PHOTO-ASSISTED FRAGMENTATION SPECTROSCOPY OF TRIATOMIC HYDROGEN

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The $R_0(0)$ line of the $3s\,^2A'_1 \leftarrow 2p\,^2A''_2$ transition of the H_3 radical has been observed in absorption by the new technique of photo-assisted fragmentation spectroscopy. A fast beam of metastable H_3 radicals produced by H_3^+/K electron transfer is interacted with visible light from a dye laser. Optical absorption is detected by observing a decrease in parent peak intensity in the H_3^+ neutralization–reionization mass spectrum, resulting from dissociation of the neutral molecule. Absorption line widths are observed to be instrumentally limited (≈ 0.05 cm^{-1}) as the upper state of the transition is spectroscopically long lived. Application of the technique to various second-row hypervalent hydride radicals is discussed.

1. Introduction

The H_3 radical has been the subject of theoretical and experimental investigations for more than 40 years. Although the ground state is dissociative [1] and will not support the existence of the molecule for lifetimes longer than about 10^{-13} s, the H_3 radical can be produced in excited states having microsecond lifetimes, as observed in several beam experiments [2–9] [#1]. The observed metastability arises in at least two distinct ways: (1) formation of the radical in high-*n*, high-*l* Rydberg states (where *n* and *l* are the electronic principal and angular momentum quantum numbers, respectively) as first demonstrated by Gaillard et al. [7] using field ionization, and (2) formation of the radical in the non-rotating $N=K=0$ level (where N and K are the rotational quantum numbers of a symmetric top molecule) of the $2p\,^2A''_2$ electronic state as first identified by Gellene and Porter [6]. The $2p\,^2A''_2$ state, which can be efficiently produced by the neutralization of H_3^+ with alkali metal atoms, was previously known from the high-resolution emission spectrum of the radical obtained and analyzed by Dabrowski and Herzberg [10]. In that work, it was shown that the $2p\,^2A''_2$ state undergoes an efficient heterogeneous predissociation through a Coriolis coupling into the repulsive $2p\,^2E'$ ground state with a lifetime on the order of 10^{-11} s. However, as the coupling requires rotational motion of the radical, the predissociation is forbidden for the non-rotating $N=K=0$ level, resulting in the formation of a metastable state with a theoretically predicted radiative lifetime of about 87 µs [11].

Additionally, radiative transitions of the radical have been observed in absorption. The ground state has recently been probed by multiphoton ionization transition state spectroscopy [12], and Helm [13], producing the radical by the method of Gellene and Porter [6], has observed several Rydberg series by field ionization following ultraviolet photo-excitation of the $2p\,^2A''_2$, $N=K=0$ metastable to high-*n*, $l=0$, 2 Rydberg levels. In the present study, the $3s\,^2A'_1 \leftarrow 2p\,^2A''_2$ transition of H_3, previously known from emission studies, is observed in absorption by photo-assisted fragmentation (PAF) spectroscopy. This technique is distinguished from other beam photodissociation spectroscopic methods [14,15] in that rotationally resolved spectra are observable because dissociation occurs following fluorescence from the spectroscopically long-lived uper state.

2. Experimental

The details of the apparatus shown in fig. 1, prior to the present modification for optical studies, have

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[#1] The results of ref. [8] have been questioned, see ref. [9].

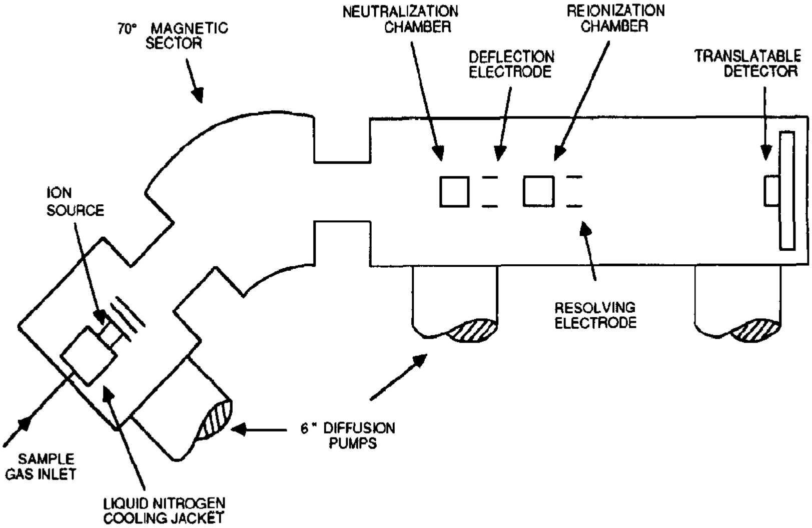

Fig. 1. Schematic of the apparatus configured to obtain non-optical neutralization–reionization mass spectra.

