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[1] See, e.g., V. I. Krylov, *The Approximate Calculation of Integrals* (MacMillan, London, 1962).

[2] For a semiempirical application of the operator see P. B. Empedocles, J. Chem. Phys. 46, 4474 (1967).

[3] R. G. Parr, J. Chem. Phys. 26, 428 (1957).

[4] I. Shavitt and M. Karplus, J. Chem. Phys. 43, 398 (1965).

[5] P. B. Empedocles, Theoret. Chim. Acta 13, 139 (1969).

[6] P. B. Empedocles, Int. J. Quantum Chem. 3, S47 (1969).

[7] R. L. Somorjai, Chem. Phys. Letters 2, 399 (1968); Phys. Letters 23, 329 (1969); R. L. Somorjai and D. M. Bishop, Phys. Rev. A 1, 1013 (1970); D. D. Shillady, Chem. Phys. Letters 3, 17 (1969); 3, 104 (1969).

[8] P. B. Empedocles, J. Chem. Phys. 52, 1703 (1970).

[9] C. B. Hazlegrove, Math. Comput. 15, 323 (1961).

[10] H. Conroy, J. Chem. Phys. 47, 5307 (1967).

[11] S. F. Boys and N. C. Handy, Proc. Roy. Soc. (London) A311, 309 (1969).

[12] C. Schwartz, J. Comput. Phys. 2, 90 (1967); S. F. Boys, Proc. Roy. Soc. (London) A309, 195 (1969); E. Szondy and T. Szondy, Acta Phys. Acad. Sci. Hung. 20, 253 (1966).

[13] I. Shavitt, in Third Canadian Symposium on Theoretical Chemistry, 1969, (unpublished).

[14] *Symposium on Monte Carlo Methods*, edited by H. A. Meyer (Wiley, New York, 1954).

[15] H. Conroy, J. Chem. Phys. 41, 1331 (1964).

[16] P. -O Löwdin, J. Mol. Spectry. 3, 46 (1959). Note however, that the scaling involved here not only allows a uniform scaling of the basis but also allows for the reoptimization of the configuration weighting coefficients for each scaling.

[17] C. Eckart, Phys. Rev. 36, 878 (1930).

[18] P. B. Empedocles, J. Comput. Phys. (to be published).

[19] W. A. Goddard III, Phys. Rev. 109, 120 (1968).

[20] E. Clementi, J. Chem. Phys. 38, 2686 (1963).

[21] P. B. Empedocles (unpublished).

[22] J. N. Lyness and B. J. J. McHugh, Computer J. 6, 264 (1963); R. Cranley and T. N. L. Patterson, (unpublished); T. N. L. Patterson and R. Cranley (unpublished).

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Radiative Lifetimes for the $2p\pi\,^3\Pi_u$ State of the Hydrogen Molecule*

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A calculation is made of the radiative electric dipole transition probabilities coupling the vibrational levels of the $2p\pi\,^3\Pi_u$ and the $2s\sigma\,^3\Sigma_g$ electronic states of hydrogen. The radiative lifetimes for those vibrational levels lying above the ground state are found to be approximately 100 μsec. The lifetime of the ground vibrational level, decaying by magnetic dipole and electric quadrupole emissions, is estimated to be 1 msec. Finally, a calculation is made of the dependence of the radiative lifetimes upon an external electric field.

I. INTRODUCTION

The $2p\pi\,^3\Pi_u$ electronic state of the hydrogen molecule is especially interesting because the radiative lifetimes for this state are three to four orders of magnitude longer than the radiative lifetimes for neighboring electronic states. The reasons for these long lifetimes are threefold: The lowest vibrational level of the $^3\Pi_u$ state lies lower than any *g* (*gerade*) level of the triplet spectrum and radiative dipole transitions from this vibrational level are forbidden[1]; for the higher vibrational levels, dipole transitions can occur to the $2s\sigma\,^3\Sigma_g$ state but here the transition probabilities are relatively small, in part due to the small energy differences and in part to large scale cancellations in the Frank-Condon factors.

