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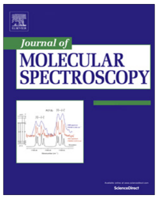

Rotational state analysis of AlH^+ by two-photon dissociation

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ABSTRACT

We perform *ab initio* calculations relevant to predict the cross-section of an experimentally accessible $(1+1')$ resonance-enhanced multiphoton dissociation (REMPD) pathway in AlH^+. Experimenting on AlH^+ ions held in a radiofrequency trap, we confirm dissociation via this channel with analysis performed using time-of-flight mass spectrometry, demonstrate the use of REMPD for rotational state analysis, and measure the rotational distribution of trapped AlH^+ to be consistent with the expected thermal distribution. AlH^+ is a particularly interesting species because its electronic level structure is compatible with proposals to perform rotational optical pumping, direct Doppler cooling, and single-molecule fluorescence detection. Potential applications of trapped AlH^+ include searches for time-varying constants, quantum information processing, and ultracold chemistry studies.

1. Introduction

Because of their rich internal structure, trapped molecules offer great potential for precision spectroscopy experiments, including searches for time-variation of fundamental constants [1–3], parity violation studies [4,5], and searches for fundamental electric dipole moments [6–8]. Trapped polar molecules have also been proposed for use in quantum information processing [9–11]. Trapped neutral and charged molecules are also excellent candidates for ultracold chemistry studies and coherent control applications.

Generally, rovibrational state control and readout present a challenge for all of these applications. In light of these challenges, it is interesting to consider a special class of "alkali-like" molecular ions. We have proposed that these species can quickly be cooled to their rovibrational ground state with a single spectrally filtered pulsed laser [12], detected by fluorescence at the single-molecule level, and in some cases directly Doppler cooled [13,14].

Here we study one such molecular ion, AlH^+. Owing largely to astrophysical interest, some spectroscopic properties of the AlH^+ molecular ion are already well understood with good agreement between experiment [15–18] and theory [13,19]. Here, we extend our previous calculations [13] to include states relevant for an experimentally convenient pathway for REMPD rotational state readout, and we predict an experimentally accessible dissociation cross-section.

We also perform experiments on Coulomb crystals of AlH^+ held in a linear radiofrequency (RF) trap and sympathetically cooled via laser cooling of co-trapped Ba^+. Using time-of-flight mass spectrometry (TOFMS), we demonstrate the first REMPD of AlH^+ and use REMPD/TOFMS for rotational state analysis of our trapped sample. Rotational state analysis by REMPD has previously been used for MgH^+ [20] and HD^+ [21], where the molecular fraction dissociated was analyzed by observing deformation of a fluorescing Coulomb crystal of co-trapped atomic ions. Also in the current issue of this journal [22], Ni et al. analyze the rotational distribution of non-crystallized trapped HfF^+ using REMPD/TOFMS.

2. Computational details

Potential energy curves and transition dipole moments for AlH^+ were computed with the multireference singles and doubles configuration interaction (MRSDCI) method. All computations were performed with the `MOLPRO` quantum chemistry package [23]. The molecular orbitals used in the MRSDCI computations were obtained from the state-averaged complete active space self-consistent field (SA-CASSCF) method [24,25]. The SA-CASSCF orbitals were optimized with an active space consisting of three electrons in the $4\sigma 2\pi_x 2\pi_y 5\sigma 6\sigma$ orbitals while averaging over the lowest four electronic states. In the MRSDCI wavefunction, the 1s Al orbital was constrained to always be doubly occupied. The aug-cc-pCVQZ basis set was used for all computations [26,27].

In a previous study [13], we found the results obtained from MRSDCI to be in excellent agreement with approximate

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coupled-cluster singles, doubles and triples (CC3) [28,29] as well as the experimentally determined bond length and vibrational frequency of AlH$^+$ [17]. In the present work, the $C^2\Sigma^+$ and $D^2\Pi$ states could not be studied with CC3, since current implementations are not fully spin-adapted (*i.e.* CC3 wavefunctions are not proper spin eigenfunctions). This led to spurious mixing of the two higher-lying doublet states with quartet states. For this reason, the present work relies on MRSDCI computations exclusively. A drawback of this approach is that the energy spacings at dissociation do not match experimental results. In order to fix the energy spacings, constant shifts were applied so that, at dissociation, the gap between the $X^2\Sigma^+$ and $A^2\Pi/B^2\Sigma^+$ is 266.9157 nm and $X^2\Sigma^+$ and $C^2\Sigma^+/D^2\Pi$ states is 167.0787 nm [30]. We expect that the nonparallelity errors of the MRSDCI method are small, and the application of a small constant shift is reasonable. Calculated potential energy surfaces and transition dipole moment functions are shown in Figs. 1 and 2.

Photodissociation cross-sections were calculated using the program BCONT 2.2 [31], using as input our calculated surfaces and transition moments. In Fig. 3, the experimentally relevant photodissociation cross-sections from the $A^2\Pi, v = 0$ state are plotted as a function of photon wavelength. Experimentally, as shown in Fig. 1, 266 nm light is used for the dissociating photon. At this wavelength the cross-section is dominated by the $D^2\Pi \leftarrow A^2\Pi, v = 0$ transition and is calculated to be $\sigma_0 = 6 \times 10^{-18}$ cm^2.

It could also be convenient experimentally to use 532 nm light to dissociate from the $A^2\Pi$ state to the $B^2\Sigma^+$ continuum. However, even though this cross-section is near its maximum at this wavelength, the calculated cross-section of 3×10^{-22} cm^2 is inconveniently small. Another experimental consideration is whether the 266 nm light might drive bound–bound transitions from $X^2\Sigma^+$ to $A^2\Pi$ or $B^2\Sigma^+$. Although such processes are energetically allowed, the vibrational overlap is expected to be small, and we see no experimental evidence for such transitions.