been described elsewhere [16] so that the non-optical component will be only briefly discussed. The H_3^+ ions were produced in a high-pressure, low-temperature ion source by chemical ionization following electron ionization of H_2 according to the reaction sequence

$$H_2 + e^- \to H_2^+ + 2e^- , \tag{1a}$$

$$H_2^+ + H_2 \to H_3^+ + H . \tag{1b}$$

Reaction (1b) produces H_3^+ in a wide range of internal energy states [17] with the $J=1$, $K=0$ rotational level having been shown [6] to be particularly efficient in producing the $2p\,{}^2A_2''$ metastable state upon neutralization with K. Thus, the ion source was operated at an H_2 pressure of 1.3 Torr and cooled with liquid nitrogen to 110 K in order to quench the internal energy of the H_3^+ ions as much as possible in our apparatus. While the degree to which the H_3^+ ions are thermalized in the ion source cannot be directly determined in the present experiment, it should be noted that lowering the ion source temperature effectively enhanced metastable H_3 production and no assumptions about the actual internal energy distribution of the H_3^+ ions are made.

The ions are accelerated to 5 keV, magnetically mass resolved and focused into a neutralization chamber, which is essentially a small oven heated radiatively to contain about 3 mTorr of K metal vapor. In this chamber approximately 40% of the ions are neutralized in the reactions

$$H_3^+ + K \to H_3^* + K^+ , \tag{2a}$$

$$H_3^+ + K \to H_2 + H + K^+ . \tag{2b}$$

Unreacted ions exiting the neutralization chamber are electrostatically deflected out of the beam so that only neutral species continue toward the reionization chamber. It should be noted that since the kinetic energy released in reaction (2b) causes the overwhelming majority of fragments to scatter off-axis, the entrance slit to the reionization chamber provides geometrical discrimination in favor of transmitting metastable molecules as opposed to neutral fragments. In the reionization chamber, which contains approximately 100 mTorr of N_2, about 1% of the transmitted neutrals undergo ionizing collisions with N_2 according to

$$\begin{aligned} &H_3^* + N_2 \to H_3^+ + N_2 + e^- , \\ &H_2 + N_2 \to H_2^+ + N_2 + e^- , \\ &H + N_2 \to H^+ + N_2 + e^- . \end{aligned} \tag{3}$$

The secondary ions exiting the reionization chamber are deflected off-axis and, as the extent of deflection is inversely proportional to the kinetic energy of the ion, a mass spectrum is obtained by translating an electron multiplier detector normal to the beam axis, in the plane of the deflection. Fig. 2 shows a typical neutralization–reionization mass spectrum obtained for H_3^+ following reactions (2) and (3). The increased width of the H_2^+ and H^+ fragment peaks relative to that of the H_3^+ ion is caused by the translational energy released in reaction (2b) resulting in a broadened kinetic energy distribution in the laboratory frame [18].

The integrated intensity of the parent ion signal in the secondary mass spectrum (i.e. H_3^+ in fig. 2) is a direct indication of the extent to which the neutral H_3^* molecules survived the transit time from the neutralization to the reionization chamber. Thus, any process which affects the stability of H_3^* before reionization can be observed with extremely high sensitivity as the secondary H_3^+ ions are detected with near unit efficiency and can be individually counted. In the present experiment, the stability of H_3^* is affected by photo-assisted fragmentation induced by the resonant absorption of a photon provided by a tunable dye laser system (Coherent 699-01 ring dye laser pumped by an Innova 90 Ar^+ ion laser) using a modified version of the apparatus as shown in fig. 3. Increased sensitivity is provided by multiple intersections of the neutral and laser beams accomplished by a pair of slightly displaced right angle prisms. Care must be taken in the alignment of the optical elements to ensure that the intersection of the beams remains normal since a deviation of only 0.1° would Doppler shift an observed transition an amount comparable to the line width of the laser (≈ 0.05 cm^{-1}). Althoug coaxial optical/neutral beam excitation would be expected to have increased sensitivity and decreased alignment requirements, the impossibility of redirecting the flight path of a neutral beam makes such an experimental arrangement unworkable in the present apparatus. A portion of the laser light is split off and directed to a wavemeter (Burleigh model WA20-VIS) which provides frequency calibration to a precision of one part in 10^6. The laser is chopped at a frequency of about 100 Hz, allowing secondary ions to be counted alternately with the laser on (N_{on}) and off (N_{off}) on a time scale fast compared to variation in the overall ion signal. The ion-counting electronics are synchronized with the light chopper by an optical trigger positioned at the exit of the laser radiation from the apparatus. The ion-counting data are used in the relationship

