VOLUME 12, NUMBER 11

sion of both Stokes and anti-Stokes radiation, contrary to our observations with calcite. Further, it was suggested to us by Dr. A. Szöke⁷ that since the Stokes radiation has the greatest gain in the forward direction it may be possible to generate cones of anti-Stokes radiation not only as a volume effect according to relation (1) but also as a surface effect according to $\bar{k}_n \cos\theta_n = (n+1)\bar{k}_0$ $-n\bar{k}_{-1}$. However, for calcite the corresponding values of the angles for the first- and secondorder anti-Stokes emission are 3.67×10^{-2} and 6.26×10^{-2} radian, considerably larger than the observed values.

In summary, we note that our experiments with calcite quantitatively confirm the wave vector relations (1) and (1'). In addition, the observed absorption cones in the first-order Stokes radiation show that in calcite the interaction of maser light with the first-order Stokes radiation produces anti-Stokes and Stokes radiation of several orders, in accordance with the theory of Garmire, Pandarese, and Townes.⁴

We are very grateful to Professor C. H. Townes

for his interest and advice during the course of this work and to Mrs. E. Garmire and Dr. A. Szöke for helpful discussions.

[†]On leave from the National Research Council, Division of Pure Physics, Ottawa, Canada.

¹R. W. Terhune, Bull. Am. Phys. Soc. <u>8</u>, 359 (1963); Solid State Design <u>4</u>, 38 (1963). B. P. Stoicheff, Phys. Letters <u>7</u>, 186 (1963).

²H. J. Zeiger, P. E. Tannenwald, S. Kern, and R. Herendeen, Phys. Rev. Letters 11, 419 (1963).

³J. W. Gifford, Proc. Roy. Soc. (London) <u>A70</u>, 329 (1902).

⁴E. Garmire, F. Pandarese, and C. H. Townes, Phys. Rev. Letters <u>11</u>, 160 (1963); see also reference

2; R. W. Hellwarth (to be published).

 5 G. Eckhart, D. P. Bortfeld, and M. Geller, Appl. Phys. Letters <u>3</u>, 137 (1963).

⁶M. Born and E. Wolf, <u>Principles of Optics</u> (Pergamon Press, New York, 1959), pp. 434-444.

⁷A. Szöke (private communication).

ENERGY LOSSES AND ELASTIC RESONANCES IN ELECTRON SCATTERING FROM H_2^{\dagger}

C. E. Kuyatt, S. R. Mielczarek, and J. Arol Simpson National Bureau of Standards, Washington, D. C. (Received 14 February 1964)

Recently developed techniques of high-resolution electron spectroscopy¹ have both given new information on the energy levels of rare gas atoms² and made possible the discovery of sharp resonances in the elastic scattering of electrons from rare gases.^{3,4} These techniques have now been used to study the simplest and theoretically best-understood molecule, hydrogen. Inelastic scattering measurements for the first time show well-resolved vibrational levels of several electronic states of H₂. Elastic scattering measurements show at least eight narrow resonances in the elastic cross section.

The experimental apparatus, previously described,⁵ consists of an electron energy monochromator, a gas-filled scattering chamber, and an electron energy analyzer. The analyzer accepts only electrons which are within a cone of half-angle 0.0125 rad about the direction of the incident electron beam. In the elastic measurements only electrons which have lost less than about 0.05 eV are accepted. Figure 1 shows the variation of the number of 33-eV electrons inelastically scattered by 0.04 Torr-cm of hydrogen as a function of electron energy loss. Two vibrational series are clearly shown, one starting at 11.19 eV and the other at 12.27 eV. The region above 14 eV appears to be composed of at least two overlapping series.

Also shown on Fig. 1 are the rotational bandheads of some of the energy levels obtained from ultraviolet emission spectroscopy by Hopfield,⁶ Herzberg and Howe,⁷ and Monfils.⁸ The ultraviolet data show that the electron energy-loss spectrum arises from excitation of the ground (X) state of molecular hydrogen, $(1s\sigma)^{21}\Sigma_g^+$, to vibrational levels of three electronic excited states: $1s\sigma 2p\sigma^1\Sigma_u^+$, $1s\sigma 2p\pi^1\Pi_u$, and $1s\sigma 3p\pi^1\Pi_u$, the so-called *B*, *C*, and *D* states.⁹ The $1s\sigma 2s\sigma$ - $^{3}\Sigma_g$ repulsive state, found by Schulz¹⁰ with the trapped-electron method, could not be seen in our measurements. We conclude from our measurements that the probability of exciting this state in forward scattering must be less than 10^{-3} of

^{*}This work was supported in part by the National Aeronautical and Space Administration under Research Grant No. NsG-330.



FIG. 1. Intensity of 33-eV electrons inelastically scattered by 0.04 Torr-cm of H_2 as a function of energy loss.

that for exciting the C state.

Figure 2 shows the intensity of electrons transmitted by the scattering chamber without energy loss as a function of energy. Curve a is for an evacuated scattering chamber. The shape of this curve is caused by a well-understood electron-optical effect associated with changing the energy. Curve b shows the transmitted intensity with 0.02 Torr of H_2 in the chamber, and all other conditions unchanged. The over-all shape is similar to curve a except in the region between about 11.5 and 14.0 eV, where proportionately more electrons are transmitted. The peak is shifted slightly due to the decrease in elastic scattering cross section with increasing energy. Several discrete resonances are apparent. Curve c shows the interval containing the resonances, magnified by suppressing the zero of the x-y recorder and increasing its gain. The lineup was changed to bring the broad peak into the resonance region. Eight resonance peaks are clearly resolved, with an indication of several more at higher energies. A small amount of asymmetry in the shape of some of the resonances is apparent.

