

## Direct and Auto-Ionization of $H_2$ near Threshold\*

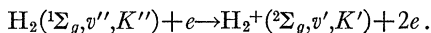
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In our experiments involving the collision of electrons with  $H_2$  ( $^2\Sigma_g^+, v=0, K$ ), the ionization-efficiency curve of  $H_2^+$  shows no structure which can be obviously related to the direct vibrational spectrum of  $H_2$ . In the first-derivative spectrum, however, the major peaks correspond to the major peaks in the photoionization spectrum, which strongly suggests, for allowed transitions, a one-to-one correspondence between  $d\sigma_e/dE_e$  and  $\sigma_{ph}$ . Other peaks no doubt are associated with auto-ionizing states of  $H_2$  which can only be reached through channels normally forbidden to photoexcitation. The major valleys can be related to the direct vibrational-excitation thresholds. From these experiments and other published results, we believe that the auto-ionizing lifetime  $\tau_a$  for many states may be long.

### I. INTRODUCTION

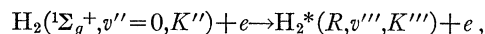
IN atoms like H described in the previous paper,<sup>1</sup> only electronic transitions are important; however, even in the simplest molecules, such as  $H_2$ , the effects of nuclear motion must also be taken into account, i.e., through vibrational and rotational energy changes:



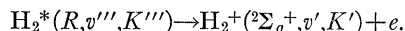
In the above relation,  $v$  and  $K$  are the nuclear vibrational and rotational quantum numbers. To a good approximation, the Born-Oppenheimer description of the transition allows one to calculate the direct ionization processes outlined in the equation above; in fact, for the case of direct vibrational excitation, the calculations of the relative transition probabilities<sup>2-6</sup> (Franck-Condon overlap integrals) appear to be substantiated by both electron<sup>7,8</sup> and photon<sup>9</sup> impact measurements. Quite recently, it was thought that direct rotational excitation by electron impact had been observed<sup>10,11</sup>;

however, the more complete study reported here indicates that the major portion of the observed structure is due to auto-ionization.

For the case of auto-ionization of molecular hydrogen,<sup>10,12-17</sup> the ion is formed first by exciting the neutral species to some electronic level ( $R$ ) above the ionization continuum:



and then in a time short with respect to the radiative lifetime, the excited neutral decays into an ion-electron pair, that is, the excited neutral auto-ionizes:



Beutler and his associates<sup>12</sup> identified this process spectroscopically many years ago. For  $H_2$ , in particular, Beutler and Junger<sup>13</sup> were able to identify the specific transition; i.e., they were able to relate the product ion in a particular vibrational and rotational state with its parent neutral. It is imperative that high-resolution spectroscopic studies like these now be extended. It is only recently that the ion spectrum has been identified under photon bombardment by Cook and Metzger,<sup>15</sup> and by Dibeler, Reese, and Krauss.<sup>16</sup> In the present paper, we compare the ion spectrum resulting from electron bombardment to the equivalent spectra resulting from photon bombardment.

A special problem has arisen in the case of electron-impact ionization of  $H_2$ , because in some high-resolution electron-impact studies, the vibrational structure of the  $H_2^+$  ion is prominent<sup>7,8</sup> while in others, including this, it is not<sup>10,17</sup>. Accepting the results of both experiments, we will argue in a later section of this paper that the lifetime of the auto-ionizing states is long.

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<sup>1</sup> J. Wm. McGowan and E. M. Clarke, preceding paper, *Phys. Rev.* **167**, 43 (1968).

<sup>2</sup> M. Krauss and A. Kropf, *J. Chem. Phys.* **26**, 1776 (1957).

<sup>3</sup> M. E. Wacks, *J. Res. Natl. Bur. Std.* **A68**, 631 (1964).

<sup>4</sup> H. von Koch and L. Friedman, *J. Chem. Phys.* **38**, 1115 (1963).

<sup>5</sup> J. Wm. McGowan and L. Kerwin, *Can. J. Phys.* **38**, 972 (1960).

<sup>6</sup> G. H. Dunn, *J. Chem. Phys.* **44**, 2592 (1966).

<sup>7</sup> P. Marmet and L. Kerwin, *Can. J. Phys.* **38**, 972 (1960).

<sup>8</sup> L. Kerwin, P. Marmet, and E. M. Clark, *Advances in Mass Spectrometry* (Pergamon Press Ltd., London, 1963), Vol. 2, p. 522.

<sup>9</sup> D. C. Frost, C. A. McDowell, and D. A. Vroom, *Phys. Rev. Letters* **15**, 612 (1965).

<sup>10</sup> J. Wm. McGowan and M. A. Fineman, in *Proceedings of the Fourth International Conference of the Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters Inc., Hastings-on-Hudson, New York, 1965), p. 429. The electron-energy scale must be shifted down by  $\sim 0.03$  eV in conjunction with the results of the study reported in Ref. 1.

<sup>11</sup> J. Wm. McGowan and M. A. Fineman, *Phys. Rev. Letters* **15**, 179 (1965). More recent data and data analysis have led to a shift in the electron-energy scale. Most of the structure which was thought to be associated with direct rotational excitation of the ion from various excited rotational levels of the molecule can now be identified as auto-ionization structure.

<sup>12</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., N. J., 1959). (See p. 414 for the work of Beutler *et al.*)

<sup>13</sup> H. Beutler, A. Deubner, and H. O. Junger, *Ann. Physik* **100**, 80 (1936).

<sup>14</sup> P. H. Doolittle and R. I. Schoen, *Phys. Rev. Letters* **14**, 348 (1965).

<sup>15</sup> G. R. Cook and P. H. Metzger, *J. Opt. Soc. Am.* **57**, 968 (1964).

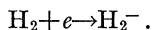
<sup>16</sup> V. H. Dibeler, R. M. Reese, and M. Krauss, *J. Chem. Phys.* **42**, 2045 (1965).

<sup>17</sup> D. D. Briglia and D. Rapp, *Phys. Rev. Letters* **14**, 245 (1965).

