Spin Polarized Alkali Clusters: Observation of Quartet States of the Sodium Trimer

J. Higgins, W. E. Ernst,* C. Callegari, J. Reho, K. K. Lehmann, and G. Scoles
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

M. Gutowski
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352
and Department of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

(Received 31 May 1996)

Using helium cluster-isolation spectroscopy we have prepared and characterized the lowest quartet state ($1^4A_2'$) of the sodium trimer. Upon excitation to the $2^4E'$ electronic state, laser induced fluorescence excitation and emission spectra have been obtained. With the aid of *ab initio* calculations, the spectra have been vibronically assigned and new insights on the nonadditivity of van der Waals interactions have been obtained. It is found that approximately 80% of the interaction energy in the $1^4A_2'$ state of Na_3 is due to nonadditive effects. [S0031-9007(96)01704-8]

PACS numbers: 36.40.Mr, 33.20.Kf

Alkali clusters are often viewed as small model systems of a metal and the size dependence of their electronic and geometrical properties has been the subject of many investigations [1]. The main goal of these studies is to understand how the covalent bond of alkali dimers evolves into the metallic binding of the bulk elements. The situation is different when aggregates of alkali atoms with parallel electron spins are formed. These high spin states are bound only by van der Waals forces due to the balance of long range dispersion attraction and short range overlap repulsion [2]. While typical model van der Waals systems (i.e., the inert gases) have rather undeformable valence electron shells, spin-polarized alkali clusters provide excellent examples of systems in which Pauli repulsion can cause large distortions in the spatial distribution of the valence electrons. Since aggregates of spin polarized alkalis possess easily accessible optical spectra, they are particularly suitable as a sensitive testing ground for the theory of van der Waals forces in systems with highly deformable outer electron shells.

Traditionally two-body forces are assumed to be dominant in van der Waals systems. However, it has been shown that many-body effects can play a crucial role in the explanation of important material properties [3]. The balance between dispersion and overlap contributions to three-body forces has been the subject of frequent discussions in the literature. The study of a system where this balance is different than in the usual closed shell systems should increase our understanding of this important question of molecular physics.

In this Letter, we report on the first spectroscopic analysis of alkali trimers in the quartet manifold. These spin-polarized clusters are produced by attaching alkali atoms to large helium clusters where the formation of the complexes can occur in the absence of spin relaxation [4]. Since the alkalis are found to reside on the surface of the clusters, the perturbations introduced by the latter are small, and for the purpose of the present work, can be neglected. Using laser excitation and emission spectroscopy, we are able to identify the lowest $^4A_2'$ state of Na_3 and obtain its vibrational frequencies. This is done with the help of *ab initio* theory, carrying out coupled cluster calculations with single, double, and noniterative triple excitations [CCSD(T)] that show the presence of strong nonadditive effects. In particular, the so determined asymmetric stretch frequency in the lowest quartet state provides a sensitive measure of the three-body contributions to the potential energy.

In a typical supersonic beam expansion, molecules and clusters are produced predominantly in their lowest energetic state that possesses the strongest bonds. Weakly bound high spin states are generated only in small quantities. Only recently, Färbert *et al.* [5] successfully studied sodium dimers in their lowest triplet state using a conventional molecular beam. Using large helium clusters as a substrate, we recently observed [4] the formation of large quantities of alkali dimers in the $1^3\Sigma_u^+$ state confirming and extending the results of Ref. [5].

To extend our investigation to the high spin state of the trimers we used a modified version of an apparatus that has been described in more detail previously [6]. Helium clusters ranging in average size up to 10^4 atoms per cluster are prepared in an expansion of helium gas through a 10 μm nozzle at a temperature of 17.5 K and a stagnation pressure of 5.4 MPa. A short distance after the beam is collimated by a 400 μm skimmer the clusters cross a pickup cell [7] that is connected to an alkali reservoir. A few centimeters downstream, the doped clusters cross the output beam of a tunable continuous wave dye laser at the center of a two-mirror laser induced fluorescence (LIF) detector. Emission spectra were obtained using a monochromator coupled to a liquid nitrogen cooled charge coupled device. Figure 1 shows the previously unassigned laser excitation spectrum taken in the region between 15 800 and 16 500 cm^{-1} that has been reported in [6] and is the starting point of the present investigation.

