Measurement of the Pure Rotational Quasibound Spectrum of HeH^+ in a Laboratory Plasma by Direct Laser Absorption

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The pure rotational quasibound spectrum of HeH^+ $X^1\Sigma^+$ has been observed in the mid infrared region using diode laser velocity modulation absorption spectroscopy. Four quasibound to quasibound (Q-Q) and three bound to quasibound (B-Q) transitions in the $v = 0$, 1, and 2 states of the ion were detected in a low pressure ac glow discharge. The highest quasibound level involved in the spectrum ($v = 0$, $J = 26$) is 2000 cm^{-1} above the dissociation limit. The measured transition frequencies are in very good agreement with *ab initio* calculations. Two of the Q-Q transitions have wider linewidths due to lifetime broadening. [S0031-9007(97)04223-3]

There has been considerable theoretical and experimental interest in the rotationally quasibound levels of diatomic molecules. Their existence arises from the centrifugal nature of rotation which contributes a term $hJ(J + 1)/8\pi^2 c\mu r^2$ to the effective potential of the rotating molecule leading to a maximum in the effective potential energy curve [1]. Energy levels lying above the asymptotic dissociation limit but below the barrier maximum may be stable and observable by high resolution spectroscopy. The energies and widths of quasibound levels are extremely sensitive to details of the interaction potential, especially to the attractive long range part of the potential [2]. The HeH^+ ion is one of the most useful model systems for both experimental and theoretical studies of these levels. It is the simplest heteronuclear ion, with only two electrons, and hence amenable to highly accurate *ab initio* calculations of its quasibound states. The calculated energies and lifetimes of the quasibound levels of HeH^+ have been reported by several groups [3–6]. The lifetimes span many orders of magnitude, e.g., for $v = 0$ from $\sim 10^7$ s in $J = 24$ to $\sim 10^{-13}$ s in $J = 27$. The quasibound levels of HeH^+ are important not only in molecular quantum mechanics but also in astrophysics. The ion has been postulated to be present in some stellar environments [3,7,8]. Dabrowski and Herzberg [3] investigated the possibility that the infrared emission from the bright nebula NGC 7027 might arise from radiative recombination transitions from the quasibound levels of HeH^+. Experimental measurement of spectra involving quasibound levels of HeH^+ is therefore important in both astrophysics and quantum mechanics.

A number of low resolution experimental techniques, e.g., translational spectroscopy [9–11] and low energy ion scattering [12], have been used to study the quasibound levels of diatomic ions. High resolution laser spectroscopy of quasibound levels using the ion beam predissociation technique has been reported by a number of workers [13–15]. Transitions involving quasibound levels are detected by monitoring predissociation products

of ions in quasibound states mass spectrometrically. Carrington and co-workers used this method to investigate the vibration rotation quasibound spectrum of HeH^+ [6,15]. In $^4HeH^+$ [15] two vibration rotation transitions between bound and quasibound levels, $(v, J) = (6, 13)-(5, 12)$ and $(7, 11)-(5, 12)$, were observed with linewidths of 0.13 and 5.17 cm^{-1}, respectively. Later Carrington *et al.* extended their measurements to the bound to quasibound transitions of other HeH^+ isotopes [6].

The quasibound levels which can be detected in this type of predissociation ion beam experiment are determined by the lifetimes of the levels. Too short a lifetime ($<10^{-13}$ s) produces a line which is too wide to detect while a level with too long a lifetime ($>10^{-6}$ s) gives too few product ions to monitor [6,14]. Many quasibound levels of HeH^+ are predicted to have very long lifetimes which are inaccessible by ion beam spectroscopy but suitable to observe by laser absorption spectroscopy with continuously tunable lasers. Although direct absorption spectroscopy is usually perceived to involve transitions in the lower part of the potential energy curve, due to its relatively low sensitivity, we have been able to observe a number of bound to quasibound (B-Q) and, more importantly, some quasibound to quasibound (Q-Q) pure rotational transitions of HeH^+ in an air cooled ac glow discharge by direct absorption.

