

Eigenvalues and Certain Expectation Values for All Bound and Quasibound Levels of Ground-State ($X\ 1\ \Sigma\ g\ +$) $H\ 2$, HD , and $D\ 2$

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³ R. E. Huffman, Y. Tanaka and J. C. Larrabee, *J. Chem. Phys.* **39**, 902 (1963).

⁴ J. A. R. Samson, *J. Opt. Soc. Am.* **54**, 6 (1964).

⁵ V. H. Dibeler, R. M. Reese, and M. Krauss, *Advan. Mass Spectry.* **3**, 471 (1966).

⁶ R. E. Fox, W. M. Hickam, D. J. Grove, and T. Kjeldaas, Jr., *Rev. Sci. Instr.* **26**, 1011 (1955).

⁷ B. Cantone, V. Emma, and F. Grasso, *Advan. Mass Spectry.* **4**, 599 (1968).

⁸ R. E. Winters, J. H. Collins, and W. L. Courchene, *J. Chem. Phys.* **45**, 1931 (1966).

⁹ J. D. Morrison, *J. Chem. Phys.* **40**, 2488 (1964).

¹⁰ B. G. Giessner and G. G. Meisels, *J. Chem. Phys.* (to be published).

¹¹ S. M. Gordon, P. C. Haarhoff, and G. J. Krige, *Intern. J. Mass Spectry. Ion Phys.* **3**, 13 (1969).

¹² C. E. Brion, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.* **44**, 1034 (1966).

¹³ F. H. Dorman, J. D. Morrison, and A. J. C. Nicholson, *J. Chem. Phys.* **32**, 378 (1960).

¹⁴ J. D. Morrison, *J. Appl. Phys.* **28**, 1409 (1957).

¹⁵ J. W. McGowan, M. A. Fineman, E. M. Clarke, and H. P. Hanson, *Phys. Rev.* **167**, 52 (1968).

¹⁶ K. Maeda, G. P. Semeluk, and F. P. Lossing, *Intern. J. Mass Spectry. Ion Phys.* **1**, 395 (1968).

¹⁷ B. G. Giessner and G. G. Meisels, paper presented at the Eighteenth Annual Meeting on Mass Spectrometry, Dallas, Texas, May 1969 (to be published).

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Eigenvalues and Certain Expectation Values for All Bound and Quasibound Levels of Ground-State ($X^1\Sigma_g^+$) H_2 , HD, and D_2^*

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A detailed knowledge of the bound and quasibound vibrational-rotational levels of diatomic molecules is necessary for an understanding of many physical and chemical properties of gases.¹⁻³ In this respect, there is considerable interest in the ground ($X^1\Sigma_g^+$) state of molecular hydrogen because of the accurate *ab initio* potential which Kotos and Wolniewicz (KW)⁴ have calculated for it.⁵ Waech and Bernstein² previously computed the energies of all the vibrational-rotational levels of ground-state H_2 from the KW potential.⁴ However, they used only the clamped-nuclei (Born-Oppenheimer) potential and omitted both the diagonal correction for nuclear motion (adiabatic correction) and the relativistic correction. In addition, they used the reduced mass of the atoms rather than that of the nuclei,⁸ which is inconsistent with the Born-Oppenheimer and adiabatic approximations.⁹ Because of the interest in this system,¹⁻³ it is appropriate to conduct a more thorough study of the properties of the bound and quasibound levels of the hydrogen isotopes, using the KW potential *with* its relativistic and adiabatic corrections⁴ and the nuclear reduced mass.