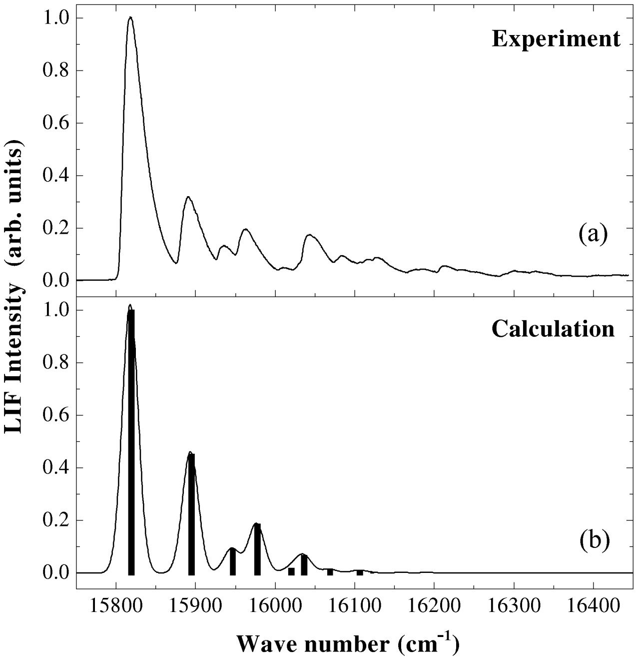

FIG. 1. (a) Excitation spectrum of the $2^4E' \leftarrow 1^4A_2'$ transition of Na_3. (b) Calculated spectrum using a linear and quadratic Jahn-Teller model. Model spectrum is constructed by convolution with a Gaussian line shape.

The intensity of this optical system depends on the third power of the Na partial pressure inside the pickup cell. This is consistent with a trimer transition. The known $B^2A_1' \leftarrow X^2B_2$ system of Na_3 lies in this wave number region but exhibits a different vibronic structure [8]. Our recent studies of the spectra of alkali dimers, carried out in the same apparatus [4,6], have revealed that triplet systems appear to be stronger than their singlet counterparts by up to 3 orders of magnitude. This can be attributed to the fact that when an Na_2 $(X)1^1\Sigma_g^+$ ground state is formed, approximately 6000 cm^{-1} of energy will be released and cause the evaporation of approximately 1000 helium atoms from the cluster or even the desorption of the alkali molecule. The $(a)1^3\Sigma_u^+$ state is bound only by 170 cm^{-1} [9] the dissipation of which poses no problem for the survival of the alkali-helium cluster complex. For the same reason, our experiment favors the observation of high spin states of trimers over the detection of the more strongly bound low spin complexes. Furthermore, multireference configuration interaction calculations predict a $2^4E' \leftarrow 1^4A_2'$ transition of the sodium trimer around 15 500 ± 1000 cm^{-1} with an oscillator strength of 0.5, in agreement with the spectrum depicted in Fig. 1. Because of the low temperature of the clusters (0.37 ± 0.05 K [10]), only the lowest vibrational level of the $1^4A_2'$ state is populated. All structure in Fig. 1 is due to the excitation of vibronic levels in the $2^4E'$ state. The large intensity of the lowest energy band indicates that the molecule has a similar geometry in both electronic states, with the Frank-Condon principle favoring $\Delta v = 0$ transitions. All bands are asymmetrically broadened to 30 cm^{-1} FWHM, with a tail towards the blue. Similar broadening is observed in our alkali dimer spectra [4] and is attributed to the interaction with the helium cluster and its excitations. Peak positions are given in Table I.

The $2^4E'$ state experiences Jahn-Teller coupling that should be weak due to similar geometries in the upper and lower states. There is no analytical expression for the energy in an intermediate case of vibronic coupling and the secular equation must be solved [11]. The variation of energy versus the magnitude of the linear coupling parameter in the $E \otimes e$ problem is depicted in [11]. In their report on the precise structure of the benzene cation, Lindner *et al.* [12] recently displayed a correlation diagram for the ordering of levels due to the linear Jahn-Teller effect. Accordingly, a linear coupling constant k between 0.5 and 1 (in units of ν_2) can produce the observed spectral structure in Fig. 1. In this parameter regime, the states are still characterized by ν_2, the quantum number for the degenerate asymmetric vibration, while l, the quantum number of the vibrational angular momentum, is not meaningful any more, but has to be replaced by the pseudorotation quantum number $j = l + 1/2$ with $j = 1/2, 3/2, 5/2, \ldots, \nu_2 + 1/2$ [11].

