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Identification of Energy Levels of Negative Ions*

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Levels of He$^-$ at 57.1 and 58.2 eV and of Hg$^-$ at 4.0_7, 4.2_9, and 4.8_9 eV, whose observation is described in an accompanying paper, are identified spectroscopically as $2s^22p\ ^2P$, $2s2p^2\ ^2D$, $6s6p^2\ ^4P_{1/2,3/2,5/2}$, respectively. The identification procedure, which combines elements of spectroscopy and collision theory, is described.

A LARGE number of resonances in the transmission of monoenergetic electrons through gases and vapors have been observed by Simpson and collaborators.[1] These resonances appear as sharp irregularities in the plots of transmitted current versus electron energy. They are attributed to the reversible formation of a negative ion according to the reaction scheme

$$e+A \rightarrow A^- \rightarrow e+A\,, \tag{1}$$

which becomes likely when the energy of $e+A$ in the initial state coincides with an energy level of the bound system A^-. Such energy levels are not defined very sharply because they correspond to autodissociating states, but level widths ranging from ~0.1 to ~0.001 eV have proved adequate for detection with present techniques.

Since additional levels are likely to be discovered in the future, some interest attaches to the spectroscopic identification of the levels observed through process (1). This problem can be solved at times by elementary considerations of spectroscopy and collision theory, but the interplay of such considerations is still somewhat novel in atomic and molecular physics, though rather familiar in nuclear physics. Therefore it might be worthwhile to outline relevant classification criteria in the context of some specific examples. For this purpose we shall consider resonances observed in the collisions of 55–60-eV electrons with He and of 4–5-eV electrons with Hg. Figures 1 and 2 reproduce tracings of transmitted current versus electron energy from Ref. 1; the observed current consists of electrons which have traversed He and Hg gas cells, respectively, emerging with energy within ~0.03 eV and direction within ~0.7° of the incidence conditions. Two resonant states of He$^-$ appearing at 57.1 and 58.2 eV and three states of Hg$^-$ between 4 and 5 eV are considered here.

The following three main criteria have been utilized thus far in the classification process; their application to an He$^-$ problem is indicated schematically in Fig. 3. These criteria will have to be supplemented by angular-distribution studies or other evidence where they prove inadequate.

(*1*) *Restrictions on the quantum numbers* of the initial, dissociated state $e+A$. Since A represents the ground state of an atom which is ^1S for both He and Hg, the LS states of $e+A$ belong necessarily to the doublet class and have parity $(-1)^l$, where l is the orbital quantum number of the incident electron. Therefore, the initial state of $e+A$ is restricted to the "parity favored" classes $^2S_{1/2}$, $^2P^\circ{}_{1/2,3/2}$, $^2D_{3/2,5/2}$, $^2F^\circ{}_{5/2,7/2}$, etc. These classification symbols are entered in the list of "available input channels" of Fig. 3, where the letter k plays the same role for a continuum state as the quantum number n for discrete levels. The parity and the total J quantum number of the input channel are invariant in the collision; therefore they must be equal for the input channel and for the A^- level. On the other hand the multiplicity $2S+1$ and the L quantum number are conserved only insofar as LS coupling prevails; specifically they should be conserved for He, but not for Hg.

(*2*) *Listing of the possible relevant configurations* of A^- and of the terms of each configuration and estimation of the relative energies and terms by spectroscopic theory. It is understood from Ref. 1 that the relevant configurations arise from the addition of the incident electron to the outermost partially occupied shell of an excited state of the atom A^* and that the electron

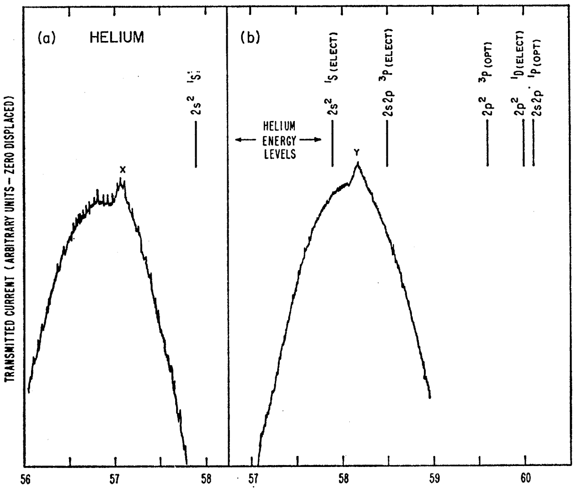

Fig. 1. Resonances in transmission in He (from Ref. 1).