The details of the infrared diode laser velocity modulation spectrometer have been given elsewhere [16,17]. The ion source was a 45 kHz glow discharge in flowing mixtures of helium and hydrogen. The air cooled Pyrex discharge tube was 90 cm long and 10 mm internal diameter with two electrodes in sidearms at either end of the tube. Optimum signals were obtained at a total pressure of approximately 2 Torr with a ratio of H_2 to He of 1:20. The maximum available power was required in order to produce the strongest signals, corresponding to discharge currents of 150 mA rms and peak-to-peak voltages of 4 kV. Ion absorption signals were recorded by phase sensitive detection either at the

TABLE I. Pure rotational bound to quasibound (B-Q) and quasibound to quasibound (Q-Q) transitions of $^4HeH^+$.

| | | | ν_{pred} (cm^{-1}) | | |
| | | | Dabrowski and | | Fournier and |
v''	J''	ν_{obs} (cm^{-1})	Herzberg [3]	Price [5]	Richard [6]
0	23	891.888[a]	892.37		891.86
1	21	781.245[a]	781.67		781.28
2	20	650.613[a]	651.14		650.67
0	24	870.298[b]		870.52	870.28
0	25	837.180[b]		837.38	837.18
1	22	760.232[b]	760.9	760.50	760.36
1	23	724.933[b]	725.5	725.17	724.98

[a] Bound to quasibound transitions.
[b] Quasibound to quasibound transitions.

discharge frequency ($1f$, velocity modulation) or at twice the discharge frequency ($2f$, concentration modulation) [18]. Line positions were calibrated with an estimated accuracy of 0.003 cm^{-1} using OCS, CO_2 [19], and C_2H_2 [20] reference spectra.

Calculations show that eleven quasibound levels exist in the $v = 0, 1$, and 2 vibrational states of $X^1\Sigma^+$ $^4HeH^+$ [3,5,6]. Of these, seven have calculated lifetimes longer than 10^{-11} s giving rise to energy widths of <0.1 cm^{-1}, which should lead to measurable linewidths in our diode laser experiment. Searches for transitions involving quasibound levels were carried out by observing their pure rotational spectra. Many HeH$^+$ pure rotational lines of $^4HeH^+$ in the $v = 0, 1$, and 2 states below the dissociation limit have already been measured [21]. However, the rotational and distortion constants from these measurements, derived from terms up to J^{12} in the rotational energy, are inadequate for predicting lines in the quasibound region. Instead, the experimental searches and the subsequent assignment relied heavily on *ab initio* calculations [3–6]. Three pure rotational bound to quasibound transitions in the $v = 0, 1$, and 2 levels and four quasibound to quasibound transitions in the $v = 0$ and 1 levels were detected. Their assignments and frequencies are given in Table I. The highest energy level involved in the observed spectrum, $v = 0$, $J = 26$, has a rotational excitation energy of about 2 eV and is 2000 cm^{-1} above the dissociation limit ($D_0 = 14865$ cm^{-1} [22]). The observed transitions are indicated in Fig. 1 along with the two previously observed vibration rotation B-Q transitions in $^4HeH^+$ [6,15].

The highest accuracy calculations of the HeH$^+$ potential are those due to Fournier and Richard [6]. Their adiabatic potential was derived by Lagrangian interpolation of $R^2 U^{AD}(R)$ between 0.9 and 9.0 bohr with extension below 0.9 bohr by an exponentially repulsive form and extrapolation to larger R using $U^{AD}(R) = -C_6/R^6 - C_8/R^8$. The measured frequencies of the pure rotational B-Q and Q-Q transitions reported here are in very good agreement with their calculations with discrepancies of less