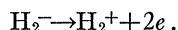
It should be remembered that the threshold laws describing photon and electron reactions are quite different. In the case of electron-impact excitation, furthermore; electron exchange, magnetic dipole, and electric and magnetic multipole transitions can give rise to possible auto-ionizing states which cannot be reached under photon impact. Therefore, one should not be surprised if the auto-ionization spectrum obtained under electron impact does not completely duplicate that associated with photon impact. Other problems arise as to the nature of the auto-ionization threshold under electron impact. If the auto-ionization threshold behaves in a manner similar to excitation (which it may not), then from Wigner's calculation<sup>18</sup> one may expect a square-root threshold law  $(E_e - E_x)^{1/2}$ , to which a step function is a rough approximation.<sup>19</sup>

The first theoretical treatments of H<sub>2</sub> auto-ionization have recently been outlined by Krauss<sup>16</sup> and by Berry<sup>20</sup>; and though no detailed calculations have been done, these discussions do give a helpful picture of the auto-ionization process.

It has also been suggested that under electron impact, the ionization of the H<sub>2</sub> spectrum might also be complicated by temporary H<sub>2</sub><sup>-</sup> compound-state formation<sup>21</sup>:



Within this mechanism, the H<sub>2</sub><sup>-</sup> formed would subsequently release two electrons, thus giving the molecular positive ion, i.e.,



As yet, there is neither experimental nor theoretical support for this mechanism, even though there are analogues in nuclear physics which support it.

In Sec. II of this report we consider briefly our experimental approach, which has been described more completely in the previous paper. In Sec. III, we will discuss data analysis particularly relevant to a study of auto-ionization of structure in electron-scattering curves. In Sec. IV, we give and discuss our H<sub>2</sub> results, while in Sec. V we summarize what is known of the electron-impact ionization of H<sub>2</sub>.

## II. APPARATUS

A complete discussion of the apparatus, its calibration and our usual operating procedure is given in the accompanying paper.<sup>1</sup> However, we will briefly summarize some salient points here. Let it suffice to point out that in our crossed beam geometry the chopped neutral beam has a density near 10<sup>10</sup> particles cm<sup>-3</sup> while the electron current is less than 3 × 10<sup>-8</sup> A. The cross section of the neutral beam is slightly greater than 5 mm by

3 mm. It is crossed on its broad side by the electron beam approximately 6 mm along the neutral beam length by 2 mm wide.

The electron spatial distribution is symmetric while the energy distribution is very near Gaussian and is  $\lesssim 0.06$  eV wide at half maximum.

The ionization-efficiency curves quoted are the sum of from five to eight runs. Each run consists usually of 100 points taken at 0.02- or 0.01-eV intervals.

Our primary electron-energy calibration is the ionization potential of atomic hydrogen, 13.60 eV. We originally thought that the ionization-efficiency curve was linear very near threshold so that we could extrapolate the known linear portion of the curve through the tail due to the electron-energy distribution to the electron-energy scale. The intercept was then fixed at 13.60 eV. However, we now find that the ionization-efficiency curve is nonlinear<sup>1</sup> and that 13.60 eV is  $\approx 0.03$  eV below the intercept of the linear extrapolation with the electron-energy scale.

## III. DATA ANALYSIS

Because of the possibility of slow drifts and/or fluctuations in the apparatus during each experimental run, a number of identical experiments were made and the results collected to make one composite set of data. In this way, we obtained sufficient signal counts so that any indication of structure could be accepted as statistically meaningful. In addition to the signal counts, other data measured in an experiment included electron energy, primary electron current, and ion current. The difficulty in trying to form a "composite" experiment was in "locking-in" the several runs with respect to the energy scale. Only those data which met the criterion of current stability were used in the final summing of the data.

Several locking-in methods were tried. These included visually matching the initial slopes of the first derivatives of the ionization-efficiency curves and then visually matching the various peaks and valleys in the first-derivative curves. Finally a method was adopted which involved mathematically smoothing the original data by: (1) binomial smoothing, (2) smoothing by fourth difference, or (3) smoothing in the large, and then taking the first derivative of the data. The initial slope and the many peaks in the first derivative of the several electron-impact spectra of molecules were visually overlapped. This procedure essentially locked-in the several runs, so that the separate data at each energy for each run were added together to form a "composite." The accumulated data of the "composite" were smoothed, and their first and second derivatives calculated. The results presented in this paper are these combined data.

To help us decide whether or not the structure in the derivative curves was real, we estimated the errors associated with signal counts at each electron energy. The signal  $S_{ij}$  was taken as the difference between the

<sup>18</sup> E. P. Wigner, Phys. Rev. **73**, 1002 (1948); *Solway Conference, Proceedings* (Interscience Publishers Inc., New York, 1963), p. 211.

<sup>19</sup> J. D. Morrison, J. Chem. Phys. **21**, 1767 (1953).

<sup>20</sup> R. S. Berry, J. Chem. Phys. **45**, 1228 (1966); also private communication.

<sup>21</sup> D. P. Stevenson, J. Am. Chem. Soc. **82**, 5961 (1960).

measured signal plus background ( $S+B$ )—when the chopper was open and the background alone, ( $B$ )—when the chopper blocked the neutral beam giving

$$S_{ij} = (S+B)_{ij} - B_{ij},$$

where  $i$  refers to the energy and the  $j$  refers to the individual run. The error associated with a number of counts was taken to be the square root of the number of counts. Thus, the error  $E_{ij}(S_{ij})$  associated with the signal ( $S_{ij}$ ) becomes

$$E_{ij}(S_{ij}) = [(S+B)_{ij} + B_{ij}]^{1/2}.$$

For the  $i$ th point of the composite run, we sum over the  $n$  sets of data so that the signal and error are

$$S_i = \sum_{j=1}^n S_{ij}$$

and

$$E_i(S_i) = \left[ \sum_{j=1}^n (S+B)_{ij} + \sum_{j=1}^n B_{ij} \right]^{1/2}.$$

The relative error  $E_i(S_i)/S_i$  for each datum of the composite run will decrease as the total number of counts increases, i.e., as more data from individual runs are included in the composite run.

Most of the results from the  $H_2$  experiments were smoothed twice, and the first and second derivatives were then taken. The statistical errors associated with the doubly smoothed data were evaluated, and with these, the errors associated with the first and second derivatives were calculated. If the function being smoothed is continuous, smoothing enhances the reliability of each signal datum point ( $S_i$ ), because the adjacent points,  $S_{i-n}, \dots, S_{i+n}$ , contain some information about  $S_i$ .

