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# Rotationally resolved infrared spectrum of the Na<sup>+</sup>-D<sub>2</sub> complex: an experimental and theoretical study

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# Rotationally resolved infrared spectrum of the Na<sup>+</sup>-D<sub>2</sub> complex: an experimental and theoretical study

## Abstract

The infrared spectrum of mass-selected Na<sup>+</sup>-D<sub>2</sub> complexes is recorded in the D-D stretch vibration region (2915-2972 cm<sup>-1</sup>) by detecting Na<sup>+</sup> photofragments resulting from photo-excitation of the complexes. Analysis of the rotationally resolved spectrum confirms a T-shaped equilibrium geometry for the complex and a vibrationally averaged intermolecular bond length of 2.461 Å. The D-D stretch band centre occurs at 2944.04 cm<sup>-1</sup>, representing a -49.6 cm<sup>-1</sup> shift from the Q<sub>1</sub>(0) transition of the free D<sub>2</sub> molecule. Variational rovibrational energy level calculations are performed for Na<sup>+</sup>-D<sub>2</sub> utilising an ab initio potential energy surface developed previously for investigating the Na<sup>+</sup>-H<sub>2</sub> complex [B. L. J. Poad et al., J. Chem. Phys. 129, 184306 (2008)] 10.1063/1.3005785. The theoretical approach predicts a dissociation energy for Na<sup>+</sup>-D<sub>2</sub> of 923 cm<sup>-1</sup> with respect to the Na<sup>++</sup> D<sub>2</sub> limit, reproduces the experimental rotational constants to within 1-2%, and gives a simulated spectrum closely matching the experimental infrared spectrum.

## Keywords

rotationally, resolved, infrared, spectrum, theoretical, na, study, d2, complex, experimental, GeoQUEST

## Disciplines

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## Rotationally resolved infrared spectrum of the Na<sup>+</sup>-D<sub>2</sub> complex: An experimental and theoretical study

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The infrared spectrum of mass-selected Na<sup>+</sup>-D<sub>2</sub> complexes is recorded in the D-D stretch vibration region (2915-2972 cm<sup>-1</sup>) by detecting Na<sup>+</sup> photofragments resulting from photo-excitation of the complexes. Analysis of the rotationally resolved spectrum confirms a T-shaped equilibrium geometry for the complex and a vibrationally averaged intermolecular bond length of 2.461 Å. The D-D stretch band centre occurs at 2944.04 cm<sup>-1</sup>, representing a -49.6 cm<sup>-1</sup> shift from the Q<sub>1</sub>(0) transition of the free D<sub>2</sub> molecule. Variational rovibrational energy level calculations are performed for Na<sup>+</sup>-D<sub>2</sub> utilising an *ab initio* potential energy surface developed previously for investigating the Na<sup>+</sup>-H<sub>2</sub> complex [B. L. J. Poad *et al.*, *J. Chem. Phys.* **129**, 184306 (2008)]. The theoretical approach predicts a dissociation energy for Na<sup>+</sup>-D<sub>2</sub> of 923 cm<sup>-1</sup> with respect to the Na<sup>+</sup>+D<sub>2</sub> limit, reproduces the experimental rotational constants to within 1-2%, and gives a simulated spectrum closely matching the experimental infrared spectrum. © 2011 American Institute of Physics. [doi:10.1063/1.3596720]

### I. INTRODUCTION

Interactions between the sodium cation (Na<sup>+</sup>) and neutral molecules are important in a variety of chemical contexts. For example, in the condensed phase, the Na<sup>+</sup> ion is a near ubiquitous constituent of natural and man-made aqueous solutions, and is one of the most important ions in biology, central to nerve action and osmotic control through translocation by enzymes such as Na<sup>+</sup>/K<sup>+</sup>ATPase.<sup>1</sup> In the gas phase, adducts of sodium have been postulated to contribute to the chemistry of interstellar clouds and extraterrestrial atmospheres.<sup>2</sup> Given the abundance of both Na and H<sub>2</sub> in interstellar space one might suspect that the Na<sup>+</sup>-H<sub>2</sub> complex is also present. However, theoretical studies on the radiative association of Na<sup>+</sup> with several abundant interstellar neutral molecules, including H<sub>2</sub>, indicate that the association rates are probably too low for Na<sup>+</sup> to play a significant role in the chemistry of the interstellar medium.<sup>3</sup>

Understanding the interaction between molecular hydrogen and alkali metal cations is particularly important for developing and optimising the storage of molecular hydrogen in zeolites in which a proportion of the framework is replaced by Li, Na, or K ions. Such zeolites and similar materials are potential candidates for reversible storage of H<sub>2</sub> gas, as required for a viable hydrogen economy.<sup>4,5</sup>