The eigenvalues and the expectation values of R , R^2 , R^{-2} and kinetic energy have been calculated for all the bound and quasibound levels of ground-state H_2 , HD, and D_2 .¹⁰ The level widths Γ were computed for all quasibounds for which $0.05 < \Gamma \leq 100 \text{ cm}^{-1}$. The heights and positions of the centrifugal barrier maxima were also determined.¹⁰ The methods of utilizing the *ab initio* potential and of solving the radial Schrödinger equation are described in Ref. (8)¹¹; the physical constants were those of Ref. 12.¹³ Quasibound levels with very small widths $\Gamma < 0.05 \text{ cm}^{-1}$ were located using the Airy-function boundary condition method,³ while the broad quasibounds lying near the centrifugal barrier maxima

were placed at the peaks of the internal amplitude functions, and hence correspond to the spectroscopically observed level positions.³ On the other hand, the widths Γ were calculated from the height of the resonance peaks in the collisional time-delay functions.¹⁵ The expectation value $\langle f \rangle$ of $f(R)$ is defined as

$$\langle f \rangle = \int_0^{R_+} |\psi_{v,J}(R)|^2 f(R) dr / \int_0^{R_+} |\psi_{v,J}(R)|^2 dR,$$

where $\psi_{v,J}(R)$ is the computed (exact) radial eigenfunction. For truly bound levels lying below the dissociation limit, $R_+ = \infty$,¹⁶ while for quasibound levels lying behind the centrifugal barrier, R_+ is the position of the barrier maximum for the given J . Of course, the present choice of R_+ for the quasibound levels [also used in Ref. 1(d)] is not unique. Switching to an alternate approach of placing R_+ at the outermost turning point would measurably change the expectation values calculated for all but the most deeply bound metastable levels. This suggests that the reported¹⁰ expectation values for the quasibound levels have only semiquantitative significance.¹⁷

The results for each property of each isotope are presented in a form analogous to Table IV of Ref. 2. As expected, the functional dependence of the expectation values on v and J is continuous at the dissociation limit separating bound and quasibound levels. Quasibounds which lie above the centrifugal barrier maxima and have widths $\Gamma \geq 100 \text{ cm}^{-1}$ are in general omitted from the eigenvalue tables. The only exception is the $v=0$ level of each isotope, which was followed to the largest J value for which the effective potential still had a minimum and maximum (this was $J=39, 45$, and 56 , for H_2 , HD, and D_2). For H_2 , HD, and D_2 , respectively, the KW potential has 301, 399, and 600

bound levels, and 47, 65, and 96 quasibounds lying below the barrier maxima.

The results described above were obtained from the *ab initio* potential alone, without empirical or non-adiabatic corrections. However, in Ref. 8 it was found that even after taking the theoretical nonadiabatic corrections into account, the KW potential still required small adjustments in order to bring the calculated vibrational eigenvalues into agreement with experiment. The recent improved measurements of the molecular dissociation energy⁷ show that the better of the two possible derived corrections⁸ is that labeled Δ'' . Although not quite optimal, Δ'' is a fair measure of the direction and magnitude of the small errors in the *ab initio* potential.^{3,18} Therefore, the H₂ eigenvalues were also calculated¹⁰ for the potential obtained on adding Δ'' to the KW results. The deeper eigenvalues were unaffected, but the higher ones are shifted deeper by as much as a few cm⁻¹.

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¹ See, e.g.: (a) J. W. Fox and E. Gal, Proc. Phys. Soc. (London) **90**, 55 (1967); (b) R. A. Buckingham and E. Gal, Advan. At. Mol. Phys. **4**, 37 (1968), and references therein; (c) R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, Chem. Phys. Letters **2**, 366 (1968); (d) J. Chem. Phys. **50**, 5163 (1969); (e) R. E. Roberts, and R. B. Bernstein, Chem. Phys. Letters **6**, 282 (1970); (f) A. C. Allison, *ibid.* **3**, 371 (1969); (g) M. E. Gersh and R. B. Bernstein, *ibid.* **4**, 221 (1969); (h) D. L. S. McElwain and H. O. Pritchard, J. Am. Chem. Soc. **91**, 7693 (1963); (i) *ibid.* **92**, 5027 (1970).

² T. G. Waech and R. B. Bernstein, J. Chem. Phys. **46**, 4905 (1967).

³ R. J. Le Roy and R. B. Bernstein, J. Chem. Phys. **54**, 5114 (1971), this issue.