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* The substance of this paper was presented as Paper HA10 at the Philadelphia American Physical Society Meeting, March 25, 1964.

[1] C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. 138, A385 (1965). This accompanying paper contains references to earlier literature.

affinity of A^* is small, generally less than 1 eV.[2] For example, states He* in the range of interest ~58 eV have both electrons in the second shell; therefore, the relevant configurations of He^- have *all three electrons* in this shell. The configurations of 3 electrons with $n=2$ are listed in the central column of Fig. 3, with all their terms arranged from bottom to top in the presumable order of increasing energy (see the experimental data for these terms in the B spectrum[3] and the calculations of Wu and Shen[4] for Li). Terms listed here that do not appear in the adjacent list of "available input channels" are crossed off. The corresponding data for Hg^- will be given below.

(*3*) *Relationship to thresholds for inelastic reactions*

$$e+A\rightarrow e+A^*. \tag{2}$$

As noted above, the relevant configurations of A^- can be regarded as derived from the addition of an electron to the outermost partially occupied shell of an excited state A^*. Thus they may be regarded as belonging to discrete spectra whose extension into the continuum is represented by $e+A^*$. One may also consider elastic scattering from an excited state, according to the reaction scheme $e+A^*\rightarrow e+A^*$ and extrapolate the parameters of this process to negative kinetic energies of the relative motion of e and A^*. The A^- states emerge then as bound states of the $e+A^*$ combination (see, e.g., Dalitz's review articles on scattering theory[5]). The correspondence pertains, of course, to states of $e+A^*$ which have the same parity and angular momentum as A^-, as well as the same values of any other "good" quantum numbers of angular momentum. Often several "channels" corresponding to different excited states $e+A^*$, $e+A^{*\prime}$, $\cdots$ have relevant quantum numbers equal to those of a state of A^-; then this state appears to result from alternative paths of formation. This circumstance is akin to resonance among bond structures in chemistry in that the bound state may be regarded as a superposition of A^*+e, $A^{*\prime}+e$, etc.; accordingly the electron affinity of A^*, $A^{*\prime}$, $\cdots$, should be increased and the energy of A^- levels should be lower than it would be if there were a single level A^*.

When many levels of A^- belong to a single configuration, the upper ones among them may lie above the inelastic threshold of reaction (2) so that the reaction

$$e+A\rightarrow A^-\rightarrow e+A^* \tag{3}$$

is energetically possible. The second step of this reaction may then be very rapid so that one or more levels of A^- are broadened to the point of escaping detection. Alternatively, the dissociation $A^-\rightarrow A^*+e$ may be slowed down by one circumstance or another so that the resonance remains sharp. An example of this type probably occurs in Hg^-, as noted below.

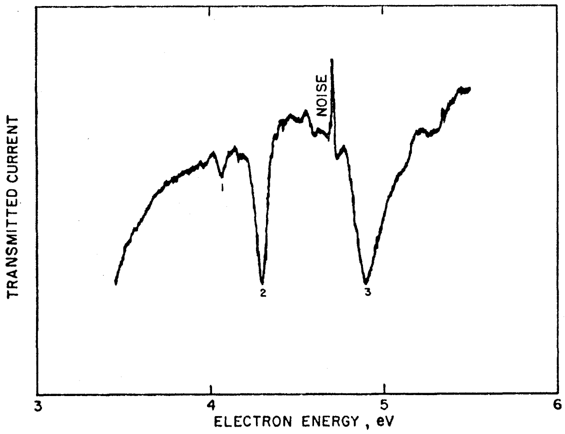

Fig. 2. Resonances in transmission in Hg (from Ref. 1).