Recognising that simple complexes composed of a metal cation (M<sup>+</sup>) and an H<sub>2</sub> ligand are good models for exploring the nature of the ion-neutral bond, we have previously

characterised the Na<sup>+</sup>-H<sub>2</sub> complex through its mid infrared spectrum.<sup>6</sup> Analysis of rotational structure in the spectrum revealed that Na<sup>+</sup>-H<sub>2</sub> has a T-shaped equilibrium structure, a vibrationally averaged intermolecular bond length of 2.493 Å, and a H-H stretch vibrational frequency of 4094.6 cm<sup>-1</sup>. In this paper we describe an analogous spectroscopic and theoretical investigation of the Na<sup>+</sup>-D<sub>2</sub> isotopologue in the D-D stretch vibration region. Ultimately, the information derived from this study should contribute to a comprehensive picture of bonds between metal cations and dihydrogen by complementing earlier gas-phase spectroscopic and theoretical studies of other M<sup>+</sup>-H<sub>2</sub> and M<sup>+</sup>-D<sub>2</sub> complexes (M<sup>+</sup> = Li<sup>+</sup>, B<sup>+</sup>, Na<sup>+</sup>, Mg<sup>+</sup>, Al<sup>+</sup>, Cr<sup>+</sup>, Mn<sup>+</sup>, Zn<sup>+</sup>, and Ag<sup>+</sup>).<sup>6-15</sup> A significant aspect of our investigations is the capacity to record rotationally resolved infrared spectra, providing quantitative structural information.

The small size of the Na<sup>+</sup>-H<sub>2</sub> and Na<sup>+</sup>-D<sub>2</sub> complexes and the fact that they are closed-shell systems makes them amenable to high level quantum chemical calculations. Several theoretical studies, using various levels of *ab initio* theory, have addressed the equilibrium structures, vibrational frequencies, and binding energies of the Na<sup>+</sup>-(H<sub>2</sub>)<sub>n</sub> clusters.<sup>3,16-25</sup> Making comprehensive contact between theory and high resolution infrared spectra for these light, floppy, triatomic systems requires calculation of the rovibrational energy levels using an approach that goes beyond the rigid rotor and harmonic oscillator approximation. To this end, we previously developed a three-dimensional (3D) *ab initio* potential energy surface (PES) for Na<sup>+</sup>-H<sub>2</sub> that was used to derive rovibrational energies that were tested against experimental spectroscopic data.<sup>6</sup> The same PES is used here to calculate Na<sup>+</sup>-D<sub>2</sub> rovibrational energy levels, with the results evaluated through comparisons with parameters extracted from the

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experimental IR spectrum. Obviously, a stringent test for the  $\text{Na}^+ + \text{H}_2$  PES is its ability to predict reliably the properties of both  $\text{Na}^+ - \text{H}_2$  and  $\text{Na}^+ - \text{D}_2$  isotopologues. The theoretical and spectroscopic results presented in this paper are also compared with the theoretical results by Page *et al.* who recently developed a 3D *ab initio* PES and calculated rovibrational energies for the  $\text{Na}^+ - \text{H}_2$  and  $\text{Na}^+ - \text{D}_2$  complexes.<sup>24</sup>

## II. EXPERIMENTAL AND COMPUTATIONAL METHODS

### A. Experimental methods

The approach used to record the IR spectrum of  $\text{Na}^+ - \text{D}_2$  was described in the previous study of  $\text{Na}^+ - \text{H}_2$  (Ref. 6). Briefly,  $\text{Na}^+ - \text{D}_2$  complexes were produced in a supersonic expansion of  $\text{D}_2$  gas (8 bar) passed over a laser-ablated alloy rod (10% Na/90% Al, *ACI Alloys*). The  $\text{Na}^+ - \text{D}_2$  ions were selected by a quadrupole mass filter and deflected through  $90^\circ$  by a quadrupole bender into an octopole ion guide, where they were overlapped by the counter-propagating output of a tunable IR optical parametric oscillator (Continuum Mirage 3000,  $0.017 \text{ cm}^{-1}$  bandwidth). Resonant excitation of the D-D stretch vibrational mode precedes migration of the energy to the weak intermolecular bond which then ruptures. Resulting  $\text{Na}^+$  photofragments were selected by a second quadrupole mass filter and passed through to the ion detector. The IR spectrum was obtained by monitoring the  $\text{Na}^+$  signal as a function of the IR frequency.