The relative magnitudes of the errors in the first derivative when there is no smoothing, when there is single quadratic smoothing, and when there is double quadratic smoothing are 1.00: 0.67: 0.57. Clearly, the largest improvement in the statistical error comes from the first smoothing of the data. Keep in mind that smoothing can effectively increase the energy distribution of the bombarding electrons, unless care is taken to be certain that the breadth of the structure under investigation is quite large compared with the energy interval between data points. If not, some structure in the data may be blurred. Remember, too, that the above treatment helps only the statistical errors and not systematic ones.

The analysis of errors, the smoothing of the data, and the removal of the energy distribution (the instrument function) are not unique to our study. Such methods have been used in spectral analysis of radar signals and of spectra for years.<sup>22</sup> Unfortunately, these methods

<sup>22</sup> The following literature is pertinent to the analysis of data and generally to collision spectroscopy studies. Many of these references have been collected with the aid of J. Cooper of the

have not found general use in ion and electron collisions spectroscopy, even though the application of them does much to improve the value of the data obtained.

#### IV. IONIZATION OF HYDROGEN MOLECULE

The probability of ionization of  $H_2$  can be generally described as the square of  $J$ , the transition probability amplitude, which includes terms for all processes involved in the ionization of  $H_2$ . The total amplitude can be separated as follows:

$$J = J_d + J_a + J_{cs} + \dots,$$

where  $J_d$  relates to the direct ionization processes, i.e., direct ionization with electronic, vibrational, and rotational excitation of the ion;  $J_a$  relates to auto-ionization; and  $J_{cs}$  relates to the process involving negative-ion compound-state formation followed by double auto-ionization. Other less important terms are not considered here. It follows, then, that the total transition probability,

$$|J|^2 = |J_d|^2 + |J_a|^2 + |J_{cs}|^2 + \dots + 2\text{Re}[J_d J_a + J_d J_{cs} + J_a J_{cs} + \dots],$$

contains terms describing each of the processes plus interference terms between the processes. It should be remembered, too, that interference may also exist between the ionizing channels and nonionizing channels, like radiation and predissociation. In the section which follows, we will discuss the terms in the above generalized expression with reference to our data, while other contributions will not be considered.

Our data for the first 0.6 eV of the ionization curve for  $H_2$  by electron impact are plotted in Fig. 1. The calibration of cross section is obtained by normalizing the slope of the long linear portion of our curve to that of Rapp *et al.*<sup>23</sup> This gives an indication of the cross section versus electron-energy curve in the vicinity of the ionization threshold, a quantity which is of interest in thermal-equilibrium situations such as is found in the upper atmosphere. Where we have paid particular attention to such details as the shape of the cross-section curve and to the calibration of the electron-energy scale, Rapp *et al.*, have given similar attention to measurements of the absolute cross section. The

Joint Institute for Laboratory Astrophysics, Boulder, Colo., to whom we owe our thanks. (a) C. Lanczos, *Applied Analysis* (Prentice-Hall Inc., Englewood Cliffs, N. J., 1965). (b) R. N. Bracewell, *Proc. IRE* **45**, 106 (1957). (c) R. N. Bracewell and J. A. Roberts, *Australian J. Phys.* **7**, 615 (1954). (d) C. P. Flynn, *Proc. Phys. Soc. (London)* **78**, 1547 (1961). (e) C. P. Flynn and E. F. W. Seymour, *Proc. Phys. Soc. (London)* **75**, 337 (1960). (f) J. D. Morrison, *J. Chem. Phys.* **39**, 200 (1963). (g) J. O. Porteus, *J. Appl. Phys.* **33**, 700 (1962). (h) S. G. Rautian, *Usp. Fiz. Nauk* **66**, 475 (1958) [English transl.: *Soviet Phys.—Usp.* **1**, 245 (1958)]. (i) J. S. Rollett and L. A. Higgs, *Proc. Phys. Soc. (London)* **79**, 87 (1962). (j) Wm. C. Sauder, *J. Appl. Phys.* **37**, 1495 (1966). (k) A. R. Stokes, *Proc. Phys. Soc. (London)* **61**, 382 (1948).

<sup>23</sup> D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).

TABLE I. Cross section for the ionization of H<sub>2</sub>[<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, v=0, K(thermal)].

Electron energy (eV)	Cross section (10 <sup>-21</sup> cm <sup>2</sup> )	Electron energy (eV)	Cross section (10 <sup>-21</sup> cm <sup>2</sup> )
15.27	0.10	15.77	168.3
15.28	0.12	15.78	175.5
15.29	0.13	15.79	181.6
15.30	0.18	15.80	188.7
15.31	0.24	15.81	196.4
15.32	0.34	15.82	204.5
15.33	0.46	15.83	212.0
15.34	0.61	15.84	219.9
15.35	0.82	15.85	227.9
15.36	1.07	15.86	235.0
15.37	1.41	15.87	242.4
15.38	1.81	15.88	249.3
15.39	2.34	15.89	255.4
15.40	2.98	15.90	261.1
15.41	3.82	15.91	267.9
15.42	4.72	15.92	274.8
15.43	5.89	15.93	280.7
15.44	7.23	15.94	286.3
15.45	9.07	15.95	292.5
15.46	10.90	15.96	299.0
15.47	13.10	15.97	304.2
15.48	15.40	15.98	309.3
15.49	18.50	15.99	316.5
15.50	21.90	16.00	323.2
15.51	25.60	16.01	329.0
15.52	29.50	16.02	334.4
15.53	33.4	16.03	340.6
15.54	37.5	16.04	346.7
15.55	42.3	16.05	354.6
15.56	47.6	16.06	363.1
15.57	52.8	16.07	371.8
15.58	58.0	16.08	379.8
15.59	63.4	16.09	387.3
15.50	69.8	16.10	392.8
15.61	75.8	16.11	399.7
15.62	81.3	16.12	406.6
15.63	86.4	16.13	413.5
15.64	92.5	16.14	418.8
15.65	98.5	16.15	425.4
15.66	104.3	16.16	430.6
15.67	110.3	16.17	435.7
15.68	116.6	16.18	440.7
15.69	121.0	16.19	447.2
15.70	125.6	16.20	452.6
15.71	131.7	16.21	458.7
15.72	138.2	16.22	466.3
15.73	143.8	16.23	475.1
15.74	149.6	16.24	483.5
15.75	155.5	16.25	492.0
15.76	161.9		

values of the cross section near threshold versus the ionizing electron energy are recorded in Table I.

