Visible line intensities of the triatomic hydrogen ion from experiment and theory

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The visible spectrum of H³⁺ is studied using high-sensitivity action spectroscopy in a cryogenic radiofrequency multipole trap. Advances are made to measure the weak ro-vibrational transitions from the lowest rotational states of H³⁺ up to high excitation energies providing visible line intensities and, after normalisation to an infrared calibration line, the corresponding Einstein B coefficients. Ab initio predictions for the Einstein B coefficients are obtained from a highly precise dipole moment surface of H³⁺ and found to be in excellent agreement, even in the region where states have been classified as chaotic.

The triatomic molecular ion H³⁺ prevails in cold hydrogen plasmas and has therefore been the subject of study for many decades in astronomy and for even longer in molecular physics. In space, H³⁺ is the cornerstone of the chemical network leading to larger molecules and it is now being widely monitored in both the dense and diffuse interstellar medium. In planetary atmospheres, it acts as a tracer of H₂, as an important coolant, and as a tracer of ionospheric activity. H³⁺ is thought to be the key of the thermal stability of hot Jupiter exoplanets. For modeling the role of H³⁺ in these environments and for interpreting related observations, precise and reliable data on the H³⁺ spectrum are required in an increasingly wide wavelength range. Such work relies heavily on comprehensive, theoretical spectral line calculations including transition energies and also line intensities. While theoretical line intensities in comparison to laboratory observations served as a guide in the assignment of complex discharge spectra in the infrared (IR) spectral region, experimental information on the intensities for independently identified lines is scarce.

By combining laser spectroscopy in a cryogenic trap with high-precision calculations of the ground-state potential energy surface of the ion, we recently identified several lines of H³⁺ in the near-visible and visible (VIS) spectral range and showed that our theoretical transition energies agreed with the measured line positions on the sub-tenth cm⁻¹ level. Here we prepare H³⁺ ions in their lowest ortho and para rotational levels only and measure the intensities of eighteen weak near-VIS and VIS spectral lines, which are directly referred to the intensity of an IR calibration transition whose value can be safely predicted. Theoretically, we developed a dipole moment surface (DMS) for H³⁺ that also covers the VIS part of its vibrational spectrum, which we used to model the line intensity measurements.

Highly excited molecular motion forms a challenge in the ab initio treatment of molecules and molecular dynamics. The Born–Oppenheimer approximation breaks down and the molecular motions couple strongly to each other, leading to ill-defined approximate quantum numbers and vibrational angular momenta. This behavior is associated with the onset of chaos in the analogous classical problem. Non-adiabatic effects are often only included as ad hoc correction factors on the calculations. Despite these difficulties, the recent advanced theoretical treatment gave spectroscopic accuracy in the predictions of H³⁺ ro-vibrational energy levels up to 2 eV internal excitation.

The investigation of high levels of excitation also constitutes a great experimental challenge as the spectra often become complex and unassignable. Carrington et al. triggered the extensive theoretical investigation of H³⁺ with their measured, rich spectrum of states near the dissociation limit, which remains unassigned. The H³⁺ internal motion already becomes chaotic at about one-third of the dissociation energy where the nuclei sample linear configurations. The first measurements just above this barrier to linearity were performed by Gottfried and coworkers using advanced absorption spectroscopy. This method reaches its limit at 13 700 cm⁻¹, where the absorption Einstein coefficient B of the transitions reaches a few 10⁻ⁱ⁸ cm³ J⁻¹ s⁻². No Einstein coefficients could be derived due to unknown initial population of the H³⁺ levels. The identification of the many lines was also hindered by the large number of initial