The signal-to-noise ratio for the  $\text{Na}^+ - \text{D}_2$  spectrum is somewhat lower than for other  $\text{M}^+ - \text{H}_2/\text{D}_2$  spectra. Contributing factors include a low  $\text{Na}^+ - \text{D}_2$  abundance due to the minor percentage of Na in the alloy ablation target (10%), and a persistent background signal due to slight leakage through the second quadrupole mass filter of the abundant  $^{27}\text{Al}^+$ , which has the same mass as  $\text{Na}^+ - \text{D}_2$ .

### B. Potential energy surface and rovibrational energy levels

The *ab initio* PES for the  $^1A_1$  symmetry electronic ground state of  $\text{Na}^+ - \text{H}_2$  is described in Ref. 6. Briefly, electronic structure calculations were performed using a aug-cc-pVQZ basis for the H atoms, a cc-pVQZ basis for the Na atom,<sup>26,27</sup> and a set of  $3s3p2d2f1g$  bond functions centred on a dummy atom situated halfway between the  $\text{Na}^+$  and the  $\text{H}_2$  center-of-mass.<sup>28</sup> The electronic correlation energy was calculated using a coupled-cluster methodology including single and double excitations and noniterative correction to triple excitations [CCSD(T)]. The complete PES is represented by the sum of the interaction PES,  $V(r, R, \theta)$  and an accurate potential energy curve for the  $\text{H}_2$  diatomic monomer  $U(r)$ .<sup>29</sup> An analytic representation of the PES was obtained using a reproducing kernel Hilbert space method.<sup>30</sup>

Rovibrational energy levels for  $\text{Na}^+ - \text{D}_2$  were calculated for the ground vibrational state ( $n_{DD} = 0$ ) and the state with one quantum of the D-D stretch vibrational mode ( $n_{DD} = 1$ ) following the method outlined in Ref. 31. Briefly, the full 3-D Hamiltonian was simplified by separating diabatically the fast  $\text{H}_2$  vibrational motion. The resulting two-dimensional prob-

lem, with effective potentials for each vibrational state of the  $\text{H}_2$  fragment ( $n_{HH} = 0$  and 1), is solved variationally using a basis set constructed from numerical radial functions and analytical symmetry-adapted free-rotor spherical functions. The latter brings the full Hamiltonian matrix for each total angular momentum quantum number  $J$  (excluding nuclear spin) into two and four blocks for  $J = 0$  and  $J \geq 1$ , respectively, according to two parity indices,  $p_i$  related to the inversion parity  $p = p_i(-1)^J$  and the permutation parity  $p_j$ . Parities  $p_j = +1$  and  $-1$  correspond respectively to complexes containing *ortho*  $\text{D}_2$  (even  $j$ ) and *para*  $\text{D}_2$  (odd  $j$ ). The calculated rovibrational energy levels are available as supplementary material.<sup>32</sup>

The parity classifications of the  $\text{Na}^+ - \text{D}_2$  rovibrational energy levels employed for the variational calculations can be related to the more standard spectroscopic notations.<sup>33</sup> In particular, it is useful to label the levels using quantum numbers for a near-prolate, asymmetric rotor ( $J, K_a, K_c$ ), where  $J$  is the quantum number referring to the rotational angular momentum, whereas  $K_a$  and  $K_c$  are quantum numbers relating to the projections of the total angular momentum along the  $a$  and  $c$ -axes in the prolate and oblate top limits, respectively. For  $\text{Na}^+ - \text{D}_2$ , the  $a$ -axis corresponds to the intermolecular axis.

## III. RESULTS AND DISCUSSION

In its  $^1A_1$  electronic ground state,  $\text{Na}^+ - \text{D}_2$  is a weakly bound complex with a T-shaped equilibrium structure, as favoured by the positively charged  $\text{Na}^+$  ion interacting with the quadrupole moment of the  $\text{D}_2$  molecule. As reported previously,<sup>6</sup> the PES features a  $C_{2v}$  minimum with an intermolecular  $\text{Na}^+ \cdots \text{D}_2$  bond length  $R_e = 2.408 \text{ \AA}$  and D-D bond length  $r_e = 0.746 \text{ \AA}$  ( $r_e$  for free  $\text{D}_2$  is calculated as  $0.741 \text{ \AA}$ ). The energy of the minimum is  $-1184 \text{ cm}^{-1}$  with respect to  $\text{Na}^+ + \text{D}_2$  fragments. Internal rotation of the  $\text{H}_2$  through a saddle point in the linear configuration has a calculated barrier of  $1001 \text{ cm}^{-1}$ .

