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DISSOCIATION ENERGY AND IONIZATION POTENTIAL OF MOLECULAR HYDROGEN

G. Herzberg
Division of Pure Physics, National Research Council of Canada, Ottawa, Canada

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The small discrepancy between experimental and theoretical values for the dissociation energies of H_2, HD, and D_2 has been resolved by new measurements of the ultraviolet absorption limits of these molecules. In addition, the ionization potential of H_2 has been more accurately determined from Rydberg series. The agreement between theory and experiment must be considered very satisfactory.

Nine years ago Monfils and I[1] obtained improved experimental values for the dissociation energies of H_2, HD, and D_2 from measurements of the onset of continuous absorption of the $B'^1\Sigma_u{}^+$-$X^1\Sigma_g{}^+$ transition near 850 Å. The values obtained were in excellent agreement with theoretical values derived at the same time by Kołos and Roothaan,[2] but more recent refinements of the calculations by Kołos and Wolniewicz[3] and others have led to theoretical values that are about 4 cm^{-1} larger than the experimental ones. In order to ascertain whether this discrepancy is caused by errors in the experimental determinations the absorption spectrum of hydrogen was reinvestigated with appreciably higher resolution than previously available, using the second order of the 10.5-m vacuum spectrograph of this laboratory (reciprocal dispersion 0.39 Å/mm). In addition, in order to remove overlapping lines of other electronic transitions as much as possible, the observations were carried out with the hydrogen at liquid-nitrogen temperature. At this temperature there are for H_2 less than 1% and for D_2 less than 20% of the molecules in rotational levels with $J > 1$. For para-H_2 this means, since there are no molecules in the levels $J=1, 3, \cdots$, that 99% of the molecules are in the lowest rotational level $J=0$.

The new experiments show that the earlier results were affected more seriously than was realized at the time by unresolved or unrecognized overlapping lines belonging to other electronic transitions. For para-H_2 even at liquid-nitrogen temperature a fairly strong line (probably belonging to $C^1\Pi_u$-$X^1\Sigma_g{}^+$) occurs near the absorption limit for $J''=0$ (near 850 Å), making an exact determination of this limit impossible. However, fairly close upper and lower bounds have been obtained. For D_2 and HD good limits free from overlapping have been observed which give directly, after subtraction of the H or D excitation energy and a very small correction for the rotational barrier in the upper state, the dissociation energies of the ground state. The experimental values obtained in this way are given in the second column of Table I and are compared with the latest theoretical values of Kołos and Wolniewicz[3] in the third column. In the fourth column slightly revised theoretical values are given which were obtained by Bunker[4] by adding corrections for nonadiabatic effects to the results of Kołos and Wolniewicz.

Only an upper and a lower bound can be given for the experimental $D_0{}^0(H_2)$ value. For HD two independent values are obtained from the two observed limits which correspond to $H+D^*$ and

Table I. Experimental and theoretical values of the dissociation energies of H_2, HD, and D_2 (in units of cm^{-1}).

	D_0^0		
		Theoretical values	
	Observed	KW[a]	Bunker[b]
H_2	<36 118.3 (>36 116.3)	36 117.4	36 117.9
HD	36 406.6 36 405.8	36 405.2	36 405.5
D_2	36 748.9	36 748.0	36 748.2

[a] Kołos and Wolniewicz, Ref. 3.
[b] Bunker, Ref. 4.

$H^* + D$. It appears likely that the lower of these two values is to be preferred.

It is seen from Table I that there is essential agreement between experiment and theory within less than 1 cm^{-1}. The experimental values are slightly larger than the theoretical values. These small differences are probably significant since the error in the absorption limits is estimated to be less than ±0.4 cm^{-1}. The deviations suggest that the calculations have not yet reached complete convergence.

At shorter wavelengths, on the same plates Rydberg series are observed which allow an accurate determination of the ionization potential. Up to now they have been studied in detail only for H_2. For para-H_2 at low temperature ($J''=0$ only) there are two series with different limits for each value of the vibrational quantum number v of the ion. The two series correspond to the $R(0)$ lines of the transitions $np\ {}^1\Sigma_u^+ - X^1\Sigma_g^+$ and $np\ {}^1\Pi_u - X^1\Sigma_g^+$; the two limits correspond to $N=0$ and $N=2$ of the H_2^+ ion (N = total angular momentum apart from spin); they are separated by about 180 cm^{-1} ($\approx 6B_{\text{ion}}$). The first series ($N=0$) is perturbed by the lower members of the second. These perturbations make a precise determination of the series limit difficult. However, using a theoretical formalism, developed by Fano,[5] for the two mutually perturbing series it was possible to get reliable values for the $v=0, 1, 2$ series limits. They are listed in Table II. Confirmation of these limits is obtained from the $Q(1)$ lines of the $np\ {}^1\Pi_u - X^1\Sigma_g^+$ bands which are observed in ordinary hydrogen at liquid-nitrogen temperature. These limits are given in the third column of Table II.