The lowest vibrational level of the $^3\Pi_u$ electronic state can undergo radiative decay to the $^3\Sigma_u$ state through a combination of magnetic dipole and electric quadrupole emissions and with a lifetime estimated to be approximately 1 msec. This level is also susceptible to spontaneous predissociation into two ground-state atoms arising from perturbations coupling the $2p\pi\,^3\Pi_u$ and $2p\sigma\,^3\Sigma_u$ states. For the "allowed predissociations," induced by rotational-electronic perturbations,[2] the Kronig selection rules[3] allow for predissociation of the $^3\Pi_u$ vibrational levels for even rotational levels in the case of orthohydrogen and odd rotational levels in the case of parahydrogen. In Lichten's experiments, only the $N=1$ rotational level of orthohydrogen and the $N=2$ rotational level of parahydrogen were observed; since the time of flight of the molecule was approximately 50 μsec, these experiments imply an upper limit of some tens of microseconds for the lifetime against allowed predissociation. In a system with strongly coupled Π_u and Σ_u states (certainly not the case here), this lifetime could be as short as 10^{-11} sec.[4] Those rotational levels which are stable against predissociation according to the Kronig selection rules may be susceptible to "forbidden predissociations" which arise from spin-orbit and spin-spin couplings. Lichten[5] and Chiu[6] have identified these forbidden predissociations as the cause for the observed decay of the para $N=2$ level and ortho $N=1$ level. The experimental lifetimes attributed to these decays lie in the range from 100 to 500 μsec; recently, Bottcher and Browne[7] have provided theoretical estimates for the forbidden predissociation lifetimes which are of the order of milliseconds.

Interest in the prospects for a long-lived $H_2(2p\pi\,{}^3\Pi_u)$ molecule arises in connection with the problem of forming energetic neutral hydrogen beams.[8] Charge-transfer collisions of H_2^+ with alkali or alkaline-earth targets are expected to lead to relatively large populations of $H_2(2p\pi\,{}^3\Pi_u)$ in the molecular beam.[9] To a large extent, these charge-transfer collisions will preserve the initial vibrational level distribution of the incident H_2^+ ion, which for typical ionization conditions, will span the entire vibrational level spectrum.[10] Those vibrational levels lying above the ground level are subject to radiative decay by electric dipole emission to the $2s\sigma\,{}^3\Sigma_g$ state. To a first approximation, the aforementioned predissociation lifetimes are applicable to the higher vibrational levels, and the problem which remains is to compare the radiative electric dipole transition rates with the different predissociation rates.

In this paper, a calculation is made of the radiative dipole transition probability for each of the vibrational levels of the $2p\pi\,{}^3\Pi_u$ electronic state. Critical features of the calculation are the magnitudes of the Frank-Condon factors coupling the ${}^3\Pi_u$ and ${}^3\Sigma_g$ states. The generation of accurate vibrational functions necessary to evaluate these factors is made possible utilizing the ${}^3\Pi_u$ potential computed by Browne[11] and the ${}^3\Sigma_g$ potential given by Wakefield and Davidson (WD)[12] and by Kolos and Wolniewicz (KW).[13] Finally, a calculation is made of the dependence of the radiative lifetime upon an external quenching electric field.

II. QUANTITATIVE DISCUSSION

The expression for the radiative electric dipole transition probability is given by[14]

$$A_{\text{ED}} = \tfrac{4}{3}\,(e^2 w^3/\hbar c^3)\,|\vec{\mathfrak{M}}_{\text{ED}}|^2\,, \tag{1}$$

where

$$\vec{\mathfrak{M}}_{\text{ED}} = \int u^*(v')u(v)\,dR \int \chi^*({}^3\Sigma_g)\chi({}^3\Pi_u)\rho\,d\rho\,dz \times\int \omega^*(N'\,\Lambda' M')\omega(N\Lambda M)\,\vec{r}\,d(\cos\theta)\,d\phi\,d\psi\,, \tag{2}$$

the product of a rotational, an electronic, and a vibrational integral. Our over-all molecular eigenfunctions, exclusive of the spin functions, are taken to be

$$\begin{aligned}\Psi({}^3\Pi_u^\pm) &= u(v;R)\chi({}^3\Pi_u;\rho,z,R)[\Theta(N\Lambda M;\theta) \\ &\quad\times e^{i\Lambda\Psi}\mp\Theta(N-\Lambda M;\theta)e^{-i\Lambda\psi}]e^{iM\phi}, \\ \Psi({}^3\Sigma_g) &= u(v';R)\chi({}^3\Sigma_g;\rho,z,R)\Theta(N'0M';\theta)\,e^{iM'\phi}\,.\end{aligned} \tag{3}$$

The symmetric-top functions $\Theta(N\Lambda M;\theta)$ are given in Herzberg.[15] In the triplet spectrum, the positive ${}^3\Pi_u^+$ functions are to be used for orthohydrogen and the negative ${}^3\Pi_u^-$ functions for parahydrogen. The coordinate R, occurring in the vibrational and electronic functions, measures the internuclear separation in units of a_0; the ρ, z are electronic cylindrical coordinates moving with the internuclear axis measured from the midpoint of the nuclei, and ψ the azimuthal coordinate measured about the internuclear axis.