Rovibrational calculations predict that the ground state of the  $\text{Na}^+ - \text{D}_2$  (*ortho*) complex lies  $D_0 = 923 \text{ cm}^{-1}$  below the  $\text{Na}^+ + \text{D}_2$  ( $j = 0$ ) limit and that the ground state of the  $\text{Na}^+ - \text{D}_2$  (*para*) complex lies  $949 \text{ cm}^{-1}$  below the  $\text{Na}^+ + \text{D}_2$  ( $j = 1$ ) limit. Due to its slightly lower vibrational zero point energy,  $\text{Na}^+ - \text{D}_2$  is bound marginally ( $81 \text{ cm}^{-1}$ ) more strongly than  $\text{Na}^+ - \text{H}_2$  [ $D_0 = 842 \text{ cm}^{-1}$  for  $\text{Na}^+ - \text{H}_2$  (*para*); Ref. 6]. Note that the calculated  $\text{Na}^+ - \text{H}_2$  binding energy agrees well with the experimental value determined from clustering equilibrium measurements ( $860 \pm 70 \text{ cm}^{-1}$  from Ref. 20).

In the remainder of this section, the results of the rovibrational calculations are compared with the experimental data. First, the infrared spectrum is presented and analysed in terms of a phenomenological Watson Hamiltonian,<sup>34</sup> which is also used to fit the theoretical rovibrational energy levels. Next, fitted parameters are used to estimate the vibrationally averaged separation and the harmonic frequency of the intermolecular stretch mode. Finally, the experimental spectrum is compared with a simulated spectrum in which infrared transition energies were determined from the rovibrational energies, and the variational wave functions were used to calculate the line in-



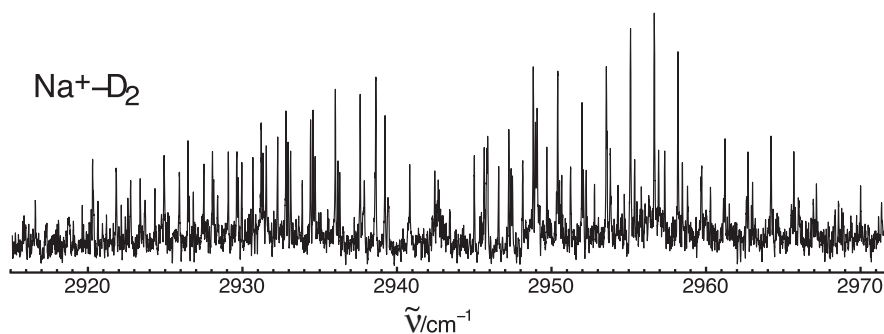


FIG. 1. Infrared spectrum of mass-selected Na<sup>+</sup>-D<sub>2</sub> complexes in the D-D stretch vibration region obtained by monitoring Na<sup>+</sup> photofragments.

tensities, employing the dipole surface and method described in Ref. 6.

### A. Infrared spectrum

The IR spectrum of Na<sup>+</sup>-D<sub>2</sub> in the  $\nu_{DD}$  region shown in Fig. 1 has the characteristic form for a parallel transition of a near-prolate asymmetric rotor, with  $K_a = 0-0$ ,  $K_a = 1-1$  and  $K_a = 2-2$  sub-bands all distinguishable. Vibrational excitation of the  $\nu_{DD}$  mode results in a transition dipole moment lying along the intermolecular axis ( $a$ -axis) producing an  $A$ -type band with selection rules  $\Delta K_a = 0$  and  $\Delta J = 0, \pm 1$  ( $\Delta J = \pm 1$ ) for  $K_a > 0$  ( $K_a = 0$ ). All observed transitions have been assigned to either the  $K_a = 0-0$ ,  $K_a = 1-1$ , or  $K_a = 2-2$  sub-bands, with the  $K_a = 0-0$  sub-band transitions being the most prominent. As seen in Fig. 2, asymmetry doublets are clearly resolved in the P and R branches of the  $K_a = 1-1$  sub-band, although assigning individual transitions in the Q-branch is difficult due to a poor signal-to-noise ratio. For the  $K_a = 2-2$  sub-band, the asymmetry doublets are not resolved and the Q-branch appears as a single peak at  $\sim 2938.6$  cm<sup>-1</sup>. A list of observed transitions, along with their assignments, is provided as supplementary material.