Calibration of the absolute energy scale was



FIG. 2. Electron current transmitted through scattering chamber as a function of incident energy. Curve *a* is for an evacuated scattering chamber. The shape is caused by a well-known electron optical effect which accompanies the change in energy. Curve *b* is for 0.04 Torr-cm of H_2 in the scattering chamber with all other conditions unchanged. The current sensitivity was increased by a factor of 2000. Curve *c* shows the resonance region at still higher sensitivity.

performed by determining the apparent appearance potential for positive ions. From the average of several measurements, the first elastic resonance peak occurs 4.28 ± 0.1 eV below the apparent appearance potential. From the work of Marmet and Kerwin,¹¹ we estimate that the apparent appearance potential, obtained by extrapolating the straight-line portion of our ionization appearance curve, should occur 0.5 eV above the calculated appearance potential of 15.4 eV.¹² With this choice¹³ the positions of the eight resonance peaks are as shown in Table I. The over-all accuracy of the energy scale is about 0.3 eV, due to the uncertainty in apparent appearance potential. Values are given to the nearest 0.01 eV since the spacing of the resonances can be reproduced to about this accuracy. Also given are the vibrational spacings of the $1s\sigma 2p\pi^{1}\Pi_{u}$ (C) state of $H_{2}^{8,9}$ and of the ground state¹² of H_2^+ . The observed spacings of the

Table I. Observed position of elastic scattering resonances in H_2 , and comparison of the resonance spacing with vibrational spacings in H_2 and H_2^+ .

		Vibrational spacing	
Resonance energy	Resonance spacing	H_2 $1s\sigma 2 \not \sigma {}^1 \Sigma_{}^+$	H ₂ ⁺ ground state
(eV)	(eV)	(eV)	(eV)
11.62	0.29	0.285	0.269
11.91	0.27	0.268	0.253
12.18	0.28	0.268	0.237
12.71	0.25 0.23	0.238 0.220	0.221
12.94	0.19	0.205	0.192
13.31	0.18	0.188	

resonances correspond closely with vibrational spacing of the C state,¹⁴ but show small but significant differences from the H_2^+ vibrational spacings.

If the resonances are ascribed to compound state formation with an excited state of H_2 , then it might be expected that the vibrational spacings would be similar to those of H_2^+ , modified in the same direction as in the excited states of H_2 . This appears to be the case.

[†]This research received partial support under Project

DEFENDER, sponsored by the Advanced Research Projects Agency, Department of Defense.

¹J. Arol Simpson and S. R. Mielczarek, J. Chem. Phys. <u>39</u>, 1606 (1963).

²J. Arol Simpson, S. R. Mielczarek, and J. Cooper, J. Opt. Soc. Am. <u>54</u>, 269 (1964).

³J. Arol Simpson and U. Fano, Phys. Rev. Letters 11, 158 (1963).

⁴J. Arol Simpson and S. R. Mielczarek, Bull. Am. Phys. Soc. 9, 89 (1963).

⁵J. Arol Simpson, Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions, London, July 1963, edited by M. R. C. McDowell (North-Holland Publishing Co., Amsterdam, to be published).

⁶J. J. Hopfield, Nature <u>125</u>, 927 (1930).

⁷G. Herzberg and L. L. Howe, Can. J. Phys. <u>37</u>, 636 (1959).

⁸A. Monfils, Bull. Classe Sci., Acad. Roy. Belg. <u>47</u>, 585, 816 (1961).

⁹O. W. Richardson, <u>Molecular Hydrogen and Its Spec-</u> <u>trum</u> (Yale University Press, New Haven, Connecticut, 1934).

¹⁰G. J. Schulz, Phys. Rev. <u>112</u>, 150 (1958).

¹¹P. Marmet and L. Kerwin, Can. J. Phys. <u>38</u>, 973 (1960); <u>Advances in Mass Spectrometry</u> (Pergamon

Press, London, 1963), Vol. 2, p. 522.

¹²E. A. Hylleraas, Z. Physik <u>71</u>, 739 (1931). ¹³G. J. Schulz, Phys. Rev. <u>113</u>, 816 (1959), gives a value of 15.56 eV for the appearance potential of H_2^+ . We are currently investigating this discrepancy.

 ^{14}It should be noted that the vibrational spacings of the $1s\sigma 2p\sigma^3\Sigma_u$ state are nearly identical with those of the C state.

RESONANT EXCITATION IN HELIUM ION-ATOM COLLISIONS*

Nyle G. Utterback[†] University of Denver, Denver, Colorado (Recieved 20 January 1964)

An energy resonance in the production of helium metastable atoms has been observed for helium ions impacting on helium atoms. The peak of the resonance occurs at 28 eV in the center-of-mass system for metastables scattered in the forward direction.

This resonance was first observed as an apparent resonance in the ionization cross section for helium atoms impacting on hydrogen molecules. The technique for measuring such ionization cross sections has been reported in detail previously.¹⁻⁴ It involves the neutralization of an ion beam by charge transfer in order to produce the fast neutral beam. The neutral beam passes between parallel plates in a low-pressure ionization chamber and all negative charge due to ionizing interactions is measured. Figure 1, curve $He-H_2$, shows the results obtained when a neutral helium beam, obtained from He^+ in He charge-transfer neutralization, impacted on molecular hydrogen.⁵ "Ionization cross section" here means total cross section for production of electrons (or negative ions). The energy scale for Fig. 1 is the kinetic energy in the He-H₂ center-of-mass system minus 15.5 eV, and is therefore the excess energy over ionization of the hydrogen molecule. The ionization cross section measured^{5,6} for H₂-He (fast neutral hydrogen molecular beam impacting on helium atoms) is also given in Fig. 1. The energy scale is the same.⁷

One would expect the $He-H_2$ results to be identical to the H_2 -He results when the energy is expressed