Under the Eulerian transformation θ, ϕ, ψ from the laboratory system to the system $\vec{r}'$ rotating with the internuclear axis, the three components of $\vec{r}$ become

$$\begin{aligned}x &= x'(\cos\psi\cos\phi-\sin\psi\cos\theta\sin\phi) \\ &\quad-y'(\sin\psi\cos\phi+\cos\psi\cos\theta\sin\phi)+z'\sin\theta\sin\phi, \\ y &= x'(\cos\psi\sin\phi+\sin\psi\cos\theta\cos\phi) \\ &\quad+y'(-\sin\psi\sin\phi+\cos\psi\cos\theta\cos\phi)-z'\sin\theta\cos\phi, \\ z &= x'\sin\psi\sin\theta+y'\cos\psi\sin\theta+z'\cos\theta\,.\end{aligned} \tag{4}$$

Using these expressions and the symmetric-top functions, the rotational integral in Eq. (2) is evaluated.

Figure 1 shows a schematic of the lower portion of the rotational spectrum for any vibrational level and for each of the electronic states: ${}^3\Pi_u$, ${}^3\Sigma_g$, and the repulsive ${}^3\Sigma_u$. The ortho levels are indicated as full lines, the para levels as dashed lines. The electric dipole transitions between ${}^3\Pi_u$ and ${}^3\Sigma_g$ for the ortho and para levels computed here are shown by connecting dashed and full lines, respectively. The fine-structure splittings are suppressed in the figure; the radiative lifetimes are determined by the N, N' values, not the J, J' values. The rotational levels for the ${}^3\Sigma_u$ state and the connecting transitions for the allowed predis-

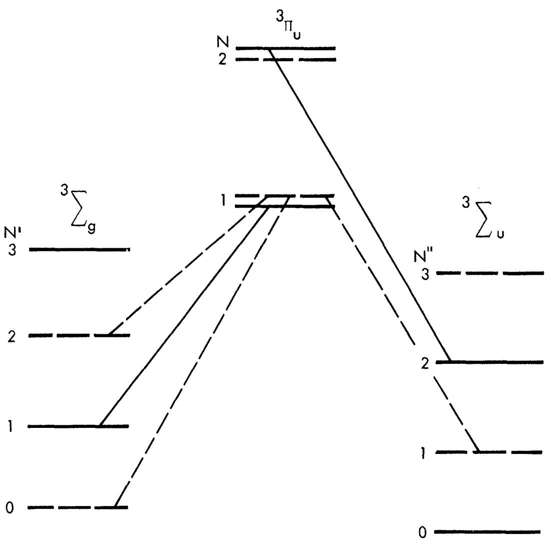

FIG. 1. Schematic representation of the lower rotational spectrum for any vibrational level belonging to the $2s\sigma\,{}^3\Sigma_g$, $2p\pi\,{}^3\Pi_u$, and $2p\sigma\,{}^3\Sigma_u$ electronic states. The para levels are shown as dashed and the ortho levels as full lines. The radiative electric dipole transitions considered in the paper are indicated by the diagonal lines joining the $^3\Pi_u$ and $^3\Sigma_g$ states. The allowed predissociation transitions are shown as diagonal lines joining the $^3\Pi_u$ and $^3\Sigma_u$ states.

sociations of the $^3\Pi_u$ state are shown on the right. The connecting transitions in the case of the forbidden predissociations are not shown on the diagram but obey the selection rule $\Delta N = \pm 1$. For the evaluation of the rotational integral in Eq. (2) we have taken the initial rotational level to be $N=1$ for both orthohydrogen and parahydrogen. Because of the Λ dependence of the $\omega(N\Lambda M)$, only the terms in Eq. (4) containing $\cos\psi$ or $\sin\psi$ contribute to the rotational integral. Setting $x' = y' = \rho$, the square of the rotational integral is found to be $\frac{1}{2}\rho^2$ for each of the three initial states.