than 0.13 cm^{-1} (Table I). The discrepancy between the experimental measurements and the best adiabatic calculations may be accounted for by including small corrections due to nonadiabatic, radiative, and relativistic effects in the calculations. Calculations of vibration rotation transition frequencies of HD$^+$ which include these small contributions agreed with experimental measurement to within 0.001 cm^{-1} [23,24]. It will be interesting to test similar calculations for HeH$^+$ using the experimental results reported here.
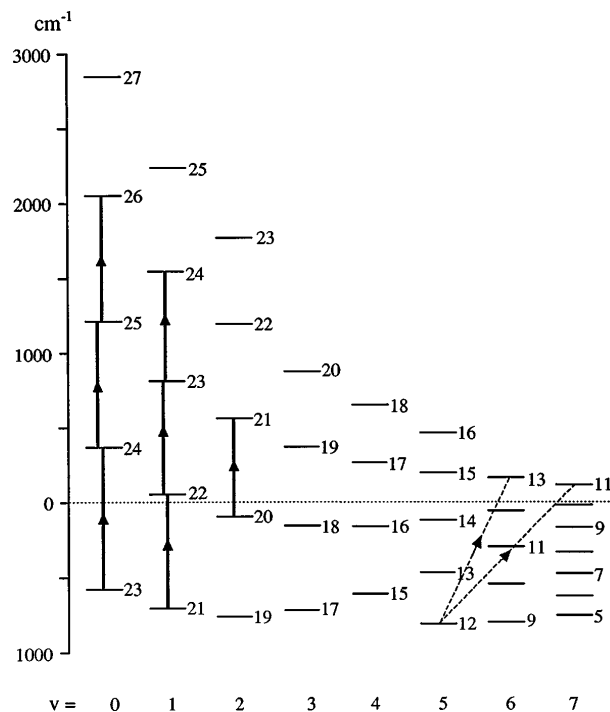

FIG. 1. Energy levels and quasibound spectra of $^4HeH^+$ $X^1\Sigma^+$. All the quasibound levels of the ion are shown. The pure rotational transitions measured in this work are indicated by solid lines and the vibration rotation transitions measured using ion beam predissociation spectroscopy by Carrington *et al.* [15] by dashed lines.
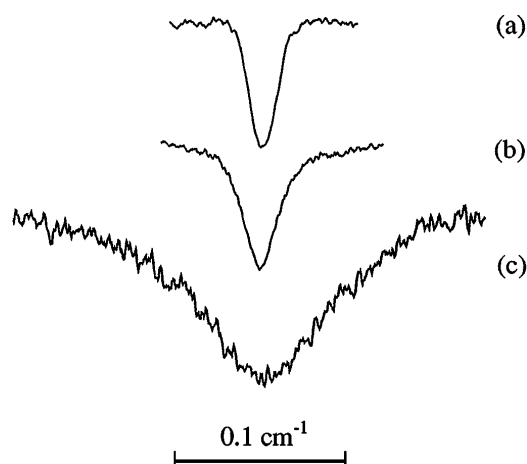
FIG. 2. Three pure rotational absorption lines of HeH$^+$ recorded by $2f$ concentration modulation. (a) $J = 21 \leftarrow 20$, $v = 1$; (b) $J = 26 \leftarrow 25$, $v = 0$; and (c) $J = 24 \leftarrow 23$, $v = 1$.

Two of the quasibound levels involved in the four Q-Q transitions measured in this work, $v = 0$, $J = 26$ and $v = 1$, $J = 24$, should have shorter lifetimes (2.9×10^{-10} and 7.8×10^{-11} s) relative to other quasibound and to bound levels according to theoretical results. The large energy widths of these levels (0.02 and 0.07 cm^{-1}) are expected to give rise to measurably wider experimental linewidths. The lifetime of other detected quasibound levels ($v = 0$, $J = 24$ and 25; $v = 1$, $J = 22$ and 23; and $v = 2$, $J = 21$) are predicted to be long ($>10^{-10}$ s) and hence no measurable lifetime broadening is expected. Figure 2 shows the $2f$ line profiles of a representative bound to bound (B-B) transition, $v = 1$, $J = 21 \leftarrow 20$, Fig. 2(a), and the two Q-Q transitions involving the lifetime broadened quasibound levels mentioned above, Figs. 2(b) and 2(c). The two Q-Q transitions are not only broader at half maximum than the B-B line but have a different profile in the wings. The experimental linewidth (0.0163 cm^{-1}) of the B-B line is significantly larger than its calculated Doppler width (0.008 cm^{-1} if $T = 1000$ K is assumed), which may be due to a contribution from modulation broadening [18]. Nevertheless, the B-B line was found to be fitted accurately with a Gaussian line shape. This was also confirmed by comparing the $1f$ and $2f$ line profiles of the B-B transition. The ratio of the $2f$ linewidth (FWHM)

and the $1f$ peak-to-peak width (1.23) was close to that expected for a pure Gaussian profile (1.18 [25]).