### A. Ionization of H<sub>2</sub> through Compound-State Formation

Although we have investigated the possibility of compound-state formation<sup>21</sup> in our data, we have not been able to find any indication that the process, if operative at all, makes any measurable contribution to the cross section. If it were a major contributor, we would have expected to find, in the ionization curve, resonance peaks similar to those found in the elastic

scattering cross sections for H<sup>24</sup> and H<sub>2</sub>.<sup>25</sup> However, we found no evidence of such structure. One must remember, however, that if the resonance structure has a natural width much less than 0.01 eV, our electron-ionization distribution would obscure such structure.

### B. Direct Ionization

The experimental ionization-efficiency curve in Fig. 1 shows none of the marked vibrational structure which has been reported previously.<sup>7,8</sup> Instead, it is apparently without structure (i.e., the usual breaks) except for the slight break which appears near 15.80 eV. This is a general over-all agreement with the work of Briglia and Rapp.<sup>17</sup> However, under close examination, it is possible to detect slight departures from the straight line, which in this instance are statistically real, and as we will show in the next section, are due to auto-ionization. The primary energy scale shown in the figure is derived from the ionization of atomic hydrogen when a nonlinear threshold is used.<sup>1</sup>

If one extrapolates either of the linear segments of

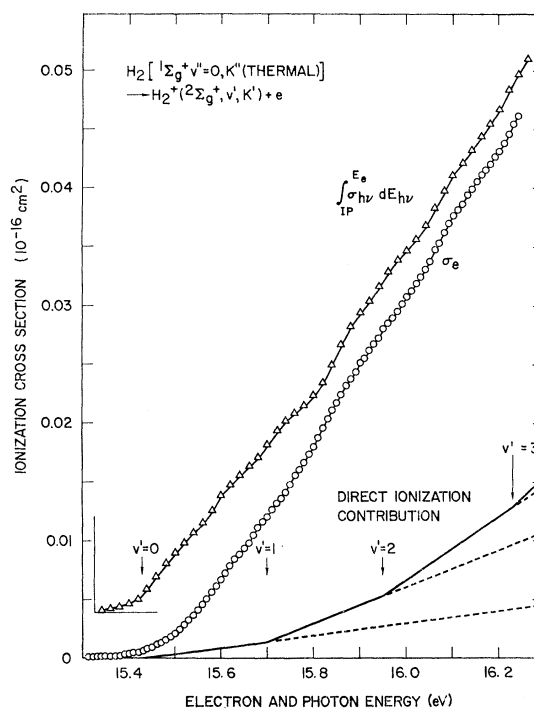


FIG. 1. The ionization cross section for H<sub>2</sub>[<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, v'=0, K''(thermal)] shown with the integrated photo-ionization-efficiency curve of Dibeler, Reese, and Kraus (DRK). Also shown is the lower portion of the direct ionization-efficiency curve estimated from the Franck-Condon factors for H<sub>2</sub><sup>+</sup>. The final slope of this synthetic direct ionization-efficiency curve is made parallel to that of ionization-efficiency curve.

<sup>24</sup> J. Wm. McGowan, E. M. Clarke, and E. K. Curley, Phys. Rev. Letters **15**, 917 (1965); **17**, 66E (1966).

<sup>25</sup> C. E. Kuyatt, S. R. Mielczarek, and J. A. Simpson, Phys. Rev. Letters, **12**, 293 (1964); G. J. Schulz, Phys. Rev. **135**, A988 (1964).

the  $\text{H}_2^+$  ionization-efficiency curve to the electron-energy scale, one finds that neither extrapolation agrees with the spectroscopic values of the ionization potential<sup>12,16</sup> 15.43 eV, thus once again demonstrating the danger in using a simple extrapolation to identify the ionization threshold. The difference between the true ionization potential and the lower extrapolation is 0.04 eV, and the difference between the two extrapolations is another 0.04 eV, leading to a possible compound error of 0.08 eV. In the work of Briglia and Rapp,<sup>17</sup> there was no attempt to identify these fine details, even though they claim an electron-energy distribution very close to our own.

Also in Fig. 1, we show the integral of the photo-ionization data of Dibeler *et al.*,<sup>16</sup> from the ionization potential (IP) to  $E_e$  in comparison with our data. The fine structure which can be seen in our ionization-efficiency curve can also be identified in the integrated-photo-ionization curve. In particular, the break near 15.80 eV is quite clear. Below 15.80 eV the two curves diverge, the integrated-photo-ionization curve lying lower than the electron-impact ionization curve. Also shown in the figure is the ionization-efficiency curve one would expect if only direct vibrational excitation occurred. The energy intervals between the levels are from Herzberg,<sup>12</sup> while the Franck-Condon factors used are calculated.<sup>2-6</sup> Rotation has not been included in our discussion, since the results are approximate, and the conclusions we draw do not depend upon its inclusion.

In order to obtain the estimate of the relative contribution of direct and indirect ionization processes, the slope of the ionization-efficiency curve derived from the Franck-Condon factors was normalized to that of experimental results at 3.0 eV above the ionization threshold. Consider the following: If the slope of the derived curve were made much larger than that for the measured curve, the two ionization-efficiency curves would soon cross, since the linear portions of the two curves, which themselves remain linear over as much as 3 eV,<sup>26</sup> would then intersect. This is not physically realistic. If, instead, the slope of the derived curve were much less than that of the measured curve, the contribution due to the indirect processes would remain unrealistically large as the electron energy increased above the ionization threshold. This is not consistent with what is observed under photon impact,<sup>27</sup> and most

<sup>26</sup> In the case of the ionization of atomic H, it appears that the ionization-efficiency curve is nearly linear over  $\sim 3$  eV. (See Ref. 1.) There is no reason to imagine that the linear portion of the ionization-efficiency curve for each of the vibrational levels (barring rotation) does not extend over a similar interval. It is under this assumption that the estimates are made in Table II. However, the case of  $\text{He}^+$  is somewhat different (unpublished data). Its threshold, too, is nonlinear but over a larger interval than that for H. This is to be expected.