The electronic integral to be evaluated has the form

$$\int \psi^*({}^3\Sigma_g;\rho,z,R)\psi({}^3\Pi_u;\rho,z,R)\rho^2\,d\rho\,dz\ . \qquad (5)$$

This integral is only weakly dependent upon the parameter R. Designating the integral by $E(R)$ and using helium functions,[16] one finds $E(0) = 3.68\ a_0$, and for hydrogen functions $E(\infty) = 4.24\ a_0$. Huzinaga[17] has given approximate one-center functions for $^3\Sigma_g$ and $^3\Pi_u$ from which we obtain $E(2) = 4.08\,a_0$. Retaining only the leading term of the Coolidge-James $^3\Sigma_g$ function[18] and the leading term of the Amemiya function,[19] and evaluating at the potential minimum indicated by these functions, one obtains $E(1.87) = 3.93\ a_0$. To summarize, $E(R)$ is a slowly varying function of R whose magnitude changes by only 15% over the entire range of R. To a good approximation we can rewrite Eq. (5) as

$$\int\Big(\psi^*({}^3\Sigma_g;\rho,z,R_0)\,\psi({}^3\Pi_u;\rho,z,R_0)\cdot + \frac{\partial}{\partial R}\,[\psi^*({}^3\Sigma_g)\,\psi\,({}^3\Pi_u)]_{R=R_0}(R-R_0)\Big)\rho^2\,d\rho\,dz \simeq 4\,a_0[1+0.025(R-1.95)]\ . \qquad (6)$$

Retaining the second term in Eq. (6) will amount to approximately a 10% correction to the total transition probability.

The integral over the internuclear coordinate R must still be evaluated. For this purpose, it has been necessary to generate the vibrational functions $u(v)$ and $u(v')$ belonging to the $^3\Pi_u$ and $^3\Sigma_g$ states, respectively, using the equation

$$\frac{d^2u(v)}{dR^2} + \left(\alpha\,[W_v - V(R)] - \frac{N(N+1)}{R^2}\right)u(v) = 0, \qquad (7)$$

where $\alpha = \frac{1}{2}\,\frac{M}{m}\left(1 + \frac{m}{2M}\right) = 918.308$.

For $V(R)$, we have used both the potential of WD and the fixed nuclei potential of KW to generate the $^3\Sigma_g$ levels and the potential of Browne for generating the $^3\Pi_u$ levels.

The vibrational eigenvalues are shown in Table I. The $^3\Pi_u$ entries are listed for $N=1$ and the $^3\Sigma_g$ entries for $N=0$, 1, 2, the corresponding three final rotational levels; the latter eigenvalues are given in double entry, appropriate to the respective potentials. If we compare the lowest four $^3\Pi_u$ levels with the experimental values given by Dieke,[20] the calculated values are found to be 0.007 Ry higher than the experimental values; better agreement is found by comparing the first differences in the calculated eigenvalues with the first differences in the spectroscopic values, the discrepancies in the differences amounting to about 0.0001–0.0002 Ry. The WD $^3\Sigma_g$ levels computed here lie about 0.0002 Ry lower than the values computed by WD; why this occurs is unclear since both calculations use the same potential. The KW levels computed here agree with those computed by KW. Of some interest is the fact that our WD $v=0$ and $v=1$ energy levels and the KW $v=0$ to $v=6$ energy levels lie lower than Dieke's spectroscopic values. In both cases, the $v=0$ eigenvalue lies between the spectroscopic values given by Beutler and Jünger[21,13] and by Dieke. A similar situation was found by Wright and Davidson[22] for the $^3\Sigma_g$ state. Inspection of the second differences in the WD $^3\Sigma_g$ levels shows a discontinuity near the $v=6$ level. This discontinuity also occurs in WD's spectrum and is of the same magnitude. We have tentatively ascribed

TABLE I. Vibrational spectrum of the $^3\Pi_u$ and $^3\Sigma_g$ electronic states measured in rydberg units below the total ionization limit. For the $^3\Pi_u$ state, the eigenvalue is given for the $N=1$ rotational level and for the $^3\Sigma_g$ state, the $N'=0,1,2$ rotational levels. The $^3\Sigma_g$ levels are given in double entry and are computed using the WD and KW potentials, respectively. Dieke's spectroscopic values are listed for the lowest rotational level. The asterisk implies an extrapolated value.

