was solved with $N=8$ and I taken as $25\times(J+1-p)$, where $p=0$ or 1 and the total parity of the state is given by $(-1)^{J+p}$. This gave rotational levels converged to better than 0.01 cm^{-1} relative to the appropriate band origin.

The calculations used the programs SELECT, TRIATOM and ROTLEV [13] which have been updated to drive a new program DIPOLE [14]. This allows for the calculation of transition dipole moments, the theory of which can be found elsewhere [15, 16]. All calculations were performed on the Cray-1S computers at the University of London Computer Centre.

RESULTS AND DISCUSSION

Table 1 presents results for the vibrational band origins of $^7Li_3^+$ as a function of N. The slight splitting between the even and odd components of the degenerate E states is caused by the failure of our method to allow for the full D_{3h} symmetry of the system. This splitting can provide a useful indication of convergence. Our results are well converged for $N=8$ and agree closely with those of SDF, which are presented for comparison.

Table 2 presents the analogous results for $^7Li_2{}^6Li^+$. Again the results are well converged at the $N=8$ level. We note that the splitting between v_2 and v_3 caused by lowering the symmetry of the system by isotopic substitution is only 0.5 cm^{-1}.

Rotational calculations were performed for values of the total angular momentum, $J\leqslant 4$. Rather than presenting the individual levels, we give the results of least-squares fits to the more compact parameterised Hamiltonians due to WATSON *et al.* [17, 18]. For a full discussion of assigning and parameterising the levels of X_3 systems see WATSON [19]. We note however that K in Tables 3 and 5 refers to the projection of J along the C_3 symmetry axis of $^7Li_3^+$. It was found that including up to quartic terms gave a very good representation of our data as can be judged by the standard deviations given in Tables 3 and 4.

$^7Li_2{}^6Li^+$ is an asymmetric top with $\kappa\simeq 0.62$. One feature of the results for $^7Li_2{}^6Li^+$ presented in Table 4 is the very strong Coriolis interaction between the nearby v_2 and v_3 fundamentals. Because the rotational manifolds of the two states not only overlap but are also strongly coupled, they were fitted simultaneously with no attempt at vibrational pre-assignment. Instead, the vibrational states were assigned by analysis of the eigenvectors produced by the fitting procedure.

Table 3. Rotational constants [19] for $^7Li_3^+$ in cm^{-1}

Parameter	Ground state	v_1	v_2
B	0.5319	0.5260	0.5321
C	0.2641	0.2603	0.2629
10^5D^{JJ}	0.9	−9.9	2.6
10^5D^{JK}	−1.4	2.6	1.4
10^5D^{KK}	0.6	−0.7	−0.7
C_ζ			−0.2588
$10^5\eta^J$			−4.4
$10^5\eta^K$			2.5
10^2q			−1.007
10^5q^J			1.0
10^5q^K			−16.5
No.*	16	16	32
$10^3\sigma$†	0.01	4.1	1.2

*Number of levels fitted.

†Standard deviation on fits.

Table 4. Rotational constants [18] for $^7Li_2{}^6Li^+$ in cm^{-1}

Parameter	Ground state	ν_1	ν_2	ν_3
A	0.5908	0.5867	0.6030	0.5777
B	0.5320	0.5293	0.5206	0.5406
C	0.2779	0.2763	0.2173	0.3343
$10^5\Delta^{JJ}$	0.5	−0.1	−185.1	224.2
$10^5\Delta^{JK}$	−0.1	1.3	443.7	−876.6
$10^5\Delta^{KK}$	0.8	−0.2	−182.0	708.6
$10^3\delta^J$			1.10	−0.91
$10^3\delta^K$			−1.88	1.78
ζ_{23}			−0.5003	
$10^3\zeta^J$			2.61	
$10^3\zeta^K$			−3.16	
$10^3\alpha_{23}$			−8.09	
No.*	24	24	48	
$10^3\sigma$†	0.0	0.0	6.9	

*Number of levels fitted.
†Standard deviation on fits.