All excitation takes place from the lowest level of the $1^4A_2'$ state that has A_1' vibronic symmetry. The vibronic levels $\nu(j)$ of the $2^4E'$ state have E symmetry for $j = 1/2, 5/2, 7/2, 11/2, \ldots$ and A symmetry consisting of an A_1, A_2 pair for $j = 3/2, 9/2, 15/2, \ldots$ [11]. The latter levels cannot be excited from the ground state. For linear Jahn-Teller coupling, only ν_2 $(j = 1/2)$ lines would appear in the spectrum. Adding quadratic coupling makes the other E symmetry levels accessible from the zero point level of the ground state [11]. Diagonalization of the Hamiltonian matrix using harmonic oscillator basis functions (see [12]) yields the result that the spectrum in Fig. 1 is consistent with a vibrational constant $\nu_2 = 88.2$ cm^{-1} and linear and quadratic Jahn-Teller interaction

TABLE I. Experimental and calculated peak positions of the $2^4E' \leftarrow 1^4A_2'$ transition of Na_3 given in cm^{-1}.

v	j	Experiment	Calculated	Difference
0	0	15 817.8	15 817.8	0.00
1	1/2	15 891.6	15 893.5	−1.9
2	5/2	15 936.2	15 945.5	−9.3
2	1/2	15 963.4	15 976.4	−13.0
3	7/2	16 011.8	16 019.0	−7.2
3	1/2	16 043.6	16 035.4	8.2
3	5/2	16 084.3	16068.0	16.3
4	5/2	16 117.9	16 105.1	12.8
4	1/2	16 128.7	16 122.0	6.7
4	7/2	16 146.0	16 155.9	−9.9
5	11/2	16 177.9	16 172.0	5.9
5	7/2	16 185.9	16 191.9	−6.0
5	1/2	16 213.3	16 214.4	−1.1
5	5/2	16 234.2	16 233.4	0.8

parameters $k = 0.72$ and $g = 0.48$, respectively, and no Franck-Condon activity in the symmetric stretching mode. These parameters indicate a rather small Jahn-Teller stabilization of about 22 cm^{-1} [12]. The corresponding quantum number assignments of the peaks and calculated transition wave numbers are included in Table I. An excitation spectrum was calculated using a Gaussian line shape function and is depicted in Fig. 1.

Information about the lowest quartet state was obtained by recording an emission spectrum with the laser frequency positioned at 15 817.8 cm^{-1} shown in Fig. 2. The strongest fluorescence occurs at about 15 792 cm^{-1}, 35 cm^{-1} to the red of the energetically lowest excitation. Additionally, other bands have been detected to the blue of the laser excitation frequency that are described and analyzed in a separate paper [13]. They are related to dissociative decay channels involving the coupling of the quartet to the doublet state followed by desorption of atomic and molecular fragments from the helium cluster. The broad line shape in the emission spectrum shown in Fig. 2 is caused by the excitation of the trimer displacement mode from the helium cluster surface. The $1^4A_2'$ has two fundamental vibrational modes of A_1' and E' symmetry. Without vibronic coupling, fluorescence emission from the lowest level in $2^4E'$ could lead into any vibrational level of the symmetric stretch of the $1^4A_2'$ state, but only into even numbered quanta of the degenerate mode. Because of the Jahn-Teller interaction in the $2^4E'$ state, decay into all vibrational states becomes allowed.

The potential energy surface of the lowest quartet state $1^4A_2'$ of Na_3 was modeled to predict the emission spectrum. The potential was calculated at the D_{3h} configuration for the symmetric stretch coordinate at the [CCSD(T)] level [14] using an extended one-electron basis set. This approach yields a satisfactory pairwise potential curve for the triplet dimer, with a calculated well depth of 176 cm^{-1} compared to the experimental value of 174.5 cm^{-1} [9]. The total interaction energy for the trimer was represented as a sum of the two-body and three-body terms. The two-body interaction energy between two sodium atoms (V_2) with parallel spins was represented by the analytical form suggested by Douketis *et al.* [15]:

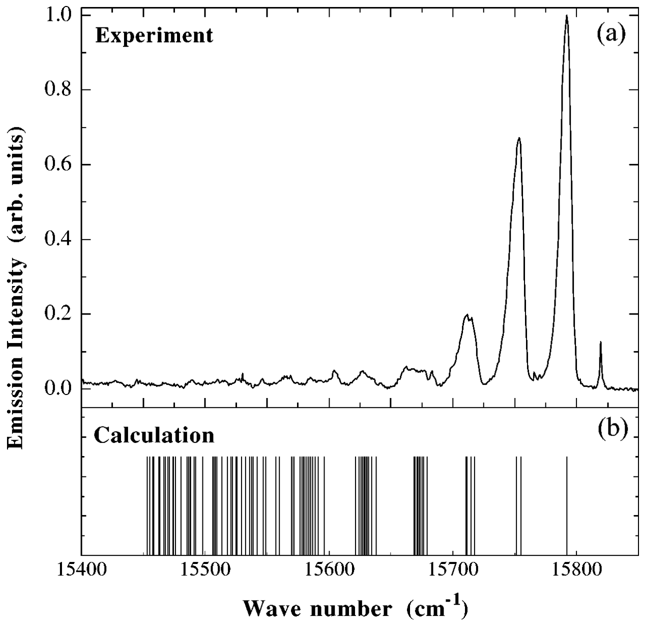

FIG. 2. (a) Emission spectrum of the $2^4E' \rightarrow 1^4A_2'$ transition of Na_3. (b) Calculated vibrational levels of the $1^4A_2'$ state of Na_3.

$$V_2(r) = \Delta E^{\text{SCF}}(r) + \Delta E^{\text{CORR}}(r), \tag{1}$$

$$\Delta E^{\text{SCF}}(r) = A_1 r^{\beta_1} e^{-\alpha_1 r} + A_2 r^{\beta_2} e^{-\alpha_2 r}, \tag{2}$$

$$\Delta E^{\text{CORR}}(r) = -\left[\sum_n C_n r^{-n} g_n(\rho r)\right] f(\rho r), \tag{3}$$

$$n = 6, 8, 10, \ldots. \tag{4}$$

The long range dispersion coefficients (C_6, C_8, C_{10}) calculated by Marinescu and Dalgarno [16] for Na 3s were used. The universal damping functions f and g scale with ρ, which is determined by the ionization potentials of the two interacting atoms [15]. The parameters of $\Delta E^{\text{SCF}}(r)$ were determined by a fit to the SCF energy of the $1^3\Sigma_u^+$ state of Na_2. This two-body functional form was adopted to obtain the nonadditivity (V_3) of the potential surface using the following equation applied to the equilateral geometry where $r = r_{12} = r_{23} = r_{31}$:

$$V_3(r_{12}, r_{23}, r_{31}) = V_{\text{CCSD(T)}}^{\text{total}}(r) - 3V_2(r). \tag{5}$$

The *ab initio* three-body D_{3h} data were fit to the empirical formula [17,18]:

$$\begin{aligned} V_3(r_{12}, r_{23}, r_{31}) = {} & A_3 f(r_{12}) e^{-\gamma r_{12}} f(r_{23}) e^{-\gamma r_{23}} \\ & \times f(r_{31}) e^{-\gamma r_{31}}, \end{aligned} \tag{6}$$

where $f(r) = 1 - r^{\eta} e^{-\lambda r}$ is a damping function used to reproduce the correct form of the nonadditivity at short internuclear separations. A_3, γ, η, and λ are adjustable parameters. Equation (6) was found to give a reliable estimation of the three-body term for an energy calculated at a C_s geometry. The result is a potential whose binding energy relative to three free ground state Na atoms is 850 cm^{-1} at an internuclear separation of 4.4 Å. At this distance, the dimer is bound by 52 cm^{-1}, showing the strong nonadditivity of the potential energies. The parameters of the potential surface are listed in Table II.

The vibrational levels of the $1^4A_2'$ state were calculated using the TRIATOM suite of programs [19]. The Hamiltonian for the triatomic system was set up using body-fixed coordinates (r_1, r_2, θ) where r_1 and r_2 are two bond lengths of the trimer and θ is the included angle. A Morse oscillator basis set consisting of 900 functions was used and the Hamiltonian was diagonalized to give the corresponding eigenvalues. The comparison of the calculated energy levels and the experimental emission spectrum is

TABLE II. Parameters of the potential energy surface of the $^4A_2'$ state of Na_3. The parameters listed in the upper portion of the table were not constrained while those in the bottom portion were constrained.

Parameter	Value[a]
A_1	1.010×10^6
β_1	5.7348
α_1	4.3736
A_2	9.6005×10^4
β_2	1.7342
α_2	1.7861
A_3	-1.3082×10^6
γ	0.5869
η	25.575
λ	9.8821
C_6	7.0789×10^6
C_8	5.3813×10^8
C_{10}	5.3236×10^{10}
ρ	0.5261

[a] Values given for r in Å and V in cm^{-1}.

given in Fig. 2. The calculated vibrational fundamentals of the two normal modes are $\nu_1 = 38$ cm^{-1} for the symmetric stretch and $\nu_2 = 41$ cm^{-1} for the degenerate asymmetric stretch and are in good agreement with the measured emission spectrum.