3. Experimental details

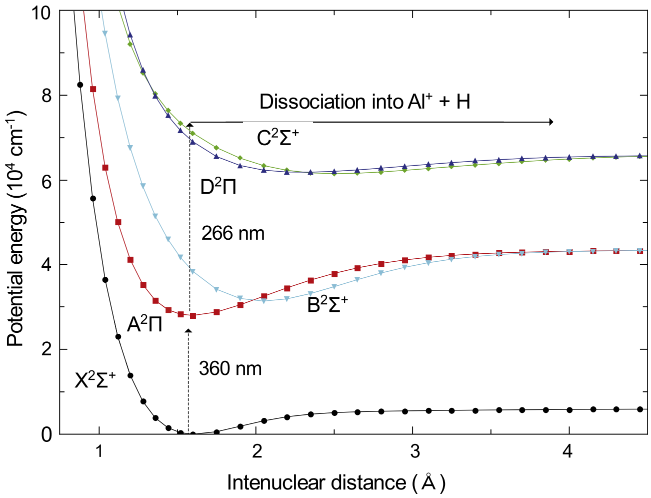

Fig. 1. Calculated potential energy surfaces of the lowest several electronic states of AlH$^+$. The resonant-enhanced two-photon dissociation pathway used in the experiment is also shown.

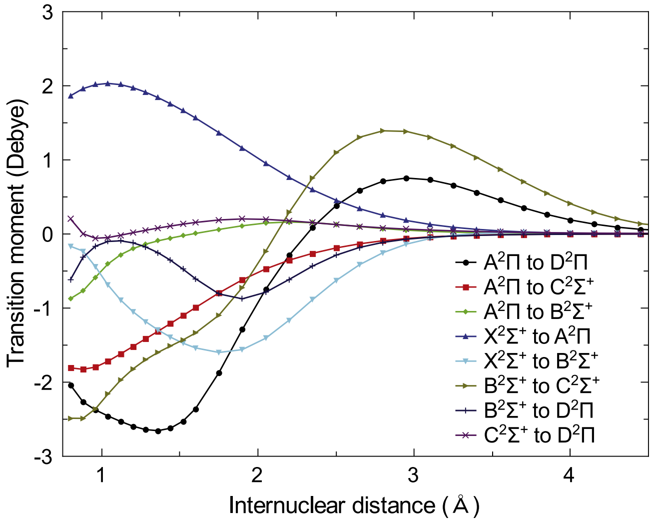

Fig. 2. Calculated transition dipole moment functions of selected electronic transitions in AlH$^+$.

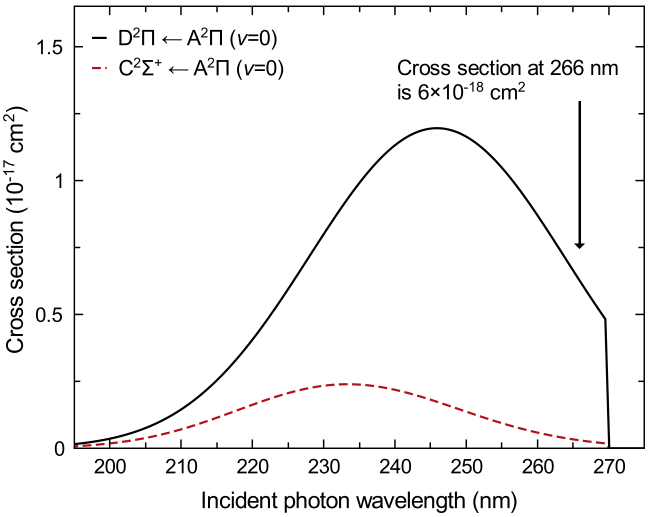

Fig. 3. Calculated photodissociation cross-sections from the AlH$^+$ $A^2\Pi, v = 0$ state. The sharp cutoff near 270 nm corresponds to a photon energy insufficient to excite to the continuum.

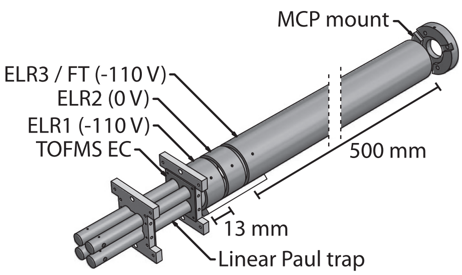

Fig. 4. Schematic of the apparatus. TOFMS EC labels the trap endcap that is switched at the start of TOFMS. Adjacent to the TOFMS EC is the einzel lens, consisting of two rings (ELR1 and ELR2) with the third doubling as the flight tube (ELR3/FT).

The experimental work is performed in a linear RF trap (Fig. 4); r_0 = 3 mm, z_0 = 15 mm, $\Omega_{RF}/2\pi = 2.35$ MHz, and $V_{pp} = 300$ V with the RF applied to two opposing rod electrodes and the other two held at ground. The trap endcaps are plates with holes in the center, similar to a trap design shown in [32,33], held at 850 V. Trapped ion species were identified and counted using TOFMS. A 3-element einzel lens utilizing a 500 mm flight tube as the last electrode spatially and temporally focuses ejected trapped ions onto a Hamamatsu F4655 multi-channel plate (MCP) operating at −3 kV with a −0.5 kV anode bias. The analog-mode MCP signal is terminated with 50 Ω at a digital oscilloscope with a sample rate

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