The transition wave numbers for the  $K_a = 0-0$  and  $1-1$  sub-bands of Na<sup>+</sup>-D<sub>2</sub> were fitted to a Watson  $A$ -reduced Hamiltonian for an asymmetric near-prolate rotor to yield effective spectroscopic constants. Adjustable parameters included the  $\nu_{DD}$  band centre and the rotational constants  $B$ ,  $C$ ,  $\Delta_J$ , and  $\Delta_{JK}$  in the  $n_{DD} = 0$  and  $n_{DD} = 1$  states. For the fits,  $A'$  was constrained to 29.907 cm<sup>-1</sup>, the rotational constant of D<sub>2</sub> in its ground vibrational state,<sup>35</sup> whereas  $A'$  was allowed to vary. It should be noted that the  $B$  and  $C$  constants have a weak dependence on  $A''$  and  $A'$ , with the form of the spectrum depending on the difference  $\Delta A = A' - A''$  rather than the values of  $A'$  and  $A''$  themselves. Similar fits were carried out for the calculated  $K_a = 0$  and 1 rovibrational energy levels to allow comparisons between the experimental and theoretical spectroscopic parameters. The resulting spectroscopic constants are presented in Table I.

The  $K_a = 0$  and 2 sub-bands are both obvious in the Na<sup>+</sup>-D<sub>2</sub> spectrum, but are essentially absent from the Na<sup>+</sup>-H<sub>2</sub> spectrum. This difference is partially due to the different nuclear spin statistics for H<sub>2</sub> and D<sub>2</sub>. For normal H<sub>2</sub> gas, for which the *ortho* and *para* nuclear spin states have been equilibrated at high (i.e., room) temperature, the *ortho* ( $j = \text{odd}$ ) and *para* ( $j = \text{even}$ ) modifications have a population ratio of 3:1 and are associated with odd and even  $K_a$  levels in Na<sup>+</sup>-H<sub>2</sub>,

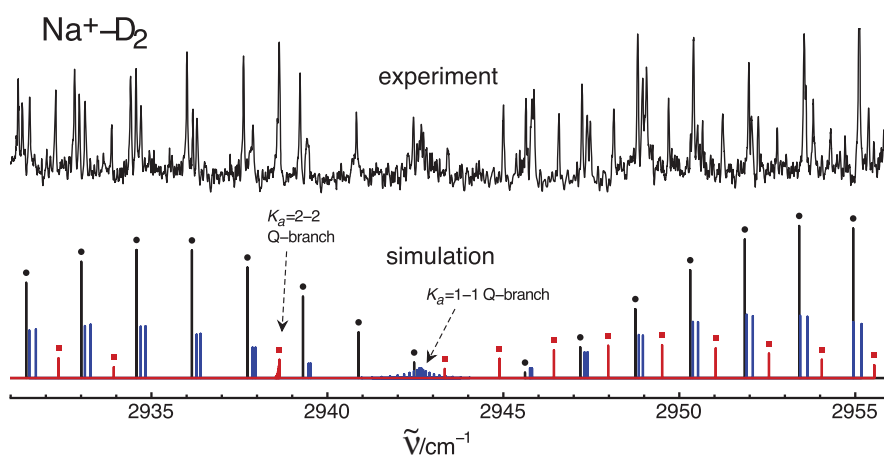


FIG. 2. Central region for the experimental and simulated infrared spectra of Na<sup>+</sup>-D<sub>2</sub>. The simulated spectrum corresponds to temperature of 25 K and has been shifted by  $-2.4$  cm<sup>-1</sup> to overlap with the experimental spectrum. The spectra contain  $K_a = 0-0$  transitions (●),  $K_a = 1-1$  transitions, and  $K_a = 2-2$  transitions (■). Note that the intensities of the  $K_a = 1-1$  and  $K_a = 2-2$  Q-branches, for which there are several overlapping transitions, are underrepresented in the simulated stick spectrum.

TABLE I. Spectroscopic constants for  $\text{Na}^+\text{-D}_2$  obtained by fitting the D-D stretch band experimental transitions and calculated rovibrational energy levels to a Watson  $A$ -reduced Hamiltonian. Units are  $\text{cm}^{-1}$  unless otherwise stated. Errors in the last significant figure are given in brackets.

	$K_a = 0,1$ (expt.)	$K_a = 0,1$ (calc.)
$A''$	...	33.34(1)
$B''$	0.8158(14)	0.8025(6)
$C''$	0.7870(14)	0.7746(6)
$\overline{B''}$	0.8014(14)	0.7886(6)
$\Delta''_J \times 10^5$	4.59(30)	4.61(60)
$\Delta''_{JK} \times 10^4$	8.5(50)	7.8(30)
$A'$	...	31.94(1)
$B'$	0.8140(14)	0.8012(6)
$C'$	0.7851(14)	0.7730(6)
$\overline{B'}$	0.7996(14)	0.7871(6)
$\Delta'_J \times 10^5$	4.37(30)	4.45(60)
$\Delta'_{JK} \times 10^4$	6.8(50)	7.2(30)
$\Delta A$	-1.40(1)	-1.40(2)
$\nu_{DD}$	2944.04(2)	2946.4
rms $\times 10^3$	11.6	2.5
$\Delta \nu_{DD}$	-49.6	-47.2
$\omega''_s$	212	
$\omega'_s$	216	
$\nu''_s$		196
$\nu'_s$		199
$\nu''_b$		336
$\nu'_b$		342
$R''_0/\text{\AA}$	2.461	2.481
$R'_0/\text{\AA}$	2.463	2.483
$D_0$		923