⁴ (a) W. Kołos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964); (b) **43**, 2429 (1965); (c) **49**, 404 (1968).

⁵ When first published, the fully-corrected KW potential⁴ yielded a more accurate ground-state dissociation energy than the best existing experimental value,⁶ as was recently confirmed by the improved spectroscopic measurements of Herzberg.⁷

⁶ G. Herzberg and A. Monfils, J. Mol. Spectry. **5**, 482 (1960).

⁷ G. Herzberg, J. Mol. Spectry. **33**, 147 (1970); see also W. C. Stwalley, Chem. Phys. Letters **6**, 241 (1970).

⁸ R. J. Le Roy and R. B. Bernstein, J. Chem. Phys. **49**, 4312 (1968).

⁹ (a) See, e.g., Refs. 4(c) and (8); (b) L. Wolniewicz, J. Chem. Phys. **45**, 515 (1966); (c) J. O. Hirschfelder and W. J. Meath, Advan. Chem. Phys. **12**, 3 (1967).

¹⁰ R. J. Le Roy, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-387 (1971). Tables of these results have been deposited as Document number 01374 with the National Auxiliary Publications Service of the A.S.I.S. CCM Information Corp., 909 Third Ave., New York. A copy may be secured by citing the Document number and by remitting \$5.00 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

¹¹ Fortran listings of the computer programs used here are available: R. J. Le Roy, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-429G (1971).

¹² E. R. Cohen and J. W. Du Mond, Rev. Mod. Phys. **37**, 537 (1965).

¹³ An improved value of the electron mass (see Ref. 8) has been reported¹⁴; however, this imputes negligible (≤ 0.075 cm⁻¹)⁸ errors to the present eigenvalues.¹⁰

¹⁴ B. N. Taylor, W. H. Parker, and D. N. Langenberg, Rev. Mod. Phys. **41**, 375 (1969).

¹⁵ Comparisons of divers means of locating quasibound levels and of estimating their widths are presented in Ref. 3. The time-delay function and a means of computing it are described there.

¹⁶ Of course, the quadratures need only be performed out to some R_+ which is sufficiently large that $\psi_{v,J}(R)$ is negligible for $R > R_+$.

¹⁷ The expectation values for the metastable levels were evaluated at the energies yielded by the Airy-function boundary condition method³; hence, they are only reported for quasibounds lying below the centrifugal barrier maxima.¹⁰ While they do not precisely correspond to the reported eigenvalues (defined by the maxima in the internal amplitude functions³), error due to this discrepancy will be negligible.

¹⁸ It is believed that the Ref. 8 estimates of the nonadiabatic corrections¹⁹ to the eigenvalues are slightly large, which implies that Δ'' underestimates the necessary corrections to the KW potential.

¹⁹ See also: (a) J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936); (b) J. D. Poll and G. Karl, Can. J. Phys. **44**, 1467 (1966).

Anisotropy of the ¹³C Chemical Shift in Hydrogen Cyanide*

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In contrast to proton chemical shifts, for which a considerable number of reliable anisotropy values are now available, only one measurement of the ¹³C chemical shift anisotropy for a noncrystalline sample has so far been reported.¹ This is somewhat surprising since the ¹³C chemical shift anisotropies can be determined experimentally with considerably less ambiguity and their theoretical interpretation is in some ways simpler. In this study, the chemical shift anisotropies for ¹H and ¹³C in H¹³CN have been measured, using an exten-

sion and modification of the double resonance technique used by Yannoni and Whipple.¹

The expected proton spectrum of H¹³CN dissolved in a nematic liquid crystal consists of a doublet,² with a separation given by

$$\Delta\nu = (-\hbar\gamma_H\gamma_{^{13}C}/\pi r_{C-H}^3) S_{33} + J_{H^{13}C} + (2/3) S_{33}\Delta J, \quad (1)$$

and a chemical shift of

$$\sigma = \sigma^i + (2/3) S_{33}\Delta\sigma, \quad (2)$$