CROSS SECTIONS FOR THE ION-MOLECULE REACTION $H_2^{+*} + H_2 \rightarrow H_3^+ + H$ AS A FUNCTION OF THE VIBRATION STATE OF THE H_2^+ ION

A. Weingartshofer and E. M. Clarke
St. Francis Xavier University, Antigonish, Nova Scotia, Canada
(Received 20 April 1964)

It is recognized that the ion-molecule reaction

$$H_2^+(\text{vib}) + H_2 \rightarrow H_3^+ + H \qquad (1)$$

is very rapid[1] and that the reactant H_2^+ ion can be in various vibrationally excited states.[2] It is the purpose of this communication to report that it is only the first four vibrationally excited states of the H_2^+ ion that contribute significantly towards the formation of H_3^+. The cross sections for the $\nu' = 4$ and higher states are very small, if not zero. These measurements have been carried out in a mass spectrometer provided with an electron selector of the Clarke[3] type in the source. To check on the possibility of these cross sections being modified by collisions with the walls of the ionization chamber or other instrumental effects, a second selector was constructed of the Marmet type[4] with 90% tungsten mesh for the ionization chamber walls. No essential difference was found. From the sharpness of the breaks in the curves, the electron spread is estimated to be of no more than 0.05 eV at half-height in the monoenergetic beam. In these measurements the H_2^+ ions drifted through the ionization chamber with thermal energies of the order of 0.04 eV. Counting techniques were used to measure the ion current.

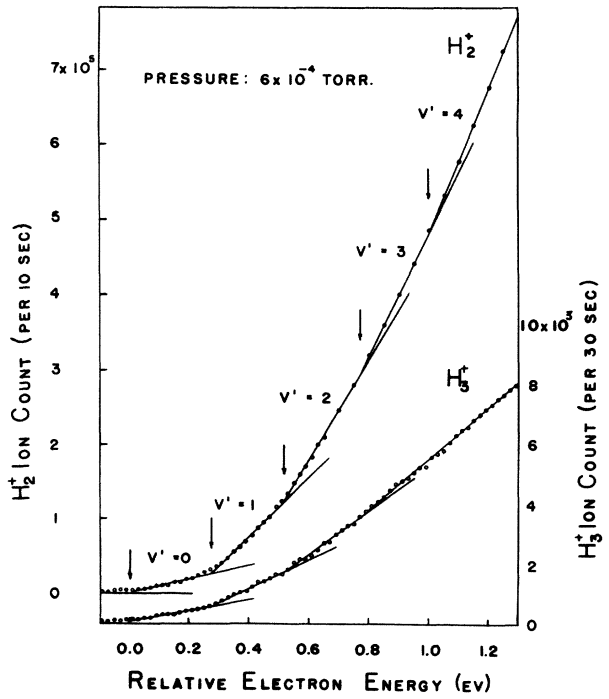

FIG. 1. Appearance potential curves for H_2^+ and H_3^+, plotted as a function of energy above threshold. (Note different ordinate axes.)

Appearance potential curves for H_2^+ and H_3^+ are presented in Fig. 1, and the relative cross sections σ_ν for the formation of H_3^+ for the various vibrational levels ν' of H_2^+ is presented in Table I. These are the averaged results from several curves, and the maximum deviation was less than 10%.

It is the experience of the authors that for the lower vibrational levels, the appearance potential curves for H_2^+ can be synthesized by superposing a series of straight-line segments that have slopes α_ν with respect to the energy axis and that start at their appropriate appearance potentials. The α_ν's are related to the Franck-Condon factors.[2,3]

At a given voltage above threshold, the number N_ν of H_2^+ ions in a particular vibrational level ν are related to the α_ν's by

$$N_\nu = \alpha_\nu (V - V_\nu), \qquad (2)$$

where V_ν is the appearance potential of the vibrational level ν.

It is found that the appearance potential curve for H_3^+ shows very distinct segments which correspond to the vibrational intervals of H_2^+. And the number N_ν' of H_3^+ ions can also be represented by an equation of the form (2), namely,

$$N_\nu' = \alpha_\nu' (V - V_\nu), \qquad (3)$$

where the slopes of the segments are now designated by α_ν'. This suggests that N_ν' represents

Table I. Values of the relative cross section σ_ν for the formation of the H_3^+ ion for various vibrational levels of the colliding H_2^+ ion.