	$2p\pi\,^3\Pi_u$		$2s\sigma\,^3\Sigma_g$		
	Computed	Dieke (Ref. 19)	Computed		Dieke (Ref. 19)
v			WD	KW	
0	−1.455 07	−1.462 56	−1.461 40	−1.462 27	−1.461 33
			−1.460 84	−1.461 66	
			−1.459 62	−1.460 45	
1	−1.433 84	−1.441 24	−1.438 43	−1.439 25	−1.438 32
			−1.437 85	−1.438 67	
			−1.436 68	−1.437 52	
2	−1.413 85	−1.421 04	−1.416 45	−1.417 47	−1.416 56
			−1.415 91	−1.416 93	
			−1.414 79	−1.415 83	
3	−1.395 11	−1.401 94	−1.395 69	−1.396 90	−1.396 00
			−1.395 15	−1.396 38	
			−1.394 11	−1.395 35	
4	−1.377 49	−1.383 9*	−1.376 31	−1.377 51	−1.376 62
			−1.375 82	−1.377 02	
			−1.374 82	−1.376 04	
5	−1.360 87		−1.358 23	−1.359 27	−1.358 40
			−1.357 77	−1.358 82	
			−1.356 88	−1.357 89	
6	−1.345 24		−1.341 34	−1.342 21	−1.341 33
			−1.340 96	−1.341 77	
			−1.340 11	−1.340 90	
7	−1.330 58		−1.325 41	−1.326 30	
			−1.325 01	−1.325 89	
			−1.324 20	−1.325 07	
8	−1.316 88		−1.310 84	−1.311 58	
			−1.310 44	−1.311 19	
			−1.309 71	−1.310 43	
9	−1.304 14		−1.297 40	−1.298 09	
			−1.297 04	−1.297 74	
			−1.296 33	−1.297 04	
10	−1.292 50		−1.285 33	−1.285 94	
			−1.285 00	−1.285 62	
			−1.284 36	−1.284 98	
11	−1.282 06		−1.274 65	−1.275 24	
			−1.274 36	−1.274 96	
			−1.273 79	−1.274 40	
12	−1.272 93		−1.265 59	−1.266 22	
			−1.265 34	−1.265 97	
			−1.264 86	−1.265 49	
13	−1.265 26		−1.258 30	−1.259 13	
			−1.258 11	−1.258 94	
			−1.257 71	−1.258 56	
14	−1.259 00				

this discontinuity as due to the properties of the potential function rather than to a feature of the numerical integration procedure.

Kolos and Wolniewicz have also computed the dynamical corrections to the ${}^3\Sigma_g$ potential; the effect of including these corrections is to lower the eigenvalues approximately 0.00004–0.00007 Ry compared with the KW eigenvalues listed in the table. The quantities that enter into the calculation of the radiative transition probabilities are the differences of the ${}^3\Pi_u$ and ${}^3\Sigma_g$ eigenvalues. Because of the relatively large errors which persist in the ${}^3\Pi_u$ levels, the energy differences are not significantly improved by inclusion of the dynamical corrections to the ${}^3\Sigma_g$ eigenvalues. The radiative transition probabilities are computed using the eigenvalues listed in the table.

In the succeeding paragraphs, the various factors which enter into the calculation of the transition probabilities have been evaluated using solutions derived from both the WD and KW potentials. A comparison of the different pairs of computed quantities provides some measure of the sensitivity of these results to further improvements of the ${}^3\Sigma_g$ potential.

From Eqs. (2) and (6), the vibrational integral to be evaluated is

$$\int [1+0.025(R-1.95)]u^*(v')u(v)\,dR\ . \qquad (8)$$

Inspection of the experimental eigenvalues for $v, v' \leq 4$ and the computed eigenvalues for $v, v' > 4$ listed in Table I shows that only those transitions for which $v' < v$ are energetically allowed. Note, however, that a comparison of the computed values for v, $v' \leq 3$ would indicate transitions $v \rightarrow v'$ are allowed; this erroneous result is a consequence of the relatively large error in the computed ${}^3\Pi_u$ levels. This selection rule on v' together with the similarity of the potentials $V(R)$ for the ${}^3\Pi_u$ and ${}^3\Sigma_g$ states causes the integral (8) to be small compared with unity. In Table II, we have listed the squared values of (8) for several values of v, v' and for $N = N' = 1$; the quantities are listed in double entry, the upper values have been computed using the WD potential, the lower values the KW potential. The values vary over several orders of magnitude; for any v, the largest values occurs for $v' = v - 1$, with magnitude of the order of one-tenth diminishing toward the highest v levels.