<sup>27</sup> Under photon impact, the contribution to auto-ionization of  $\text{H}_2$  appears to be localized in the first 1.4 eV above the ionization threshold. Although the threshold law for auto-ionization under electron impact is different than that for photon impact, the major contribution is most likely close to threshold, since the direct process is increasing almost linearly, while the contribution from auto-ionization is decreasing or at most nearly constant.

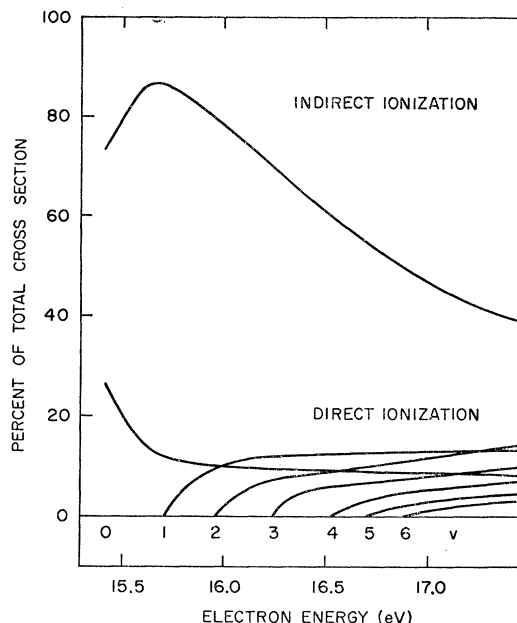


Fig. 2. An estimate of the percentage of the total cross section due to direct vibrational excitation of  $\text{H}_2^+$  and due to indirect ionization primarily through auto-ionization.

likely does not occur here. Therefore, it is reasonable to normalize the slope of the constructed curve to that of the measured curve in order to obtain a first approximation of the contributions from the direct and indirect processes. In Fig. 2, for each electron energy, we estimate the percentage of the total ionization due to indirect processes (primarily auto-ionization), and that fraction due to each of the direct vibration channels, simply by measuring the relative vertical distance between the assumed direct ionization curve and the measured ionization-efficiency curve. In this way we see that the indirect process clearly dominates, and that a Franck-Condon distribution of states is not to be expected until much higher electron energies are used.

In a previous publication,<sup>11</sup> we discussed the possibility of direct rotational excitation of the ion near the ionization threshold. The details of these results depended heavily upon our calibration of the electron-energy scale. When a linear threshold law was used to fix the energy scale, structure appeared below what was identified as the ionization potential of  $\text{H}_2(^1\Sigma_g^+ v''=0, K''=0)$ . It was proposed and crudely demonstrated that this structure, which was very clear in the second-derivative ionization spectrum within the resolution of our apparatus, could have been due to the direct ionization of the various rotational levels,  $K'' \neq 0$ , populated in our room-temperature  $\text{H}_2$  target. A simple model was suggested which gave results which were consistent with them. However, since the electron-energy scale has now been shifted to conform with a nonlinear ionization threshold law for atomic H,<sup>1</sup> the main structure which before was thought to lie below

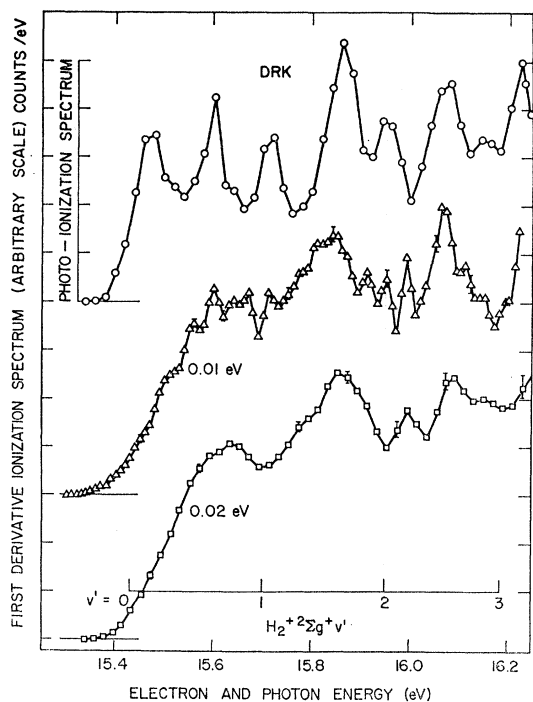


FIG. 3. The first-derivative ionization spectrum of H<sub>2</sub> ( $dH_2^+/dE_e$ ) for two separate runs shown in comparison with the photo-ionization results of Diebler *et al.*, (DRK). The energy resolution in both electron-impact experiments is the same, i.e.,  $<0.06$  eV, but the spacing between data points is different.

the ionization threshold now lies above it and is now found to agree with previous observed auto-ionization levels.<sup>16</sup> Some hint of what may be ionization of a rotationally excited molecule remains. Whether this structure is due to direct or indirect processes is not yet clear.

### C. Auto-Ionization

The second, and largest contributing process to the total ionization cross section of H<sub>2</sub>, is auto-ionization. Estimates of the fraction of the total cross section attributable to direct ionization have been given in Fig. 2, and have been partially discussed in the previous section. The remaining fraction, we contend, results from auto-ionization and from the interference between the direct and indirect processes. Whether or not the contribution from interference to the total signal is large is questionable. The magnitude of the interference will depend upon the physical coupling which exists between the two processes. In the case at hand, the contribution from interference may be completely negligible, because the characteristic lifetime for auto-ionization is different by many orders of magnitude from that for direct ionization<sup>28</sup> This is discussed in the following section.

In Fig. 3, we show the first derivative curves for two sets of data, where each set represents a composite of

<sup>28</sup> This is not the case with regard to elastic scattering resonances where the shape of the resonance depends largely upon the interference between nonresonance and resonance effects.

TABLE II. Structure in first-derivative ionization spectrum of H<sub>2</sub>( $^2\Sigma_g^+$ ,  $v=0, K$ ).

