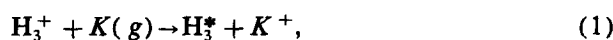


tral lines increased with lower state rotational quantum numbers as $[N(N+1) - K^2]$ and concluded that the $2p, ^2A''_2$ state was undergoing heterogeneous rotational predissociation into the ground $^2E'$ state through Coriolis interaction. From their measurements the lifetime for the first excited rotational level with $N = K = 1$ is estimated to be about 3×10^{-11} s which would be too short for observation in slow molecular beams. However this predissociation process is strictly forbidden quantum mechanically for the non-rotating $N = K = 0$ level.

Further evidence for the identity of the metastable state of H_3 is provided in the papers of Porter and co-workers³⁻⁵ who generated neutral beams of H_3 by a near resonant electron transfer process



involving a fast (6 keV) beam of H_3^+ ions. In their experiments H_3^+ ions produced by the exothermic ion molecule reaction



will carry excess internal energy unless they are quenched by collisional relaxation before exciting the ion source. These investigators found that the relative abundances of metastable/dissociative states of H_3 in the beam increased as the ion source temperature decreased and/or as the source pressure of H_2 increased. These effects were quantitatively interpreted as indicating that metastable H_3 was produced in reaction (1) only from H_3^+ ions with low rotational quantum numbers.

Additional information is available from a comparative study⁴ of the relative abundances of H_3 and D_3 metastables observed when reaction (1) was investigated for both isotopic species under similar experimental conditions. For example, the H_3^*/D_3^* ratio was found to be approximately 17 when the ion source temperature was 135 K and the beam flight time was 0.5 μ s. This ratio was found to increase at higher source temperatures and decrease for shorter flight times. The effect can be explained if the long-lived metastables in the slower beams are predominately in the $N = K = 0$ rotational levels since the thermal populations of the lower rotational levels of the precursor ions, calculated⁶ with the

appropriate nuclear spin statistics for protons and deuterons for an ion with D_{3h} symmetry, predict a disproportionately high relative abundance of H_3^* ($H_3^*/D_3^* \approx 20$ for $T_s = 135$ K). In their beam experiments Garvey and Kuppermann found nearly equal abundances of H_3 and D_3 metastables when their gas sample contained equimolar concentrations of H_2 and D_2 . From the foregoing observations it is difficult to explain this result for their beams with flight times much greater than 0.5 μ s. The source of this disagreement is not yet understood.

Finally we cite the photo assisted field ionization study of H_3 by Helm.⁷ In his experiment a UV laser beam interacted in a coaxial configuration with a molecular beam of H_3 generated by H_3^+ / Cs charge exchange. He found no evidence for transitions from rotational levels in the $2p, ^2A''_2$ state above the $N = K = 0$ level although his experiment had sufficient resolution to observe those transitions. His work also provided an accurate value for the ionization energy of the metastable (3.7 eV).

As Garvey and Kuppermann point out the optically allowed transition, $2p, ^2A''_2 \rightarrow 2s, ^2A'_1$ in H_3 has a low emission coefficient and the radiative lifetime of the $2p, ^2A''_2$ state, which is estimated to be about 90 μ s, is a major factor accounting for its metastability. This factor with the quantum restriction on the predissociation rate of the $N = K = 0$ rotational level comprises a rather unique set of circumstances contributing to the lifetime of this species. This information may be useful for spectroscopists intending to observe the metastable under high resolution conditions.

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¹J. F. Garvey and A. Kuppermann, *J. Chem. Phys.* **86**, 6766 (1987); see also, *Chem. Phys. Lett.* **107**, 491 (1984).

²I. Dabrowski and G. Herzberg, *Can. J. Phys.* **58**, 1238 (1980).

³G. I. Gellene and R. F. Porter, *J. Chem. Phys.* **79**, 5975 (1983). This work was initiated several months before we became aware of the experiments of Garvey and Kuppermann.

⁴S. J. Jeon, A. B. Raksit, G. I. Gellene, and R. F. Porter, *J. Chem. Phys.* **82**, 4916 (1985).

⁵S. J. Jeon, A. B. Raksit, G. I. Gellene, R. F. Porter, W. P. Garver, C. E. Burkhardt, and J. J. Leventhal, *Natl. Bur. Stand. Publ.* 716 (1985), p. 364.

⁶Details of these calculations are given in Refs. 3 and 4.

⁷H. Helm, *Phys. Rev. Lett.* **56**, 42 (1986).