TABLE II. Tabulation of the square of the vibrational integral, Eq. (8), for several values of v, v'. Parenthetic values are base ten exponents. The upper entry is computed using the WD potential, the lower entry from the KW potential.

$v' \backslash v$	1	2	5	10	14
0	0.042 0.039	0.0032 0.0027	1(−5) 2(−6)	1(−6) 2(−6)	7(−8) 1(−7)
1		0.069 0.069	1(−7) 1(−7)	8(−6) 1(−5)	3(−7) 1(−7)
4			0.11 0.10	1(−4) 1(−4)	5(−5) 4(−5)
9				0.077 0.084	7(−4) 7(−4)
12					0.020 0.023

The electric dipole transition probability for all transitions v, v' are listed in Table III again in double entry as in Table II. The probabilities listed in the table correspond to the $N = N' = 1$ transitions shown in Fig. 1 for orthohydrogen. In calculating the transition probabilities, we have used Dieke's spectroscopic energy levels for $v \leq 3$, a linear extrapolation of these experimental values for $v = 4$, and the computed energy levels listed in Table I for $v \geq 5$; we have used Dieke's values for $v' \leq 3$ and the calculated values for $v' \geq 4$. In the range $v \leq 4$, the computed energy levels give a transition probability larger by a factor of 2 or 3 compared to the transition probabilities computed using the experimental energy levels.

The transition probabilities listed in Table III are very small in comparison with the transition probabilities of order 10^8 sec^{-1}, characteristic of the neighboring $2s\sigma\ {}^3\Pi_g$, $3p\pi\ {}^3\Pi_u$, and $3d\delta\ {}^3\Delta_g$ electronic states, and sufficiently small to warrant consideration of the higher multiple contributions. The magnetic dipole and electric quadrupole transition probabilities are given by

$$A_{\mathrm{MD,EQ}} = \tfrac{4}{3}(e^2 w^3/\hbar c^3)\,|({}^3\Pi_u\,|D_{\mathrm{MD,EQ}}|\,{}^3\Sigma_u)|^2\ , \quad (9)$$

where either $D_{\mathrm{MD}} = |\vec{r} \times \vec{p}\,|/2mc$ or $D_{\mathrm{EQ}} = wyz/2c$. We shall ignore here the possibility of interference between the D_{MD} and the D_{EQ}. Evaluating the rotational integrals for $N = 1$, evaluating the electronic integrals using the single-center Huzinaga functions, and bearing in mind that the $\phi(v')$ belonging to the ${}^3\Sigma_u$ repulsive state form a continuous spectrum, the transition probabilities are found to be

$$A_{\mathrm{MD,EQ}} = \tfrac{4}{3}\,(e^2 a_0^2/\hbar c^3) \int w^3 |\phi^*(v')\phi(v)|^2\, dw \times E_{\mathrm{MD,EQ}}\ \mathrm{sec}^{-1} \qquad (10)$$

with $E_{\mathrm{MD}} \simeq 5\times10^{-6}$ and $E_{\mathrm{EQ}} \simeq 1\times10^{-6}$. We can estimate the value of the integral in Eq. (10) using the James-Coolidge[23] electric dipole transition probability for the ${}^3\Sigma_g$-${}^3\Pi_u$ transition and taking advantage of the similarity of shape of the ${}^3\Sigma_g$ and ${}^3\Pi_u$ potentials. James and Coolidge found $A_{\mathrm{ED}}({}^3\Sigma_g - {}^3\Pi_u) \simeq 10^8$ sec^{-1} for the five lowest vibrational levels of the ${}^3\Sigma_g$ state. Using their results, we obtain

$$\tfrac{4}{3}(e^2 a_0^2/\hbar c^3) \int w^3\, |\phi^*(v')\,\phi(v)|^2\, dw = 1.5\times10^8\ \mathrm{sec}^{-1}. \qquad (11)$$

TABLE III. Electric dipole radiative transition probabilities for orthohydrogen in the $N=1$ rotational level. The entries are listed in units of 10^3 sec^{-1}. The upper and lower entries are based on the WD and KW potentials, respectively.