H <sub>2</sub> <sup>+</sup> ( $^2\Sigma_g^+$ ) Vibrational level	Position of peaks-scale based on $n=1.127$ power law in eV	Photo-ionization results		Position of peaks-scale based on linear threshold law in eV
		Dibeler, Reese, and Krauss	Cook and Metzger	
v=0 (15.427 eV)	15.38 <sup>a</sup>	...	...	...
	15.42 <sup>a</sup>	...	15.43	...
	15.47 <sup>a</sup>	15.48 <sup>c</sup>	15.47	15.49
	15.52 <sup>a</sup>	...	15.52	15.54
	15.57 <sup>a,b</sup>	...	...	15.58 <sup>c</sup>
	15.61 <sup>a,c</sup>	15.60 <sup>c</sup>	15.60	15.62
	15.65 <sup>b,d</sup>	...	...	15.65
v=1 (15.72 eV)	15.68 <sup>d</sup>	...	15.69	15.69
	15.72 <sup>a</sup>	15.72	15.73	15.75
	15.78 <sup>d</sup>	...	15.78 <sup>c</sup>	15.79
	15.82 <sup>a,b</sup>	...	...	15.83 <sup>c</sup>
	15.86 <sup>a</sup>	15.86 <sup>c</sup>	15.84	15.89
	15.92 <sup>a</sup>	...	...	15.93
v=2 (15.95 eV)	15.96 <sup>b</sup>	15.94	15.96 <sup>c</sup>	15.97
	16.00 <sup>a</sup>	...	...	16.04 <sup>c</sup>
	16.07 <sup>a,c</sup>	16.08 <sup>c</sup>	16.06	16.09
	16.12 <sup>d</sup>	...	16.12	16.12
	16.15 <sup>d</sup>	16.14	...	16.17
	16.20 <sup>d</sup>	16.22	...	16.23 <sup>c</sup>
v=3 (16.18 eV)	16.27 <sup>a</sup>	16.26 <sup>c</sup>	16.24 <sup>a</sup>	...
		16.32	16.33	...
		16.38	...	...
		...	16.42	...
		16.46	16.47	...
		16.50	...	...

<sup>a</sup> Statistically sound peaks.

<sup>b</sup> Size of peak depends heavily on few data.

<sup>c</sup> Major peaks in spectra.

<sup>d</sup> Statistically questionable peaks.

many runs. The data points for the lower curve were taken at 0.02-eV intervals and for the middle curve at 0.01 eV. The upper curve is the photo-ionization results of Dibeler *et al.*<sup>16</sup> There are obvious similarities and differences between the two sets of our data. The lower curve appears to be an unresolved version of the middle, even though in both cases, the energy resolution of the electron beam is the same. The lack of definition in the lower curve reflects in part, the smearing which results from the superposition of a number of data which are slightly out of register. In effect, this lack of definition is a result of the coarseness of the energy grid. From a cursory examination, it appears that an even finer energy mesh than 0.01 eV is desirable. Some smearing also results from mathematical smoothing of the data. This has already been discussed in Sec. III.

The positions of the peaks in the middle curve of Fig. 3 are listed in Table II with reference to two experimental energy scales.<sup>29</sup> The scale in the figure and the third column in the table are obtained when a nonlinear threshold law for ionization of atomic H is

<sup>29</sup> The peaks in the first-derivative ionization spectrum are expected to correspond to the excitation potentials of the auto-ionizing states because the law governing the excitation is likely to approach  $(E_e - E_x)^{1/2}$  (or a step function), the derivative of which goes to infinity when  $E_e \approx E_x$ .

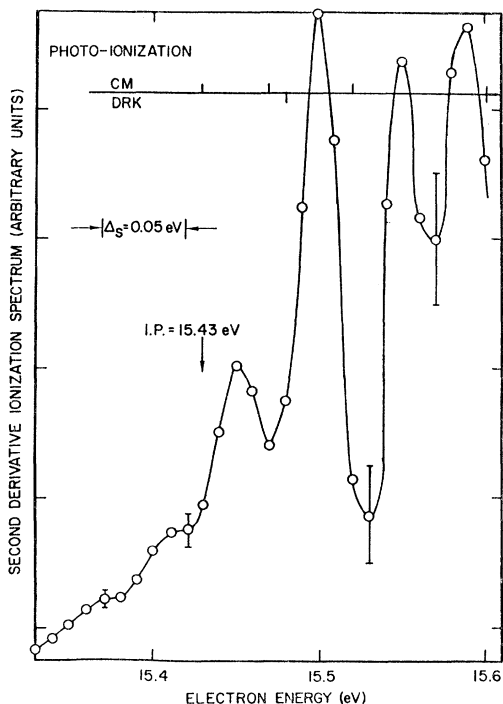


FIG. 4. The second-derivative ionization spectrum of  $H_2$  ( $d^2H_2^+/dE^2$ ). The electron-energy scale is that derived from the nonlinear dependence of the ionization threshold of atomic hydrogen. Most of the structure to the right of  $IP = 15.43$  eV for  $H_2$  ( $\Sigma_g^+, v''=0, K''=0$ ) can be related to auto-ionization peaks identified by Cook and Metzger (CM) or Dibeler, Reese, and Krauss (DRK). That to the left is statistically questionable but may result from the thermal distribution of the rotational levels of  $H_2$  which would form ionization peaks below the IP either through direct rotational excitation of the ion or through auto-ionization.

used for calibration, while the upper scale and the right-hand column give the positions derived when a linear-threshold law is used. It is clear in Table II that the fit in the third column leads to better agreement between the experiment and the photo-ionization results given in the Table. In particular, note that when the nonlinear-threshold law is used to calibrate the  $H^+$  scale, the prominent maxima in the electron-impact spectrum agree extremely well with those in the photo-impact spectrum of Dibeler *et al.* Note also that the positions of the vibrational level can be assigned to each of the major valleys in the curve. The reason for this is not clear. In Table II, the results are separated into sections associated with the bumps in the first-derivative ionization spectrum.

The energy resolution of the electrons used in our electron-impact research compares well with the energy resolution of the photons used by Dibeler and co-workers.<sup>16</sup> However, the photoresolution used by Cook and Metzger<sup>15</sup> is nearly four times better. There is substantially no difference between these two results as to the position of peaks, but there is marked difference with regard to peak magnitude.