He⁻ levels at 57–58 eV. Inspection of the information assembled in Fig. 3 makes the identification of the two resonances of He at 57.1 and 58.2 eV rather straightforward and dependable. The resonance at 57.1 is the only one that lies below the lowest inelastic threshold in its proximity, namely, the ($2s^2\,{}^1S$) threshold at 57.9 eV. The lowest configuration of 3 electrons with $n=2$, namely, $2s^22p$, is also the only one that can be associated with this threshold and yields a single term ${}^2P°$. Therefore, it appears very likely that He^- has a 57.1-eV term with the quantum numbers $2s^22p\;{}^2P°$; more accurately, the observed resonance appears to pertain to a pair of unresolved levels that constitute the doublet ${}^2P°_{1/2,3/2}$. The further association of the $2s^22p$ configuration with the threshold $2s2p\;{}^3P°$ at 58.4 eV probably contributes to lowering the He^- level so that it lies as much as 0.8 eV below the next He* threshold.

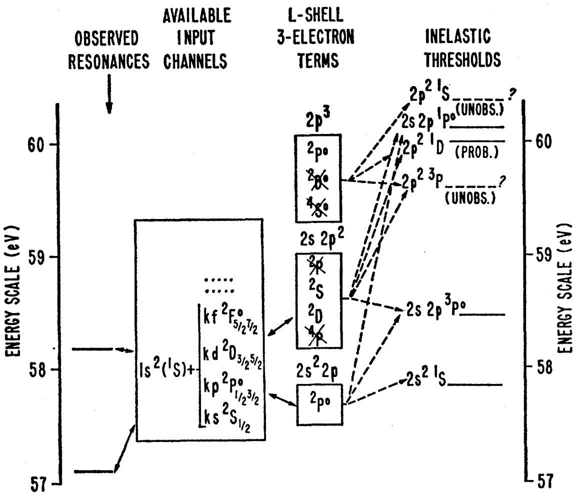

Fig. 3. Available states and channels for e+He.

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[2] The presumable electron affinity of excited states A^* has been emphasized long ago by J. Franck and W. Grotrian, Z. Physik 4, 89 (1921).

[3] C. M. Sitterly, Natl. Bur. Std. (U. S.) Circ. 467 (1949).

[4] T. Y. Wu and S. T. Shen, Chinese J. Phys. 5, 150 (1944).

[5] R. H. Dalitz, Ann. Rev. Nucl. Sci. 13, 339 (1963); Rev. Mod. Phys. 33, 471 (1961).

The second $e+\mathrm{He}$ resonance in this range lies above the $2s^2$ level of He*, but still below the $2s2p\ {}^3P^\circ$ and belongs probably to the next higher configuration of He$^-$, namely, $2s2p^2$. The lowest and the highest terms of this configuration, namely, ${}^4P$ and ${}^2P$, are exluded for the reasons indicated under (2) above. The lower one of the two remaining terms, namely, ${}^2D$ is then the principal candidate for identification with the resonance under consideration. One would then expect the next higher term, ${}^2S$, to lie above the $2s2p\ {}^3P$ threshold and to be broadened beyond present detection capability. The small stability of the 58.2 level of He$^-$ with respect to the 58.4-eV threshold (that is, the small apparent affinity of the 58.4-eV He*) is not surprising in view of the fact that ${}^2D$ is only the second lowest term of the configuration $2s2p^2$.

The 58.2-eV resonance might actually belong to ${}^2S$, in which case the ${}^2D$ resonance would presumably lie further below and have accidentally escaped detection. It is also conceivable that the anomaly at 58.2 eV is not a resonance at all, but corresponds to the threshold of excitation of $2s2p\ {}^3P$ at 58.4 eV. This interpretation would require an error of 0.2 eV in the estimated energies. Since the estimated error is ±0.1 eV, this is unlikely.

Hg$^-$ levels at 4–5 eV. The levels of Hg* in the energy range of interest belong to the configuration $6s6p$ and are ${}^3P^\circ{}_{0,1,2}$ between 4.67 and 5.46 eV and ${}^1P^\circ{}_1$ at 6.7 eV. The configurations $6s^2$, $6s6d$, $6p^2$, and $6s7s$ lie several eV away; different subshells should really be treated separately rather than as parts of a single shell when they are separated by several eV as they are in Hg. Therefore, it appears very probable that the levels of Hg$^-$ under consideration, at 4.0_7, 4.2_9, and 4.8_9 eV, belong to the configuration $6s6p^2$.