v' \ v	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	6.6	4.3	1.1	0.026	0.22	0.63	0.68	0.50	0.29	0.10	0.011	0.0002	0.004	0.012
	6.2	3.6	0.89	0.069	0.033	0.19	0.30	0.31	0.27	0.20	0.14	0.083	0.047	0.026
1		6.9	5.7	1.2	0.001	0.67	1.3	1.3	0.92	0.59	0.33	0.14	0.072	0.036
		6.9	5.9	1.6	0.056	0.27	0.80	1.0	0.99	0.83	0.62	0.41	0.24	0.016
2			4.1	5.8	1.7	0.005	0.78	1.6	1.6	1.4	1.0	0.75	0.46	0.36
			4.1	6.5	2.5	0.014	0.59	1.6	1.8	1.7	1.4	1.0	0.70	0.50
3				3.3	9.7	1.9	0.009	0.53	1.5	2.2	2.2	2.0	1.6	1.1
				3.3	11.0	2.5	0.011	0.66	1.7	2.1	2.0	1.8	1.4	0.99
4					7.6	9.4	2.4	0.006	0.55	1.4	1.8	2.2	2.1	1.8
					9.2	9.4	2.6	0.059	0.46	1.4	1.7	1.9	1.7	1.4
5						4.0	6.9	2.8	0.10	0.48	1.3	1.5	1.3	1.2
						5.5	7.6	2.9	0.26	0.14	0.81	1.3	1.6	1.3
6							2.2	4.8	2.5	0.39	0.053	0.53	0.93	1.0
							3.1	6.0	3.1	0.65	0.0033	0.24	0.81	0.71
7								1.0	3.6	2.6	0.78	0.083	0.039	0.20
								1.6	4.7	3.1	1.0	0.19	0.0003	0.08
8									0.46	2.5	2.3	1.3	0.50	0.15
									0.72	3.4	3.0	1.5	0.55	0.15
9										0.16	1.7	2.1	1.4	0.82
										0.26	2.2	2.5	1.6	0.88
10											0.034	0.94	1.4	1.2
											0.065	1.2	1.7	1.4
11												0.0024	0.39	0.76
												0.0072	0.52	0.95
12														0.11
													0.001	0.17

Combining Eqs. (9) and (10), the transition probability for these higher multipoles is

$$A_{\text{MD}} + A_{\text{EQ}} \simeq 10^3 \ \text{sec}^{-1} . \qquad (12)$$

It follows that the radiative lifetime for the $v=0$ level of the $^3\Pi_u$ state is approximately 1 msec and that the higher multipole radiation represents about a 10 to 20% correction to A_{ED} for the higher vibrational levels.

The radiative lifetimes for each of the vibrational levels of the $^3\Pi_u$ state are summarized in Fig. 2. Here we have plotted the lifetime

$$\tau(v) = [\sum_{v'} A_{\text{ED}}(v, v') + A_{\text{MD}} + A_{\text{EQ}}]^{-1} , \qquad (13)$$

as a function of the vibrational level v for orthohydrogen using the WD entries listed in Table III. The lifetimes computed using the KW entries will range from 1 to 16% less than those shown in the figure; a calculation for parahydrogen yields lifetimes which differ by less than 10% from those shown. The gap in the curves at $v=5$ corresponds to the first level at which the theoretical eigenvalues were employed in calculating A_{ED}. Using the theoretical eigenvalues in A_{ED} for the $v=1, 2, 3, 4$ levels results in radiative lifetimes for these levels which are about half the values shown in the figure. This is an indication that the lifetimes for those levels near $v=5$ are about a factor of 2 larger than shown in the figure. We have no way of estimating the error due to the uncertainties in the eigenvalues for the uppermost levels.

The vibrational integral equation (8) is sensitive to the shape and to the relative positions of the potentials $V(R)$. Comparing the spacing of the potential minima of the theoretical potentials with the spacings derived from spectroscopic data listed in Herzberg, one obtains a difference of about -0.005 a_0. To test the sensitivity of the lifetimes to the potential spacing, we have arbitrarily shifted the $^3\Pi_u$ potential an amount -0.01 a_0 and reevaluated the lifetimes for the $v=2$, 5, and 14 levels; the adjusted lifetimes are indicated by crosses on Fig. 2.

