tral lines increased with lower state rotational quantum numbers as \(N(N + 1) - K^2\) and concluded that the 2p,\(^5\)A\(^g\) state was undergoing heterogeneous rotational predissociation into the ground \(^2\)E\(^r\) state through Coriolis interaction. From their measurements the lifetime for the first excited rotational level with \(N = K = 1\) is estimated to be about \(3 \times 10^{-11}\) 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-workers\(^3\)-\(^5\) who generated neutral beams of H\(_3\) by a near resonant electron transfer process

\[
H_3^+ + K(g) \rightarrow H_2^+ + K^+ + H
\]

(1)

involving a fast (6 keV) beam of H\(_3^+\) ions. In their experiments H\(_3^+\) ions produced by the exothermic ion molecule reaction

\[
H_3^+ + H_2 \rightarrow H_4^+ + H
\]

(2)

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 as increased as the ion source temperature decreased and/or as the source pressure of H\(_3\) 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 study\(^4\) 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\(_2^+\)/D\(_2^+\) ratio was found to be approximately 17 when the ion source temperature was 135 K and the beam flight time was 0.5 \(\mu\)s. This ratio was found to increase at higher source temperatures and decrease for slower 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, calculated\(^6\) with the appropriate nuclear spin statistics for protons and deuterons for an ion with \(D_{\infty h}\) symmetry, predict a disproportionately high relative abundance of H\(_2^+\) (H\(_2^+\)/D\(_2^+\) \(\approx 20\) 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 \(\mu\)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,\(^5\)A\(^g\) 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,\(^5\)A\(^g\) \(\rightarrow\) 2s,\(^2\)A\(^g\), in H\(_3^+\) has a low emission coefficient and the radiative lifetime of the 2p,\(^5\)A\(^g\) state, which is estimated to be about 90 \(\mu\)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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3. G. 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.
6. Details of these calculations are given in Refs. 3 and 4.

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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,\(^5\)A\(^g\) state of H\(_3\) which can have a lifetime of the order of 1 \(\mu\)s or greater is the \(N = K = 0\) one, as clearly demonstrated by Dabrowski and Herzberg. Under the experimental conditions of Gellene, Porter, and co-workers,\(^2\)-\(^5\) 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 H₂ species detected in our experiments are formed3−7 are radically different. Our arc source is operated with H₂ 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 cm², corresponding to a current density of the order of 2 × 10²² electrons/cm²/s. The residence time of molecules or ions in this region is estimated to exceed 10 μs. 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 H₃ molecules, having a lifetime of the order of 40 μs or longer. On the basis of emission spectroscopy, surface conization, photoionization, and total scattering experiments performed with that beam3,4 and the spectroscopic work of Herzberg and co-workers1−6−11 we conclude that the metastable state involved is 2p²2Δ^⁺.

This assignment poses two questions which Gellene and Porter’s Comment raise explicitly or implicitly: (a) If the 2p²2Δ^⁺ metastable H₃ 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 H₃/D₃ population ratio between their and our results be explained?

The answer to these questions must reside in the completely different mechanism by which the H₃ we detect is formed. This mechanism is presently unknown, but could involve three-body processes [such as H₃⁺ (N) + e⁻ + H → H⁺(N⁺) + H], where the star represents either the 2p²2Δ^⁺ 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 H₃ 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 H₂ 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 H₂ and D₂ flows through the arc, the resulting beam has a proportion of H₂ : H₂D : HD₂ : D₃ 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 H₃ over D₃, 2p²2Δ^⁺. In summary, the mechanism for formation of the 2p²2Δ^⁺ metastable H₃ 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 H₃/D₃ 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.

ERRATA

Erratum: Scattering of highly vibrationally excited Li₂ from He and Kr [J. Chem. Phys. 85, 7062 (1986)]

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

\[ V_i(R,r) = \frac{e^4}{\epsilon^2} \left[ 3 \rho_i(R,r) - 4 \rho_i(R,r) g_i(R) \rho_i(R + z_i \frac{\Delta r_i}{r}) \right] \delta(r - z_i), \]

where \( z_i = 1 \) and \( z_i = -f \). In the correct formula the \( \nu \) 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.


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