ν'	0	1	2	3	4	5
σ_ν	1.0	0.5	0.4	0.5	0.0	0.0

the number of H_3^+ ions that have been produced from the N_ν H_2^+ ions in the vibrational level ν. Defining the relative cross section for this process as

$$\sigma_\nu = N_\nu'/N_\nu, \tag{4}$$

it follows immediately that

$$\sigma_\nu = \alpha_\nu'/\alpha_\nu. \tag{5}$$

The values for σ_ν reported in Table I have been obtained from Eq. (5) and are expressed in terms of the value for $\sigma_{\nu=0}$ which has been set arbitrarily equal to 1.0.

Our interpretation is based on the assumption of identical collection efficiencies for H_2^+ and H_3^+ ions. Evidence for this has been discussed extensively by Reuben and Friedman.[5] Their discussion centers around a conjecture of Polanyi[6] on energy transfer processes in elementary reactions. Polanyi predicts the appearance of heat of reaction as vibrational energy rather than kinetic energy in the secondary ions. Experiments with retarding potentials are presently being attempted in this laboratory to confirm the above assumption. These experiments are complicated by the fact that the retarding potentials interfere with the electron selector.

To our knowledge, cross sections for the reaction (1), with such great detail and such low ionizing electron energies, have not been reported in the literature. However, Gutbier,[7] and Reuben and Friedman[5] have published values for the absolute cross sections corresponding to ionizing electron energies of 75 eV and 50 eV, respectively.

This research was supported by the National Research Council of Canada. We are glad to express our appreciation for this support, as well as helpful advice and encouragement from Dr. Wm. McGowam.

[1]D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 29, 282 (1958).
[2]P. Marmet and L. Kerwin, Can. J. Phys. 38, 972 (1960).
[3]L. Kerwin, P. Marmet, and E. M. Clarke, Advances in Mass Spectrometry (Pergamon Press, New York, 1963), Vol. 2, p. 522.
[4]P. Marmet and L. Kerwin, Can. J. Phys. 38, 787 (1960).
[5]B. G. Reuben and L. Friedman, J. Chem. Phys. 37, 1636 (1962).
[6]J. C. Polanyi, J. Chem. Phys. 31, 1338 (1959).
[7]H. Gutbier, Z. Naturforsch. 12A, 499 (1957).

STIMULATED BRILLOUIN SCATTERING AND COHERENT GENERATION OF INTENSE HYPERSONIC WAVES*

R. Y. Chiao and C. H. Townes
Massachusetts Institute of Technology, Cambridge, Massachusetts

and

B. P. Stoicheff†
National Research Council, Ottawa, Canada

(Received 6 May 1964)

Stimulated Brillouin scattering of an intense maser beam, involving coherent amplification of a hypersonic lattice vibration and a scattered light wave, has been detected in quartz and sapphire. This process is analogous to Raman maser action, but with molecular vibration replaced by an acoustic wave of frequency near 3×10^{10} cps, and with both the acoustic and scattered light waves being emitted in specific directions.

Either compressional or shear waves can be excited, but for a compressional wave the coupling between acoustic and optical waves is simplest, and describable as electrostriction. Electrostrictive pressure is given by $p=(E^2/8\pi)\rho d\epsilon/d\rho = (E^2B/8\pi)d\epsilon/dp$, where E is the electric field, ρ the density of material, ϵ its dielectric constant, and B the bulk modulus. Thus two optical waves whose frequencies differ by ω_S can drive a pressure wave of this frequency, due to the quadratic dependence of pressure on E and the consequent generation of a beat frequency. Similarly, a pressure wave of frequency ω_S couples to an electromagnetic wave E through the varying induced dipole moment density $(E/4\pi)(d\epsilon/dp)p$.

If one assumes an intense driving wave, as from an optical maser, of form $E_0\cos(\omega_0 t-\vec{k}_0\cdot\vec{r})$, a scattered electromagnetic wave $E_{-1}\cos[(\omega_0-\omega_S)\times t-\vec{k}_{-1}\cdot\vec{r}+\varphi_{-1}]$, and an acoustic wave $p_0\cos(\omega_S t$