respectively. On the other hand, for normal  $\text{D}_2$ , the *ortho* ( $j = \text{even}$ ) and *para* ( $j = \text{odd}$ ) modifications have a 2:1 population ratio and are associated with even and odd  $K_a$  levels in  $\text{Na}^+\text{-D}_2$ , respectively. Additionally, the slightly greater stability of complexes containing  $j = \text{odd}$   $\text{H}_2/\text{D}_2$  means that they become enriched in the ion source through ligand switching reactions that are slightly more exothermic for  $\text{H}_2$  ( $46 \text{ cm}^{-1}$ ) than for  $\text{D}_2$  ( $26 \text{ cm}^{-1}$ ).<sup>36,37</sup>

## B. Comparison between the experimental and simulated infrared spectra

The central region of the experimental IR spectrum is plotted together with a spectrum simulated using the calculated rovibrational energies and IR line strengths in Fig. 2. The simulated spectrum was uniformly shifted by  $-2.4 \text{ cm}^{-1}$  to align the experimental and simulated  $\nu_{DD}$  band centres. Once this is done, there is a clear correspondence between the predicted and observed transitions, supporting the assignments for the experimental transitions. This validation is particularly welcome for the overlapping R-branch lines of the  $K_a = 0-0$  and  $K_a = 1-1$  transitions where the assignments are not immediately obvious.

Although not clear in Fig. 2, the alignment between the recorded and simulated transitions gradually deteriorates with increasing  $J$ , due to the slight difference between the measured and calculated rotational constants (e.g.,  $\overline{B''} = 0.8014$  vs.  $0.7886 \text{ cm}^{-1}$ ).

For the simulations, the population of the  $J$  levels in each  $K_a$  manifold were characterised by a rotational temperature of 40 K, chosen to replicate best the experimental intensities and in the range commonly achieved by our laser ablation ion source. A higher temperature of 120 K was necessary to describe the relative population of the  $K_a = 0, 1$ , and 2 manifolds. The need for two temperatures to replicate the observed intensities suggests collisional cooling between the closely spaced  $J$  levels within each  $K_a$  manifold is relatively efficient, whereas collisional relaxation between the  $K_a$  manifolds is impeded by large energy spacings (e.g., the  $K_a = 2$  manifold lies  $134 \text{ cm}^{-1}$  above the  $K_a = 0$  manifold).

## C. Comparisons between experiment and theory

In this section we compare the measured and calculated rotational constants, vibrationally averaged intermolecular separations, and assess the calculated PES. The vibrationally averaged intermolecular separation, estimated from the experimental  $B''$  and  $C''$  rotational constants is  $2.461 \text{ \AA}$ , increasing by  $0.002 \text{ \AA}$  in the  $\nu_{DD} = 1$  state. Note that  $R_0$  for  $\text{Na}^+\text{-D}_2$  is slightly less than for  $\text{Na}^+\text{-H}_2$  ( $2.493 \text{ \AA}$ ) due to the presence of the heavier  $\text{D}_2$  sub-unit and reduced amplitude for the zero-point vibrational excursions. The vibrationally averaged  $\text{Na}^+\text{-H}_2$  and  $\text{Na}^+\text{-D}_2$  separations derived from the calculated rovibrational levels exceed the experimental values by  $0.02 \text{ \AA}$  indicating that the PES marginally underestimates the strength of the intermolecular bond.

Vibrational excitation of the  $\text{H}_2$  or  $\text{D}_2$  sub-unit might be expected to cause a contraction and stiffening of the intermolecular bond because of enhanced electrostatic and induction interactions associated with the increase in the vibrationally averaged quadrupole moment and polarisability of the  $\text{H}_2$  or  $\text{D}_2$  molecule.<sup>38</sup> Indeed there is a slight increase in the frequency of the intermolecular stretch mode for  $\text{Na}^+\text{-D}_2$  (from  $212$  to  $216 \text{ cm}^{-1}$ ), consistent with a stiffening of the intermolecular bond. However, the vibrationally averaged intermolecular separation,  $R_0$ , actually increases by  $0.002 \text{ \AA}$  following excitation of the  $\text{D}_2$  sub-unit. This slight expansion of the intermolecular bond is apparently a trait of complexes containing alkali metal cations ( $\text{Li}^+\text{-H}_2$ ,  $\text{Li}^+\text{-D}_2$ ,  $\text{Na}^+\text{-H}_2$ , and  $\text{Na}^+\text{-D}_2$ , Refs. 6 and 8), distinguishing them from other  $\text{M}^+\text{-H}_2$  and  $\text{M}^+\text{-D}_2$  complexes that we have investigated, all of which exhibit a vibrationally induced decrease in  $R_0$ .<sup>9-14</sup>