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duced ArH. There is a background from non-laser-produced ArH ions excited above the endothermic reaction products per storage cycle is the spectroscopic signal and is limited by ro-vibrational excitation of H\(^+_3\) ions. The near-VIS to VIS transitions were measured by chemical probing with Ar (1 × 10\(^{12}\) cm\(^{-3}\)). The reaction H\(^+_3\) + Ar → ArH\(^+\) + H\(_2\) is endothermic but activated by ro-vibrational excitation of H\(^+_3\) above 4500 cm\(^{-1}\). The count of extracted ArH\(^+\) reaction products per storage cycle is the spectroscopic signal and is limited by H\(^+_3\) ions excited above the endothermicity barrier. There is a background from non-laser-induced ArH\(^+\), originating from the initially hot H\(^+_3\) ions. The decay rate of this background ArH\(^+\) is determined by the back reaction of ArH\(^+\) with H\(_2\) (2 × 10\(^{10}\) cm\(^{-3}\)), while the forward reaction is stopped within a few ms by the buffer-gas cooling of H\(^+_3\). A pre-cooling time of 200 ms was chosen to achieve a sufficiently low ArH\(^+\) background level of less than 0.1 counts on average per storage cycle. Afterwards, the H\(^+_3\) ions were irradiated for 100 ms yielding, when on resonance, internal H\(^+_3\) ion energies much higher than the required reaction barrier. The reaction time of ~0.5 ms for ArH\(^+\) formation, estimated from the Langevin cross section, is shorter than the effective radiative decay time of at least several ms\(^{[2]}\). Collisional de-excitation of vibrations can be neglected, even for He which has the highest partial pressure. After irradiation, the ion cloud was released into a mass spectrometer (MS) that could be set to either ArH\(^+\) and H\(^+_3\) detection from one 300-ms storage cycle to the next. The ions were counted on a Daly stamp with a scintillator and a photomultiplier detection system\(^{[19,21]}\) that is sensitive enough to single-ion count the low ArH\(^+\) and the high H\(^+_3\) (normalization) ion numbers.

To determine the intensity of the spectral lines, we performed scans of the laser wavelength in small steps around the central wavelength pre-located in wider search scans\(^{[19]}\). The strength of the ArH\(^+\) counting signal exceeding the background level was determined from a Gaussian fit to the scanned line. The observed lines were Doppler-broadened corresponding to a kinetic temperature near 85 K. The experimental challenge for reliable intensity measurements is not only to increase the spectroscopic sensitivity to a level where we can measure these very weak, line\(^{[19]}\) but also to increase the dynamical counting range for both the ArH\(^+\) signal and the H\(^+_3\) normalization signal, whilst retaining linearity and constant (within the Poisson noise) experimental parameters. To increase the dynamic range to 10\(^4\), we applied a voltage ramp on the trap exit electrode to gradually release the ions, leading to a stretched ion pulse train of 0.5–1 ms.
ms and yielding a factor of 25 improvement in dynamic range. Group recordings of 10 storage cycles each were alternately performed with the MS set on $H^+_3$ (normalization) or on ArH$^+$ with (signal) and without (background) laser. Two spectroscopy lasers were applied along the trap axis: a single-mode Ti:sapphire or a dye laser for measuring a near-VIS or VIS line, and a single-mode IR laser diode for measuring an IR reference line, $03^1 \leftarrow 00^0 R(1, 1)$ at 7144.235 cm$^{-1}$. Both lasers filled identical apertures, ensuring their spatial overlap inside the trapping region. A measurement on a near-VIS or VIS line typically lasted 15 h, and immediately before and after this, 2-h measurements were performed on the IR reference line. In a campaign extending over several months, intensity measurements relative to the IR reference line were performed on 18 near-VIS or VIS lines of $H^+_3$. These intensity measurements were performed separately from the runs aiming at the line frequency determination described earlier.

The intensity ratios, linking the near-VIS to VIS lines to a single IR calibration line far below the barrier to linearity, are listed together with the measured transition wave numbers $\tilde{\nu}$ in Table I. In the line assignments, $J'''$ and $J'$ refer to the lower and upper level, respectively. Also listed are values of the absolute rate coefficients obtained for the Einstein coefficient of the IR calibration line from the theoretical method of the present work; previous theoretical calculations yielded essentially the same result ($B = 1.55 \times 10^{21}$ cm$^3$ J$^{-1}$ s$^{-2}$).

In our calculations on the two-electron system $H^+_3$, the spatial component of the electronic wave function $\Phi_M(r)$, is expanded in terms of a set of $M$ explicitly correlated Gaussians (ECGs), $\{g_k\}_{k=1,\ldots,M}$, as:

$$\Phi_M(r) = \sum_{k=1}^{M} C_k \mathcal{P} g_k(r), \quad (1)$$

where $\mathcal{P}$ is the permutational-symmetry projection operator which symmetrizes each ECG with respect to the permutation of the electron labels. The ECGs are the following 6-dimensional functions:

$$g_k(r) = \exp\left[-(r - s_k)\mathbf{A}_k(r - s_k)\right], \quad (2)$$

where $r$ and $s_k$ are 6-dimensional vectors of the electronic Cartesian coordinates and of the coordinates of the Gaussian shifts, respectively, and the prime denotes vector transposition. $\mathbf{A}_k$ is a $6 \times 6$ symmetric matrix of the Gaussian exponential parameters defined as:

$$\mathbf{A}_k = \mathbf{A}_k \otimes \mathbf{I}_3, \quad (3)$$

with $\mathbf{I}_3$ being the $3 \times 3$ identity matrix and $\otimes$ denoting the Kronecker product and $\mathbf{A}_k$ is a $2 \times 2$ symmetric matrix. More details on how the spatial wave function is constrained to satisfy the Pauli exclusion principle, and to be square integrable are given elsewhere.