Table 5. Dipole allowed ro-vibrational transitions for $^7Li_3^+$. All transitions are for the ν_2 fundamental. The energy levels are given relative to the $J=0$ state of the vibrational ground state. (Powers of ten in brackets)

$J'G'_U$–$J''K''$	E' (cm^{-1})	E'' (cm^{-1})	w_{if} (cm^{-1})	$S(f$–$i)$ (Debye^2)
01_{+1} 11	225.986	0.796	225.190	0.661(−3)
10_{-1} 10	227.291	1.064	226.227	0.195(−2)
11_{+1} 11	227.053	0.796	226.256	0.977(−3)
10_{-1} 00	227.312	0.000	227.312	0.130(−2)

Even for $J=1$ there was up to 20% mixing between the levels. As in the equivalent bands of H_2D^+ [20], any experimental analysis of these fundamentals will undoubtedly prove difficult.

Tables 5 and 6 present dipole allowed transitions for $^7Li_3^+$ and $^7Li_2{}^6Li^+$. Only transitions involving the vibrational ground state where J equals 0 or 1 for either level are given. These give a representative sample of the transition intensities to be expected for this system. Intensities for other transitions are available from the authors on request.

For $^7Li_3^+$ the only allowed transitions involve excitation of the ν_2 fundamental. For the ν_2 state the l doubling introduces the extra quantum numbers G $(=K+U)$ and U $(=\pm 1)$ [19]. For this band there is the additional selection rule $G=K$.

In contrast, for $^7Li_2{}^6Li^+$ all three fundamentals are i.r. active and the ion also has a pure rotational spectrum as a result of its permanent dipole along the b axis. If Li_3^+ was a rigid system, the transition dipole for the 1_{11}–0_{00} transition would be equal to the permanent dipole of $^7Li_2{}^6Li^+$. In fact this transition

Table 6. Dipole allowed rotational and ro-vibrational transitions from the vibrational ground state of $^7Li_2{}^6Li^+$. The energy levels are given relative to the $J=0$ state of the vibrational ground state. (Powers of ten in brackets)

v'	$J'_{K_{-1}K_{1}}$–$J''_{K_{-1}K_{+1}}$	Type	E' (cm^{-1})	E'' (cm^{-1})	ω_{if} (cm^{-1})	$S(f$–$i)$ (Debye^2)
0	$1_{10}\,1_{01}$	*b*	1.123	0.810	0.313	0.261(0)
0	$1_{11}\,0_{00}$	*b*	0.869	0.0	0.869	0.174(0)
2	$0_{00}\,1_{11}$	*b*	231.400	0.869	230.531	0.151(−3)
2	$1_{01}\,1_{10}$	*b*	231.888	1.123	230.765	0.165(−3)
3	$0_{00}\,1_{01}$	*a*	231.925	0.810	231.115	0.169(−2)
2	$1_{10}\,1_{01}$	*b*	232.527	0.810	231.717	0.231(−3)
2	$1_{11}\,0_{00}$	*b*	231.917	0.0	231.917	0.152(−3)
3	$1_{11}\,1_{10}$	*a*	233.105	1.123	231.982	0.259(−2)
3	$1_{10}\,1_{11}$	*a*	233.047	0.869	232.178	0.251(−2)
3	$1_{01}\,0_{00}$	*a*	233.100	0.0	233.100	0.168(−2)
1	$0_{00}\,1_{11}$	*b*	307.299	0.869	306.430	0.126(−3)
1	$1_{01}\,1_{10}$	*b*	308.106	1.123	306.983	0.187(−3)
1	$1_{10}\,1_{01}$	*b*	308.416	0.810	307.606	0.186(−3)
1	$1_{11}\,0_{00}$	*b*	308.163	0.0	308.163	0.122(−3)

gives a value of μ of 0.4172 D in very close agreement with the value calculated for the equilibrium geometry at the centre of mass of 0.4157 D. For the ro-vibrational transitions, the ν_3 a-type transitions are roughly an order of magnitude stronger than the ν_1 and ν_2 b-type lines.

In conclusion, we have presented results for those ro-vibrational transitions of Li_3^+ which would appear to be most promising for a laboratory observation of the system. As our ro-vibrational calculations are of proven accuracy it is necessary to concentrate on the potential energy surface in estimating any errors in our results. Error estimates for the potential are difficult. However, we note that our rotational constants for the vibrational ground state of $^7Li_3^+$ agree not only with SDF's estimates using the same potential, but also those of MARTIN *et al.* [21] obtained from a pseudo-potential calculation.

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