The IR spectrum of  $\text{Na}^+\text{-D}_2$  provides no direct information on the D-D bond length, which for a rigid complex would be related to the  $A$  rotational constant. For a rigid, T-shaped, planar molecule,  $A$  could be determined from  $B$  and  $C$  via the inertial defect ( $\Delta = 1/C - 1/B - 1/A = 0$ ). However, for a weakly bound complex such as  $\text{Na}^+\text{-D}_2$ , the large-amplitude zero-point bending motion leads to an exaggeration of the  $K_a = 1-1$  asymmetry splitting and a non-zero inertial defect.<sup>39</sup>

The  $\nu_{DD}$  band centre for  $\text{Na}^+\text{-D}_2$  lies at  $2944.0 \text{ cm}^{-1}$ , representing a shift of  $\Delta \nu_{DD} = -49.6 \text{ cm}^{-1}$  with respect to the  $Q_1(0)$  transition of the free  $\text{D}_2$  molecule ( $2993.6 \text{ cm}^{-1}$ ; Ref. 35). As expected, the fractional band shifts for  $\text{Na}^+\text{-D}_2$  and  $\text{Na}^+\text{-H}_2$  are very similar ( $\Delta \nu_{DD}/\nu_{DD} = 0.0166$  and  $\Delta \nu_{HH}/\nu_{HH} = 0.0160$ ). The calculations predict a slightly

smaller shift ( $\Delta\nu_{DD} = -47.2 \text{ cm}^{-1}$ ), with the underestimation possibly being connected with the fact that the predicted intermolecular bond is marginally longer; short intermolecular bonds are normally associated with large  $\Delta\nu_{DD}$  band shifts.

The intermolecular stretch and bend vibrational modes are predicted to have frequencies of 196 and 336  $\text{cm}^{-1}$ , respectively, with the frequency of both modes increasing slightly when the D-D stretch mode is excited (Table I). The fundamental and first overtone frequencies for the intermolecular stretch in the  $n_{DD} = 0$  and  $n_{DD} = 1$  states were fitted to an anharmonic function [ $\nu_s = \omega_s(v + 1/2) - \omega_s x_s(v + 1/2)^2$ ] to estimate the harmonic stretch frequency. Doing this, one arrives at  $\omega_s'' = 223.0 \text{ cm}^{-1}$  and  $\omega_s x_s'' = 13.5 \text{ cm}^{-1}$  for the ground state and  $\omega_s' = 225.5 \text{ cm}^{-1}$  and  $\omega_s x_s' = 13.2 \text{ cm}^{-1}$  for the excited state. For comparison, an estimate for the harmonic frequency ( $\omega_s$ ) of the intermolecular stretch vibrational mode can be obtained from  $\bar{B}$  and  $\Delta_J$ , treating Na<sup>+</sup>-D<sub>2</sub> as a pseudo-diatomic molecule. This analysis leads to  $\omega_s$  values of 212 and 216  $\text{cm}^{-1}$  in the  $n_{DD} = 0$  and  $n_{DD} = 1$  states, respectively, very close to the theoretical values.

In summary, there is a satisfactory agreement between the parameters determined from the rovibrational calculations and the experimental spectrum, although it does seem that the PES slightly underestimates the intermolecular bond length and possibly the strength of the Na<sup>+</sup>+H<sub>2</sub> interaction.

#### D. Comparisons with other theoretical results

The measured and predicted properties of Na<sup>+</sup>-H<sub>2</sub> and Na<sup>+</sup>-D<sub>2</sub> can also be compared with the theoretical results of Page *et al.* who recently calculated an *ab initio* PES for Na<sup>+</sup>+H<sub>2</sub> and conducted rovibrational calculations for the Na<sup>+</sup>-H<sub>2</sub> and Na<sup>+</sup>-D<sub>2</sub> complexes using a variational method based on the truncated Watson Hamiltonian.<sup>24</sup> The *ab initio* points were calculated using all-electron relativistically-corrected CCSD(T) with an ANO-RCC basis set for Na and an aug-cc-pVQZ basis set for H.