$$A = 1 - N_{on}/N_{off} \qquad (1)$$

to provide a normalized measure of the effect of laser radiation on the mass-resolved secondary ion signal. In the case that the laser has no effect, then ideally $N_{on} = N_{off}$ and $A = 0$. Alternatively, if the absorption of laser radiation causes the neutral molecule to dissociate, then $N_{on} < N_{off}$ and $A > 0$.

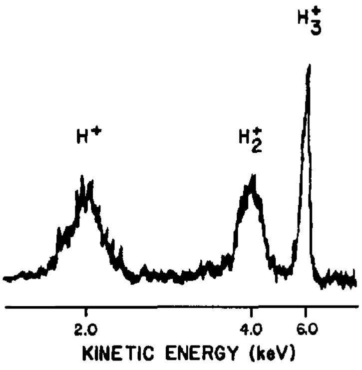

Fig. 2. Neutralization–reionization mass spectra of H_3^+ obtained using K as the neutralization target and N_2 as the reionization target.

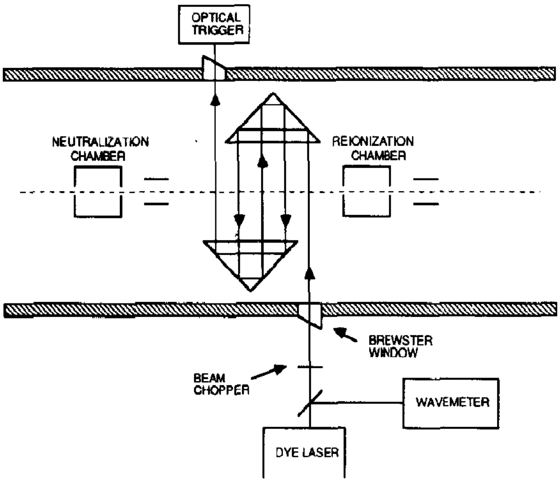

Fig. 3. Partial schematic of the apparatus depicting modifications for obtaining photo-assisted fragmentation (PAF) spectra.

3. Results and discussion

Fig. 4 shows a plot of A versus photon energy for secondary H_3^+ ions produced by reactions (2a) and

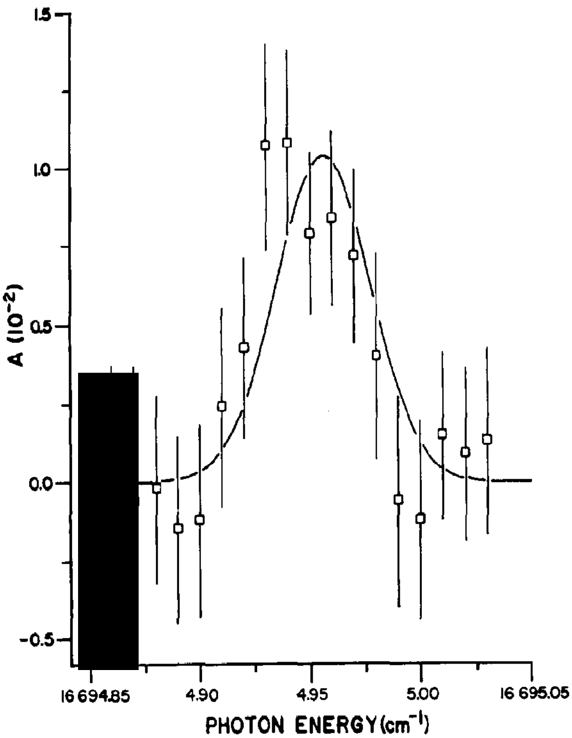

Fig. 4. Photo-assisted fragmentation spectrum of the H_3 radical. Vertical lines represent one standard deviation error bars. The smooth curve represents a least-squares fit of the data to a Gaussian function with a 0.05 cm^{-1} full width at half maximum.