Reply to Comment on "Total scattering, surface ionization, and photoionization of a beam of H_3 metastable molecules"^{a)}

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In response to the Comment of Gellene and Porter, we agree with them that the only rovibrational level of the $2p, ^2A''_2$ state of H_3 which can have a lifetime of the order of 1 μ s or greater is the $N = K = 0$ one, as clearly demonstrated by

Dabrowski and Herzberg.¹ Under the experimental conditions of Gellene, Porter, and co-workers,^{2,3} this state is produced by near-resonant electron transfer in single collisions of H_3^+ with K atoms, and we agree with their interpretation

that only low rotational quantum numbers of that ion are involved. A similar conclusion has been reached in Helm's elegant work.⁴

The experimental conditions under which the metastable H_3 species detected in our experiments are formed⁵⁻⁷ are radically different. Our arc source is operated with H_2 pressures of the order of 70 Torr and currents of the order of 100 A. The cross sectional dimensions of the region traversed by the electrons is about 0.03 cm^2 , corresponding to a current density of the order of $2 \times 10^{22} \text{ electrons/cm}^2/\text{s}$. The residence time of molecules or ions in this region is estimated to exceed $10 \mu\text{s}$. Under these conditions, each species present in the system is expected to undergo a large number of collisions, resulting in a potentially very complex reaction mechanism. Out of this arc emerges a beam which contains a significant proportion (1% to 10%) of metastable H_3 molecules, having a lifetime of the order of $40 \mu\text{s}$ or longer. On the basis of emission spectroscopy, surface ionization, photoionization, and total scattering experiments performed with that beam^{5,7} and the spectroscopic work of Herzberg and co-workers^{1,8-11} we conclude that the metastable state involved is $2p^2A_2''$.

This assignment poses two questions which Gellene and Porter's Comment raise explicitly or implicitly: (a) If the $2p^2A_2''$ metastable H_3 species we detect are all in the $N=0$, $K=0$ rotational state, what mechanism can result in the significant population of this level we find in our beam? (b) How can the difference in the H_3/D_3 population ratio between their and our results be explained?

The answer to these questions must reside in the completely different mechanism by which the H_3 we detect is formed. This mechanism is presently unknown, but could involve three-body processes [such as $H_3^+(N) + e^- + H \rightarrow H_3^*(N') + H$, where the star represents either the $2p^2A_2''$ state or a higher Rydberg predecessor state]. Processes of this type may occur via smaller impact parameters than charge exchange ones, and as a result N' may be significantly smaller than N due to rotational deexcitation. In particular,

if the fraction of such processes for which $N'=0$ is in the range 0.02 to 0.2, this would explain the H_3 metastable populations we observed, thereby answering question (a) above.

Concerning question (b), the conditions in our arc source lead to an almost complete dissociation of the H_2 gas entering it, as evidenced by the fact that 90% or more of the beam produced consists of H atoms. When an equimolar mixture of H_2 and D_2 flows through the arc, the resulting beam has a proportion of $H_3:H_2D:HD_2:D_3$ of approximately 1:3:3:1. This result implies that isotope effects in the triatomic metastable formation mechanism compensate for the nuclear spin statistics which, for $N=0$, strongly favor the formation of H_3 over D_3 $2p^2A_2''$. In summary, the mechanism for formation of the $2p^2A_2''$ metastable H_3 in our source is apt to be so different from that in Gellene and Porter's charge exchange cell that major differences in the observed H_3/D_3 population ratios in these two experiments are not unexpected.

One of the authors (J.F.G.) would like to thank Professor Harry F. King for helpful discussions.

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^{b)} Contribution No. 7682.

¹I. Dabrowski and G. Herzberg, *Can. J. Phys.* **58**, 1238 (1980).

²G. I. Gellene and R.F. Porter, *J. Chem. Phys.* **79**, 5975 (1983).

³S. J. Jeon, A. B. Raksit, G. I. Gellene, and R. F. Porter, *J. Chem. Phys.* **82**, 4916 (1985).

⁴H. Helm, *Phys. Rev. Lett.* **56**, 42 (1986).

⁵J. F. Garvey and A. Kuppermann, *Chem. Phys. Lett.* **107**, 491 (1984).

This work was initiated one year before we became aware of the experiments of Gellene and Porter.

⁶J. F. Garvey and A. Kuppermann, *Rev. Sci. Instrum.* **57**, 1061 (1986).

⁷J. F. Garvey and A. Kuppermann, *J. Chem. Phys.* **86**, 6766 (1987).

⁸G. Herzberg, *J. Chem. Phys.* **70**, 4806 (1979).

⁹G. Herzberg and J. K. G. Watson, *Can. J. Phys.* **58**, 1250 (1980).

¹⁰G. Herzberg, H. Lew, J. J. Sloan, and J. K. G. Watson, *Can. J. Phys.* **59**, 428 (1981).

¹¹G. Herzberg, J. T. Hougen, and J. K. G. Watson, *Can. J. Phys.* **60**, 1261 (1982).

ERRATA

Erratum: Scattering of highly vibrationally excited Li_2 from He and Kr [J. Chem. Phys. **85**, 7062 (1986)]

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Equation (18) is incorrect as it stands and should read

$$V_i(R,r) = \epsilon_i \left[3\rho_i(R,r)^{-8} - 4c_i(r)g_i(R)\rho_i\left(R + z_i \frac{\Delta r}{2}, r\right)^{-6} \right], \quad i = \parallel, \perp,$$

where $z_{\parallel} = 1$ and $z_{\perp} = -f$. In the correct formula the v dependence is restricted to the short range repulsive term. The results and conclusions are not affected since the correct formula was used in the paper throughout. We are grateful to H.-G. Rubahn for calling this error to our attention.