At first sight there is little difference between the two theoretical approaches. The equilibrium configuration for the PES of Page *et al.* ( $R_e = 2.392 \text{ \AA}$  and  $r_e = 0.748 \text{ \AA}$ ) is very similar to ours ( $R_e = 2.408 \text{ \AA}$  and  $r_e = 0.746 \text{ \AA}$ ). The calculated dissociation energy of  $D_0 = 860 \text{ cm}^{-1}$  also compares well with the measured value ( $860 \pm 70 \text{ cm}^{-1}$  from Ref. 20) and our theoretical value ( $842 \text{ cm}^{-1}$  from Ref. 6).

Despite these agreements for the dissociation energy and equilibrium geometry, the calculated rovibrational energy levels derived by Page *et al.* deviate considerably from the levels deduced experimentally and from our theoretical study. For example, fitting the calculated transition energies of Page *et al.* for Na<sup>+</sup>-H<sub>2</sub> gives rotational constants  $\bar{B}'' = 1.49 \text{ cm}^{-1}$  and  $\bar{B}' = 1.54 \text{ cm}^{-1}$ , which are somewhat larger than the experimental constants (1.446 and 1.442  $\text{cm}^{-1}$ , respectively). The corresponding vibrationally averaged intermolecular separations are  $R_0'' = 2.455 \text{ \AA}$  and  $R_0' = 2.415 \text{ \AA}$ , underestimating the experimental values by 0.038 and 0.080  $\text{\AA}$ , respectively. Furthermore, the predicted 0.04  $\text{\AA}$  contraction of the intermolecular bond following excitation of the H-H stretch

mode contrasts with our experimental and theoretical results which both give a 0.002  $\text{\AA}$  bond expansion.

For Na<sup>+</sup>-D<sub>2</sub>, the frequencies of the  $\nu_s$  and  $\nu_b$  modes are reported by Page *et al.* as 229 and 405  $\text{cm}^{-1}$ , respectively, which both exceed our corresponding theoretical values (196 and 336  $\text{cm}^{-1}$ ). The value for  $\nu_s$ , in particular, appears to be somewhat high considering the experimental estimate for  $\omega_s$  (212  $\text{cm}^{-1}$ ).

Although Page *et al.* did not report the  $\nu_{DD}$  frequency for Na<sup>+</sup>-D<sub>2</sub>, the  $\nu_{HH}$  frequency for Na<sup>+</sup>-H<sub>2</sub> was given as 4114.2  $\text{cm}^{-1}$ , overestimating the experimental frequency by 19.6  $\text{cm}^{-1}$  and underestimating the band shift by the same amount. It is unusual that the intermolecular bond length and the vibrational band shift are both underestimated; normally, strong intermolecular bonds are associated with large red shifts for the H-H stretch mode.

In conclusion, it appears that the approach outlined in this paper and Ref. 6 provides a somewhat better representation for the properties of the Na<sup>+</sup>-H<sub>2</sub> and Na<sup>+</sup>-D<sub>2</sub> complexes than that of Page *et al.*,<sup>24</sup> although both PESs give similar equilibrium geometries and binding energies.

#### IV. SUMMARY AND CONCLUSIONS

The Na<sup>+</sup>-D<sub>2</sub> complex has been investigated by high-resolution IR photodissociation spectroscopy and through variational rovibrational calculations based on a previously developed *ab initio* PES. The main outcomes are summarised below.

1. The  $\nu_{DD}$  band centre for Na<sup>+</sup>-D<sub>2</sub> occurs at 2944.04  $\text{cm}^{-1}$  corresponding to a shift of  $\Delta\nu_{DD} = -49.6 \text{ cm}^{-1}$  with respect to the fundamental transition of the free D<sub>2</sub> molecule.
2. The rotational constants imply a vibrationally averaged intermolecular separation of  $R_0 = 2.461 \text{ \AA}$ , with a 0.002  $\text{\AA}$  bond lengthening accompanying excitation of the D-D stretch vibrational mode.
3. Experimental spectroscopic parameters and those derived from the theoretical rovibrational calculations based on an existing PES are in good agreement; the magnitude of  $\Delta\nu_{DD}$  is underestimated by 2.4  $\text{cm}^{-1}$  and  $R_0$  is overestimated by 0.02  $\text{\AA}$ .
4. A good correspondence between the simulated and recorded Na<sup>+</sup>-D<sub>2</sub> IR spectra, once the simulated spectrum has been shifted by 2.4  $\text{cm}^{-1}$ , confirms the assignments for the experimental transitions and underlines the utility of the PES for describing the physical properties of the complex.

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