(3). The spectrum was obtained using about 80 mW of cw laser power with an average secondary ion beam flux of 200 counts/s. The low laser power employed was a consequence of the diminished performance of an aged Ar$^+$ ion pump laser. Increased laser power would be expected to result in a corresponding increase in signal for the levels presently observed. The peak occurring at 16694.96 cm^{-1} is the $R_0(0)$ transition of the 3s $^2A'_1 \leftarrow$ 2p $^2A''_2$ band and compares extremely well with the value of 16694.972 ± 0.01 cm^{-1} from the high-resolution emission spectrum of Dabrowski and Herzberg [10]. It should be noted that, due to the absence of Doppler broadening, the present instrumentally limited spectral width of the transition is almost an order of magnitude narrower than that observed in the discharge emission work.

The results are readily understood in terms of a metastable H_3^* radical absorbing a photon, making a transition to the 3s $^2A'_1$, $N'=1$, $K'=0$ state which then fluoresces back to the 2p $^2A''_2$ electronic state branching between the $(N'', K'') = (0, 0)$ and $(2, 0)$ rotational levels in a 1:2 ratio. Although those molecules returning to the $N''=K''=0$ level are again metastable, those in the $N''=2$, $K''=0$ level predissociate with a lifetime of about 2×10^{-11} s. Alternatively, the 3s A'_1 state may radiate directly to the repulsive ground state or cascade through the 3p $^2E'$ to the 2s $^2A'_1$ state [19,20], which is strongly predissociative ($\tau \approx 10^{-12}$ s) with no observed rotational level dependence. Therefore, at least two thirds of the H_3^* radicals which undergo the optical absorption ultimately dissociate following fluorescence, but because the upper state is spectroscopically long lived ($\tau_{\mathrm{rad}} \approx 75$ ns) [11], the theoretical lifetime broadening of the transition, determined in fact by the molecular transit time through the laser radiation field (≈ 20 ns), is less than 2×10^{-4} cm^{-1}.

The possibility of hyperfine structure in the transition should be considered due to the increased optical resolution of the present technique. The hyperfine Hamiltonian (H_{hyp}) can be written [21]:

$$H_{\mathrm{hyp}} = b(\boldsymbol{I}\cdot\boldsymbol{S}) + c(\boldsymbol{I}\cdot\hat{\boldsymbol{n}})(\hat{\boldsymbol{n}}\cdot\boldsymbol{S}) + d(\boldsymbol{S}\cdot\boldsymbol{N}) , \qquad \text{(II)}$$

where $\boldsymbol{I}$ is the total angular momentum of the protons required by the Pauli principle to have a magnitude of 3/2 for the states observed, $\boldsymbol{S}$ is the spin of the Rydberg electron, $\hat{\boldsymbol{n}}$ is a unit normal in the direction of the H_3 symmetry axis, and $\boldsymbol{N}$ is the nuclear rotational angular momentum. Currently, there is no direct information concerning the values of the constants b, c and d in eq. (II) for H_3 in either the 2p $^2A''_2$ or 3s $^2A'_1$ states. An estimate, however, can be made by a comparison to the H_2^+ ion where b, c and d have been determined [22] to be 888.551, 128.432, and 42.399 MHz, respectively. These values would most probably be considerably reduced for the H_3 radical due to the increased spatial extent of the wavefunction of the Rydberg electron [21] as compared to that of the core electron of H_2^+. On this basis, the major contribution to a hyperfine splitting of the observed transition would be a $\Delta F = \Delta(\boldsymbol{I}+\boldsymbol{S}) = \pm 1$ component for which the splitting in H_2^+ of 1.1–1.3 GHz [22] is already less than the laser linewidth of ≈ 1.5 GHz. The analysis of the spectrum in fig. 4 in terms of a single transition is therefore appropriate.

The preceding discussion may imply that the unique conditions necessary to observe sharp, well-resolved PAF spectra would limit further application of the technique. However, all that is required is a lower state having a greatly decreased lifetime with increased internal energy and an upper state which is radiatively stable. These stability characteristics have been identified theoretically [23,24] and experimentally [25–28] for the second-row hypervalent hydrides, NH_4, H_3O, H_2F and NeH, which will be the focus of future PAF spectroscopic investigations in this laboratory.

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