This configuration has four terms, like the configuration $2s2p^2$ in Fig. 3, with the levels ${}^4P_{1/2,3/2,5/2}$, ${}^2D_{3/2,5/2}$, ${}^2S_{1/2}$, ${}^2P_{1/2,3/2}$. In the Hg spectrum, the separations of the fine structure levels ${}^3P^\circ{}_{0,1,2}$ amount to 0.2 and 0.6 eV, whereas their center of gravity lies 2.1 eV below ${}^1P^\circ{}_1$; intercombination transitions between triplets and singlets are rather intense. Therefore, no serious obstacle should be encountered in forming ${}^4P_{1/2,3/2,5/2}$ levels of Hg$^-$ from the ${}^2S_{1/2}$ and ${}^2D_{3/2,5/2}$ channels of $e+\mathrm{Hg}$. In fact, it is suggested that the resonances shown in Fig. 2 actually correspond to the three ${}^4P$ levels of Hg$^-$. Levels isoelectronic to them are known in the optical spectrum of Tl; their separations, $E_{J=3/2}-E_{J=1/2}=0.57$ eV and $E_{J=5/2}-E_{J=3/2}=0.40$ eV are comparable to those of the Hg$^-$ resonances in order of magnitude but different in ratio. The same levels are also known in the spectra of Pb$^+$ and Bi^{++}. Extrapolation along the isoelectronic sequence to obtain a rather definite prediction for the positions of these three levels in Hg$^-$ does not prove straightforward or dependable because of configuration interactions in some of the spectra. Levels of the other terms of the configuration $6s6p^2$, namely, ${}^2D$, ${}^2S$, and ${}^2P$, are known in the spectra isoelectronic to Hg$^-$ and lie a few eV higher than the ${}^4P$ levels. The corresponding levels of Hg$^-$ may, therefore, be altogether unstable toward dissociation into $e+\mathrm{Hg}^*$ ($6s6p\ {}^3P^\circ$). These considerations provide some confidence in the suggested identification for Hg$^-$:

$$4{,}0_7\ \mathrm{eV}=6s6p^2\ {}^4P_{1/2},\ 4.2_9\ \mathrm{eV}=6s6p^2\ {}^4P_{3/2},\quad 4.8_9=6s6p^2\ {}^4P_{5/2}.$$

The three resonances, which are thus attributed to the ${}^4P$ term, have quite different profiles as seen in Fig. 2; indeed, the detection of the lowest one offered some difficulty. This difference, which might be surprising at first sight, is regarded as an interesting consequence of a difference of input channels. A ${}^4P_{1/2}$ resonance with *even* parity must occur in the ${}^2S_{1/2}$ channel of $e+\mathrm{Hg}$, whereas ${}^4P_{3/2,5/2}$ resonances must occur in the ${}^2D_{3/2,5/2}$ channels. The shape of the ${}^2S_{1/2}$ resonance—with a slight excess of transmission followed by a somewhat larger dip—and its smallness indicate that the phase shift of s-wave elastic scattering near resonance lies at $\sim150°$ (modulo 180°) and that the resonance is much narrower than the instrumental resolving power.[6] The shape and the well-resolved width of the ${}^2D_{3/2,5/2}$ resonances indicate, instead, that the phase shift of d-wave elastic scattering near resonance is $\sim10°$ (modulo 180°) and that the resonances are quite broad.

Notice that the ${}^4P_{5/2}$ resonance lies above the ${}^3P_0{}^\circ$ Hg* threshold and practically coincides with the ${}^3P_1{}^\circ$ threshold. However, in a reaction

$$e+\mathrm{Hg}\rightarrow\mathrm{Hg}^-\rightarrow e+\mathrm{Hg}^*,\tag{4}$$

with $\mathrm{Hg}^-={}^4P_{5/2}$ and $\mathrm{Hg}^*={}^3P_0{}^\circ$, the electron should emerge in a $kf_{5/2}$ high-angular momentum state. Similarly the final electron state should be $kp_{3/2,5/2}$ when $\mathrm{Hg}^*={}^3P_1{}^\circ$. The centrifugal forces associated with these angular momenta reduce the transition amplitudes of reaction (4) at the position of the resonance sharply, so that their influence on the resonance shape of reaction (1) may remain undetected.

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[6] J. A. Simpson and U. Fano, Phys. Rev. Letters **11**, 158 (1963).