In column 2 of Table II, we give some indication of the reliability of our various experimental peaks. This is primarily based upon whether or not the peak lies within the statistical limits, although some further weight is given to the reproducibility of the peak in all of the individual runs. For example, the peak or near-peak at 15.65 eV is likely not to be real, although it is identifiable in most of the experimental runs which make up our final data. On the other hand, the peaks at 15.38, 15.42, 15.52, and 16.00 eV, which have no equivalent in Dibeler's data, are real. The peaks most likely result from processes which are not allowed under photon impact: processes such as excitation through electron exchange, magnetic dipole, and multipole excitation of the molecule.

It is significant that the over-all trend in peak heights associated with electric dipole transitions, which is apparent in photo-ionization, also appears in the first-derivative electron-impact ionization spectrum. This situation, which is evident not only in  $H_2$ , but also in  $O_2$ ,<sup>30</sup> and  $N_2$ ,<sup>31</sup> strongly suggest that for photon impact, the production of excitation probability times the probability of the excited intermediate auto-ionizing is simply related to the derivative of this product for electron impact, e.g.,

$$d\sigma_e/dE_e \propto \sigma_{h\nu}$$

This has also been repeatedly observed in the past by Morrison and co-workers.<sup>32</sup>

In Fig. 4, we show the second derivative of the  $H_2^+$  ionization-efficiency curve through the first 0.2 eV, with the scale shifted to correspond to the nonlinear-threshold law for the ionization of atomic hydrogen. The data shown in this curve have been published in the past, but the energy scale has here been shifted to correspond with the new energy calibration. If the structure above the ionization threshold is now properly identified as due to auto-ionization,<sup>33</sup> then, in the figure, the center of the auto-ionization peak should correspond to the center of the dispersionlike curve. This indeed appears to be the situation for auto-ionizing peaks at 15.47 and 15.52 eV and probably for 15.42 eV, which is very close to the ionization threshold. The hint of a peak at approximately 15.38 eV, below the ionization threshold, combined with the structure near 15.42 eV, may be all that can be associated with the thermal rotational distribution in the target  $H_2$  molecule.

<sup>30</sup> J. Wm. McGowan, E. M. Clarke, H. P. Hanson, and R. F. Stebbings, *Phys. Rev. Letters* **13**, 620 (1964).

<sup>31</sup> M. A. Fineman, E. M. Clarke, H. P. Hanson, and J. Wm. McGowan, in *Proceedings of the Fourth International Conference on Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters Inc., Hastings-on-Hudson, New York, 1965), p. 426.

<sup>32</sup> J. D. Morrison, *J. Chem. Phys.* **40**, 2488 (1964); F. H. Dorman, J. D. Morrison, and A. S. C. Nicholson, *ibid.* **32**, 378 (1960).

<sup>33</sup> With the present interpretation of this spectrum, it appears clear that if we take the width of the dispersionlike curve in the second derivative as an indication of the energy distribution, the width agrees very well with our measured width of nearly 0.05 eV.

#### D. Lifetime of H<sub>2</sub> Auto-Ionizing States

It is significant that the ionization-efficiency curves obtained with 127 deg electrostatic electron selectors in different laboratories, with different experimental arrangements apparently do not agree. In low-density molecular-beam experiments, auto-ionization is the dominant ionization mechanism for all diatomic molecules thus far studied.<sup>11,30,31,34</sup> However, it is generally found in experiments where a closed ionization chamber is used that linear segments dominate the ionization-efficiency curves for H<sub>2</sub><sup>+</sup>,<sup>7,8,35</sup> D<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>+</sup>, and O<sub>2</sub><sup>+</sup><sup>36-38</sup>. These segments (or curvature which can be related to segments) are normally assigned to direct vibrational excitation of the product ion since the intervals between the onsets of the segments normally correspond to the intervals between the vibrational levels of the ion. However, it is only in the case of H<sub>2</sub><sup>+</sup> that the relative slopes of these segments appear to agree with the relative values of the Franck-Condon overlap integrals associated with the ionization of the different vibrational levels.

It is not clear what discriminatory process apparently distorts the results of the closed-box experiments so that varying amounts of auto-ionization are observable in the results of different experiments. However, it is clear that for discrimination to be important the excited molecules which subsequently auto-ionize must be long lived in order that they may be either quenched by collision or drift from the focal plane of the weak ion lens which are used. If indeed the lifetime is long and is the important parameter, then we would estimate it to be between 1.0 and 0.1  $\mu$ sec.<sup>39-41</sup>

If the above implications are correct, and the auto-ionizing lifetime of a particular state of H<sub>2</sub><sup>\*</sup> is long, then

<sup>34</sup> J. Wm. McGowan (unpublished).

<sup>35</sup> By using an open-ended box based on a de Laval nozzle, D. Keenan and E. M. Clark [ASTM E-14, Dallas, May 1966 (unpublished)] obtained an ionization cross-section curve for H<sub>2</sub><sup>+</sup> which shows strong auto-ionization and whose first-derivative plot is nearly identical to the bottom curve of Fig. 2.

<sup>36</sup> J. D. Carette and L. Kerwin, *Rev. Sci. Instr.* **36**, 537 (1965).

<sup>37</sup> P. Marmet and J. D. Morrison, *J. Chem. Phys.* **36**, 1238 (1962); and the thesis of Paul Marmet, Department of Physics, Laval University, 1960 (unpublished).

<sup>38</sup> C. Brion, *J. Chem. Phys.* **40**, 2995 (1964).

<sup>39</sup> In Berry's recent calculation, the method of calculation used cannot give an accurate indication of this lifetime since no allowance is made for the distortion of the H<sub>2</sub><sup>+</sup> core.

<sup>40</sup> The higher states of atomic H are long-lived [H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1958)]. By analogy, the upper Rydberg states of H<sub>2</sub> are probably long-lived. Evidence for this can be found in the intensity distribution of the spectral lines of H<sub>2</sub> (see Herzberg, Ref. 12).

<sup>41</sup> Recent calculations by Krauss (private communication) have shown the *B*, *B'*, *C*, *D*, and *D'* states of H<sub>2</sub><sup>\*</sup> to have radiative lifetimes lying between 10<sup>-8</sup> and 10<sup>-10</sup> sec, too short to fit the picture suggested herein. Some of the above states have tentatively been identified as auto-ionizing states. However, the bulk of the auto-ionizing levels have not yet been identified.

not only is the radiative lifetime of the state long, i.e., comparable to that for auto-ionization, but the lifetime toward predissociation must be long as well.