The intensities of the ν_2 progression in the emission spectrum arising from the excitation of the 0-0 level can be calculated using the Jahn-Teller coupling parameters given above. The intensities are also in good agreement with the experimental results which confirms that the Jahn-Teller distortion in the excited state is small in magnitude but large enough to allow significant intensity in the transitions to both even and odd quanta of the asymmetric stretch.

In summary, we have shown that aggregates of spin-polarized alkalis can be formed and spectroscopically studied by our helium cluster isolation technique. The first optical quartet system of the sodium trimer has been investigated at vibrational resolution. Information has been obtained on the vibronic structure of the $2^4E'$ excited state. With the aid of *ab initio* calculations, potential parameters have been obtained for the lowest quartet state. The nonadditive contributions to the interaction energy of this triatomic system have been found to be large. In fact, 80% of the van der Waals binding energy of the spin-polarized Na trimer is due to nonadditive effects. The analysis of similar spectra obtained for the potassium trimer is in progress and will be reported later.

We thank E. R. Grant for providing us with the computer program to perform the Jahn-Teller calculations. We thank W. S. Warren for the use of the laser that made these experiments possible. This work was carried out with the support of the AFOSR (HEDM program) under Grant No. F49620-95-1-0086.P0001.

---

*On sabbatical leave from the Department of Physics, Pennsylvania State University, University Park, PA 16802.

[1] T. Reiners, C. Ellert, M. Schmidt, and H. Haberland, Phys. Rev. Lett. **74**, 1558 (1995); J. Blanc, V. Bonacic-Koutecky, M. Broyer, J. Chevaleyre, Ph. Dugourd, J. Koutecky, C. Scheuch, J. P. Wolf, and L. Wöste, J. Chem. Phys. **96**, 1793 (1992), and references therein.

[2] G. Chaasiński and M. Gutowski, Chem. Rev. **88**, 943 (1988).

[3] M. J. Elrod and R. J. Saykally, Chem. Rev. **94**, 1875 (1994).

[4] F. Stienkemeier, W. E. Ernst, J. Higgins, and G. Scoles, J. Chem. Phys. **102**, 615 (1995).

[5] A. Färbert, J. Koch, T. Platz, and W. Demtröder, Chem. Phys. Lett. **223**, 546 (1994); A. Färbert, P. Kowalczyk, H. v. Busch, and W. Demtröder, Chem. Phys. Lett. **252**, 243 (1996); A. Färbert, J. Lutz, T. Platz, and W. Demtröder, Z. Phys. D **36**, 249 (1996).

[6] F. Stienkemeier, J. Higgins, W. E. Ernst, and G. Scoles, Phys. Rev. Lett. **74**, 3592 (1995).

[7] T. E. Gough, M. Mengel, P. A. Rowntree, and G. Scoles, J. Chem. Phys. **83**, 4958 (1985).

[8] W. E. Ernst and S. Rakowsky, Phys. Rev. Lett. **74**, 58 (1995).

[9] Li-Li, S. F. Rice, and R. W. Field, J. Chem. Phys. **82**, 1178 (1985).

[10] M. Hartmann, R. E. Miller, J. P. Toennies, and A. Vilesov, Phys. Rev. Lett. **75**, 1566 (1995).

[11] I. B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry* (Plenum Press, New York, 1984).

[12] R. Lindner, K. Müller-Dethlefs, E. Wedum, K. Haber, and E. R. Grant, Science **271**, 1698 (1996).

[13] J. Higgins, C. Callegari, J. Reho, F. Stienkemeier, W. E. Ernst, K. K. Lehmann, M. Gutowski, and G. Scoles, Science **273**, 629 (1996).

[14] R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry* (VCH Publishing Inc., New York, 1994), Vol. V.

[15] C. Douketis, G. Scoles, S. Marchetti, M. Zen, and A. J. Thakkar, J. Chem. Phys. **76**, 3057 (1982).

[16] M. Marinescu and A. Dalgarno (to be published).

[17] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, Molecular Potential Energy Functions (John Wiley and Sons, Chichester, 1984).

[18] T. P. Lybrand and P. A. Kollman, J. Chem. Phys. **83**, 2923 (1985).

[19] J. Tennyson, S. Miller, and C. R. Le Sueur, Comput. Phys. Commun. **75**, 339 (1993).