For the two broader Q-Q transitions shown in Figs. 2(b) and 2(c) the line widths contain not only Doppler broadening but also lifetime, i.e., Lorentzian, broadening due to the predissociation of the upper levels. The profiles of these two lines should therefore be more accurately represented by a Voigt line shape. To extract the lifetime broadening component, the Q-Q lines were fitted to a Voigt line shape function [26]. Assuming the Lorentzian linewidth is mainly due to the lifetime broadening, then its contribution can be determined by fixing the Gaussian linewidth component to the linewidth of a B-B transition in the fit. The resulting $\Delta\nu_L$ values 0.0189 ± 0.0004 cm^{-1} for Fig. 2(b), and 0.092 ± 0.001 cm^{-1} for 2(c), are in satisfactorily good agreement with the theoretical predictions (Table II). The predissociation lifetimes of the upper levels, $v = 0$, $J = 26$ and $v = 1$, $J = 24$, are then determined to be $2.81 \pm 0.06 \times 10^{-10}$ s and $0.577 \pm 0.006 \times 10^{-10}$ s, respectively.

This appears to be the first time that quasibound levels of an ion have been detected in a conventional laboratory glow discharge plasma. Glow discharges are usually employed as sources of ions in their ground or lower energy states. In contrast, in this study we have detected very high levels of rotational and vibrational excitation. It is therefore interesting to briefly consider some of the processes which could lead to such high excitation. For example, in discharges containing both hydrogen and helium the quasibound states of HeH$^+$ could be generated from reactions of helium metastables with hydrogen or via inverse predissociation. The reactions between He* (2^3S_1, 2^1S_0) and H$_2$,

$$\text{He}^*(2^3S, 2^1S) + \text{H}_2 \rightarrow \text{HeH}^+ + \text{H} + e, \quad (1)$$
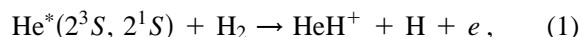
are exoergic enough [27] (4.37 and 3.57 eV, respectively) to exceed the dissociation energy of the ground state of the ion ($\sim$1.85 eV). It is reasonable to expect that some of this energy could be channeled into rotational excitation. HeH$^+$ can be formed in quasibound levels by inverse predissociation following collisions between protons and helium atoms [3]. An ion formed in a quasibound level in this way can either dissociate again or radiate to a lower quasibound or bound level.

TABLE II. Linewidths and predissociation lifetimes of the Q-Q pure rotational transitions of HeH$^+$.

	$\Delta\nu_L$ (cm^{-1})		$\tau (\times 10^{10}$ s)[a]	
	Experiment	Theory	Experiment	Theory
$v = 0$, $J = 26 \leftarrow 25$	0.0189 ± 0.0004	0.018^b, 0.020^c	2.81 ± 0.06	2.79^b, 2.90^c
$v = 1$, $J = 24 \leftarrow 23$	0.092 ± 0.001	0.07^b, 0.07^c	0.577 ± 0.006	0.76^b, 0.78^c

[a] The predissociation lifetime of the upper quasibound level.
[b] Reference [3].
[c] Reference [6].

The radiative recombinationspectrum of HeH^+ ($Q \rightarrow B$) has been considered as a source of the unidentified infrared emission in space [3]. Although the laboratory plasma is very different from astrophysical environments a possible extension of the present study is to search for the recombination spectrum of HeH^+ in a laboratory plasma.

Diode laser absorption spectroscopy and ion beam dissociative spectroscopy are complementary to each other as far as the lifetimes of the quasibound levels which are detected are concerned. The former detects lifetimes longer than 10^{-11} s and the latter levels with lifetimes between 10^{-6} and 10^{-13} s. Recent interest in the dissociative recombination of HeH^+ has focused attention on the $a^3\Sigma^+$ and $b^3\Sigma^+$ excited states of HeH^+ [28] which have lifetimes of $>10^{-8}$ s. While the fundamental band of the $a^3\Sigma^+$ state lies in the far infrared, that of the much more strongly bound b state lies at 400 cm^{-1}, and R branch lines in this band fall within the frequency range of diode lasers. Extended measurements of the quasibound spectrum of other HeH^+ isotopes are being carried out and it is also possible to use the direct absorption technique used here to study the long lifetime quasibound levels of other fundamental diatomic ions like HD^+.

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