#### V. SUMMARY

One of the most surprising discoveries of this study has been the marked similarity that exists between the photo-ionization and the first-derivative electron-impact ionization spectra of H<sub>2</sub>. Although one cannot extract from our present data a meaningful one-to-one correspondence for the peak heights, there is every indication that this exists. As one would expect, there are extra auto-ionization peaks in the electron-impact spectrum which no doubt correspond to optically forbidden transitions allowed under electron impact.

Although there is little hint of direct vibrational excitation in the ionization-efficiency curve, there is very marked structure in the first derivative of this curve which relates to the known vibrational spacing of H<sub>2</sub><sup>+</sup>. It is clear from our present study that the structure we originally identified in the very threshold region is primarily due to auto-ionization and not to direct rotational excitation of the ion. The nature of the identified structure which remains after the lower auto-ionizing peaks are identified is at the moment uncertain, although there is every reason to expect that it reflects the rotational distribution of the target molecule.

The glaring discrepancies which exist between our results for ionization of H<sub>2</sub>, as well as D<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, and the other high-resolution studies in closed boxes, are still not completely resolved; however, it would seem that the closed-box ionization studies somehow universally tend to suppress auto-ionization or the ions formed through auto-ionization. From our analysis we conclude that the lifetime of the auto-ionizing levels in H<sub>2</sub> can be long, of order 10<sup>-7</sup> to 10<sup>-6</sup> sec, which suggests that the states involved are primarily long-lived Rydberg states rather than lower-lying, shorter-lived states.

Considerable theoretical<sup>42</sup> and parallel experimental work is needed before the ionization thresholds of both H and H<sub>2</sub> are completely understood. In the case of H<sub>2</sub>, no doubt, high-resolution photo-ionization experiments<sup>43</sup> will prove most useful as a test of theoretical details, since even the best resolution available today

<sup>42</sup> Calculations by J. C. Y. Chen and N. F. Lane presented at the Fifth International Conference on Physics of Electronic and Atomic Collisions, Leningrad, July 1967 (to be published).

<sup>43</sup> Since this paper has been submitted for publication, high-resolution photo-ionization experiments with H<sub>2</sub> have been reported at American Physical Society meetings by W. A. Chupka, *Bull. Am. Phys. Soc.* **12**, 273 (1967) and J. Berkowitz, *ibid.* **12**, 515 (1967).



in electron-impact studies cannot hope to resolve clearly the rotational structure or determine the widths of auto-ionization lines. Although there does not appear to be a simple theoretical relationship between photoionization and electron-impact ionization of H (1s), it does experimentally appear to exist for all the simple diatomic molecules considered thus far, H<sub>2</sub>, D<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NO, and CO.

#### ACKNOWLEDGMENTS

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### Correlation Energies of the Lithium Sequence

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The nonrelativistic eigenvalues of the  $1s^2 2p \ ^2P$  states of the lithium sequence are calculated to be  $E(Z) = -1.125Z^2 + 1.09352614Z - 0.52717136 + O(Z^{-1})$  a.u., where  $Z$  is the nuclear charge; and the energy of the  $1s^2 2p \ ^2P - 1s^2 2s \ ^2S$  transition is calculated to be  $\Delta E(Z) = 0.07072093Z - 0.11902237 + O(Z^{-1})$  a.u. For large nuclear charges, the addition of a  $2p$  electron to the  $1s^2 \ ^1S$  core increases the magnitude of the correlation energy by 0.30 eV to give a value of 1.57 eV, most of which arises from the electron-pair energies.

#### 1. INTRODUCTION

WE have recently calculated the nonrelativistic eigenvalue of the  $1s^2 2s \ ^2S$  states of the lithium sequence as a series in inverse powers of the nuclear charge  $Z$ , using a method that expresses the correlation energy as a weighted sum of electron-pair energies and certain single-electron nonadditive terms.<sup>1</sup> The addition of the  $2s$  electron to the  $1s^2 \ ^1S$  core increases the magnitude of the correlation energy by 0.19 to 1.46 eV, most of which arises from the pair energies.

The method can be extended to states of higher angular momentum and in particular to the  $1s^2 2p \ ^2P$  states of the lithium sequence.

#### 2. THEORY

We choose a set of units in which the scale of distance is  $Z$  atomic units (a.u.) and the scale of energy is  $Z^2$  a. u. If  $\mathbf{r}_i$  is the position vector of the  $i$ th electron, the Hamiltonian is given by

$$H = H_0 + V/Z, \quad (1)$$

where

$$H_0 = -\frac{1}{2} \sum_{i=1}^3 \nabla_i^2 - \sum_{i=1}^3 \frac{1}{r_i} \quad (2)$$

and

$$V = \sum_{i < j}^3 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3)$$

Then to second order in  $Z^{-1}$ , the energy  $E$  is given by

$$E(Z) = Z^2 E_0 + Z E_1 + E_2, \quad (4)$$

where

$$E_1 = \langle \psi_0 | V | \psi_0 \rangle, \quad (5)$$

$$E_2 = \langle \psi_0 | V - E_1 | \psi_1 \rangle, \quad (6)$$

$\psi_0$  and  $\psi_1$  being the well-behaved solutions of

$$(H_0 - E_0)\psi_0 = 0, \quad (7)$$

$$(H_0 - E_0)\psi_1 + (V - E_1)\psi_0 = 0. \quad (8)$$

The solution of (8) is

$$\begin{aligned} \psi_1(1s^2 2p \ ^2P) = & \alpha \left[ \frac{1}{3} \sqrt{3} \{ \psi_0(2p \ ^2P), \psi_1(1s^2 \ ^1S) \} \right. \\ & - \left. \left( \frac{1}{6} \sqrt{6} \right) \{ \psi_0(1s^2 \ ^2S), \psi_1(1s2p \ ^1P) \} \right. \\ & \left. + \frac{1}{2} \sqrt{2} \{ \psi_0(1s^2 \ ^2S), \psi_1(1s2p \ ^3P) \} \right], \quad (9) \end{aligned}$$

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<sup>1</sup> C. D. H. Chisholm and A. Dalgarno, Proc. Roy. Soc. (London) **A292**, 264 (1966).