Here calculations of the dipole moment surface (DMS) are presented. The dipole moment is determined as an expectation value of the dipole operator with the variationally optimized electronic wave function containing 900 ECGs for each of roughly 42,000 geometry points.

The dipole moment vector associated with a certain $H^+_3$ molecular configuration defined by the Cartesian position coordinates $(R_1, R_2, R_3)$ is:

$$\mu = \sum_{k,l} C_k C_l \langle g_k(r) | \left( - \sum_{i=1}^2 r_i \right) \mathcal{P} g_l(r) \rangle + \sum_{\alpha=1}^3 R_\alpha \quad (4)$$

where $r_i$ are the coordinates of electron $i$, $R_\alpha$ are the coordinates of nucleus $\alpha$ both expressed in a Cartesian coordinate system whose origin is the center of the positive charge of the $H^+_3$ system. In eq. (4) we use the fact that the electronic dipole-moment operator, $-\sum_{i=1}^2 r_i$, is symmetric with respect to the permutation of the electrons and $\mathcal{P} = \mathcal{P} \mathcal{P}$. The spatial wave function is assumed to be normalized. The dipole moment matrix element involving two ECGs, $g_k(r)$ and $g_l(r)$ is given as

$$\langle g_k(r) | r_i | g_l(r) \rangle = S_{kl} \left\{ \left[ \mathbf{A}_k + \mathbf{A}_l \right]^{-1} \mathbf{A}_k s_k + \mathbf{A}_l s_l \right\}, \quad (5)$$

where $\{v\}_i$ denotes the $i$-th component of vector $v$, $S_{kl} = \langle g_k | g_l \rangle$ is the overlap integral.

Since the fits to produce a DMS were not entirely stable we only used dipole components from 4257 points lying up to 30,000 cm$^{-1}$ above the minimum generated by the ECG calculations in the form $\mu_x$ and $\mu_y$. Previous $H^+_3$ DMSs were based on a grid of only 69 points; following these studies, the dipole moments were transferred to effective charges $d_x$ and $d_y$ which were expanded into...
a power series in terms of symmetry coordinates. Since our DMS showed sensitivity to the fitting procedure, we opted for the simplest form and used only 7 constants and the function of Ref. 27 which reproduce the computed dipoles for points lying below 18 000 cm⁻¹ with a standard deviation of 0.001 a.u. Appropriate functional forms for fits of a global DMS will be the subject of further work. Transition intensities were computed using nuclear motion program DVR3D,23 the non-adiabatic model of Polyansky and Tennyson24 with other parameters chosen as in our previous studies of H₂⁺ VIS transition frequencies.25 Since the major uncertainty in the calculations is given by the fit of the DMS, we used the extremes of plausible fits to estimate uncertainties in our calculated intensities; these uncertainties (see Table 1) are systematic rather than statistical errors and roughly represent a 1-σ confidence level.

The high agreement between experiment and the present calculations is shown in Table I and Fig. I and covers the entire range of B coefficients whose magnitude varies by a factor of 300. For comparison, the figure also shows the results of Neale, Miller and Tennyson26 (NMT), the only previous intensity calculation extending into the VIS. The NMT results also agree well with the observations which is somewhat surprising given that the study was not designed to be accurate above the barrier to linearity and that NMT’s frequencies are significantly less accurate than the ECG ones.27 H₂⁺ spectra provide a unique probe of the Universe but their interpretation relies heavily on the reliability of ab initio intensity calculations. The present studies suggest that, with care, the intensities can be computed over a wide wavelength range. Following the confirmation of the accuracy of our ab initio H₂⁺ model for both transition frequencies28 and, with the present study, intensities, work on a new, experimentally tested, comprehensive H₂⁺ line list for astronomical and other applications is now in progress. This will make highly excited levels of H₂⁺ broadly available as a tool of precision laser spectroscopy, enabling ultra-sensitive spectroscopic detection of H₂⁺ by multistep photodissociation.29 It will also pave the way to the reliable modeling of broadband spectral emission from H₂⁺ in astrophysical environments, as considered regarding the formation20 and evolution21 of metal-poor stars, and the stability of the atmospheres of hot exoplanets.22 Furthermore, the use of accurate intensities for interpreting the Carrington-Kennedy near-dissociation H₂⁺ will allow the division of the spectra in hierarchies, greatly simplifying its analysis.23

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