The averages of the Rydberg limits derived from the $R(0)$ and $Q(1)$ series are given in the fourth column of Table II. The first of these, for $v=0$, represents a reliable experimental value for the ionization potential of H_2, namely, 124 418.4 cm^{-1} or 15.425 56 eV. The differences between the $v=0$, 1, and 2 limits give precise values for the vibrational differences $\Delta G(\frac{1}{2})$ and $\Delta G(\frac{3}{2})$ of the ground state of the ion. The ΔG values, together with the ionization potential of molecular hydrogen [$I(H_2)$], are listed in Table III and compared with the latest theoretical values (Kołos,[6] Jeziorski and Kołos,[7] and Hunter and Pritchard[8]). The dissociation energy of H_2^+ is immediately obtained from the ionization potential and dissociation energy of H_2, and its upper and lower bounds corresponding to those of $D_0^0(H_2)$ are included in Table III. The agreement between the experimental and theoretical values of $I(H_2)$, $D_0^0(H_2^+)$, $\Delta G(H_2^+)$, as in the case of $D_0^0(H_2, HD, D_2)$, is

Table II. Observed Rydberg limits in H_2 (in units of cm^{-1}).

v_{ion}	From $R(0)$ lines of $np\sigma\ {}^1\Sigma_u^+ - X'\Sigma_g^+$	From $Q(1)$ lines of $np\pi\ {}^1\Pi_u - X^1\Sigma_g^+$	Weighted average
0	124 418.3	124 418.5	124 418.4
1	126 609.5	126 609.7	126 609.6
2	128 673.6	(128 674.2)[a]	128 673.8

[a] This value is substantially less accurate than the others in the table.

Table III. Experimental and theoretical values of the ionization potential (I) of H_2 and the dissociation energy and first vibrational quanta of H_2^+.

	$I(H_2)$ (cm^{-1})	$D_0^0(H_2^+)$ (cm^{-1})	$\Delta G(\frac{1}{2})$ (cm^{-1})	$\Delta G(\frac{3}{2})$ (cm^{-1})
Observed	124 418.4 ± 0.4	<21 378.7 ± 0.4 (>21 376.7)	2191.2 ± 0.3	2064.2 ± 0.3
Calculated	124 417.3	21 379.3	2191.2_3	2163.9_3

rather satisfactory and indicates that no important terms have been neglected in the theoretical (*ab initio*) evaluation of these quantities. It is too early to say whether the very small remaining differences between observed and calculated values are significant.

A detailed account of the work on the dissociation energies is being published elsewhere.[9] The work on the ionization potential will be expanded and will be published in more detail later.[10]

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[1] G. Herzberg and A. Monfils, J. Mol. Spectry 5, 482 (1960).

[2] W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

[3] W. Kołos and L. Wolniewicz, J. Chem. Phys. 49, 404 (1968).

[4] P. R. Bunker, private communication.

[5] U. Fano, to be published.

[6] W. Kołos, Intern J. Quantum Chem. 2, 471 (1968).

[7] B. Jeziorski and W. Kołos, to be published.

[8] G. Hunter and H. O. Pritchard, J. Chem. Phys. 46, 2153 (1967).

[9] G. Herzberg, to be published.

[10] G. Herzberg, B. J. McKenzie, and P. Thurnauer, to be published.

SPECTROSCOPIC IDENTIFICATION OF EXCITED ATOMIC AND MOLECULAR STATES IN ELECTRON-BOMBARDED LIQUID HELIUM*

W. S. Dennis,† E. Durbin, Jr., W. A. Fitzsimmons,‡ O. Heybey, and G. K. Walters
Rice University, Houston, Texas 77001

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Optical and infrared emission spectra of electron-bombarded liquid helium reveal the presence of a number of excited singlet and triplet states of the He_2 molecule, including the $a^3\Sigma_u{}^+$ metastable state. The observed liquid spectra show vibrational and unresolved rotational structure. There is also preliminary evidence that excited atomic states, including the metastable 2^3S_1 state, are populated in the liquid.

The existence of energetic neutral localized excitations, created in liquid helium by an immersed radioactive source, has been established in recent work by Surko and Reif.[1] Also, indirect evidence of long-lived excitations and of an effective energy-transfer mechanism to colloidally suspended impurities has been reported by Jortner *et al.*[2] (See also Fischbach, Roberts, and Hereford.[3]) However, none of these experiments has provided any information on the identity or structure of the excitations. In this Letter we report the spectroscopic identification of electronically excited He_2 molecules in electron-bombarded liquid helium. In particular, it is found that the metastable $a^3\Sigma_u{}^+$ state is populated at a rapid rate. Preliminary spectroscopic data also suggest the presence in the bombarded liquid of metastable 2^3S_1 atoms. Both species are known to have very long natural lifetimes and to be quite stable against collisions in gaseous helium.[4] Thus both would appear to be good candidates for the unidentified localized excitations found by Surko and Reif.[1,5]

Our experimental arrangement is illustrated in Fig. 1. A beam of electrons with nominal energy 160 keV is incident upon the liquid-helium sample through a thin (0.000 125-in.) metal foil,[6] which serves to separate the cryostat interior from the common vacuum space of the Dewar flask and electron-accelerator beam tube. This technique for exciting liquid samples has several advan-

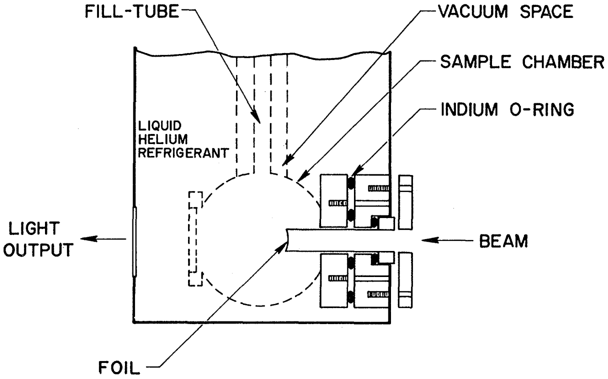

FIG. 1. Experimental apparatus.