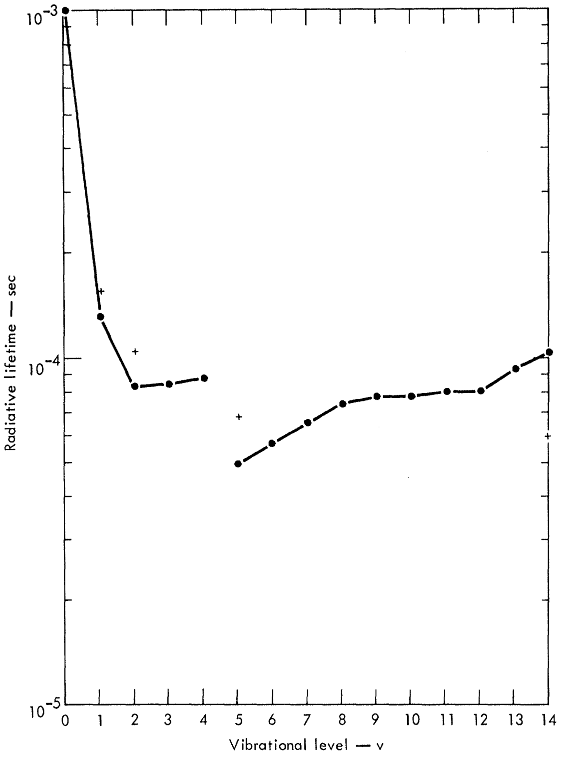

FIG. 2. Radiative lifetimes calculated as a function of vibrational level for orthohydrogen in the $N=1$ rotational level. The crosses refer to the radiative lifetime calculated for the $v=1, 2, 5$, and 14 levels for a relative shift in the potentials of $-0.01a_0$.

III. QUENCHING ELECTRIC FIELDS

We shall consider next the dependence of the radiative lifetimes on an external electric field. An electric field couples the electronic states $2p\pi\,^3\Pi_u$ and $2s\sigma\,^3\Sigma_g$ to first order. Because of the large radiative decay probability of the $^3\Sigma_g$ to the $^3\Sigma_u$ state, which is of the order of 10^8 sec^{-1}, and the small energy differences separating the $^3\Pi_u$ and $^3\Sigma_g$ levels, one would suspect that even a moderate field could lead to a significant change in the $^3\Pi_u$ lifetime.

If the electric field $\mathcal{E}$ is taken along the z axis in the laboratory system, the perturbation in the molecular system is

$$S = -e\mathcal{E}(\rho\sin\theta\ \sin\psi + \rho\sin\theta\cos\psi + z'\cos\theta)\,, \qquad (14)$$

from Eq. (4). The perturbed $^3\Pi_u$ function is now $\Psi'(^3\Pi_u) = \Psi(^3\Pi_u) + a\mathcal{E}\Psi(^3\Sigma_g)$, and the induced radiative transition probability coupling the $^3\Pi_u$ and $^3\Sigma_u$ states becomes

$$A^I_{\mathrm{ED}}(^3\Pi_u - {}^3\Sigma_u) = a^2\mathcal{E}^2 A_{\mathrm{ED}}(^3\Sigma_g\,, v'; - {}^3\Sigma_u)\ , \qquad (15)$$

where the $A_{\mathrm{ED}}(^3\Sigma_g, v' - {}^3\Sigma_u)$ are given by James and Coolidge and

$$a^2 = (4e^2a_0^2)\left[\,\left|\int u^*(^3\Sigma_g, v')u(^3\Pi_u, v)\,dR\right|^2\right]$$
$$\times[W(^3\Pi_u; N=1) - W(^3\Sigma_g; N')]^{-2}\,. \qquad (16)$$

$N' = 1$ for orthohydrogen and 0, 2 for parahydrogen. The main contribution to a^2 occurs for $v' = v$.

In Fig. 3 are plotted the radiative lifetimes as a function of electric field for the lowest four vibrational levels. The dependence for these levels is given for both the para and ortho forms. Appreciable quenching occurs only for moderately high electric fields, of the order of 10^4 to 10^5 V/cm. Inspection of the energy differences which occur in Eq. (16) will show that higher quenching fields are required for the vibrational levels not shown in the figure.

IV. CONCLUSIONS

The radiative lifetimes for the vibrational levels lying above the ground vibrational level are found to be approximately 100 μsec. The lifetimes for these vibrational levels are about one-tenth the radiative lifetime of the metastable ground vibrational level, but most probably are longer than the lifetimes for allowed predissociation. The apparent distribution of the lifetimes for the different decay modes arranged according to increasing lifetime is allowed predissociation, radiative dipole emission, and forbidden predissociation. The primary source of error in the dipole transition probabilities is due to the uncertainty in the $^3\Pi_u$ eigen-

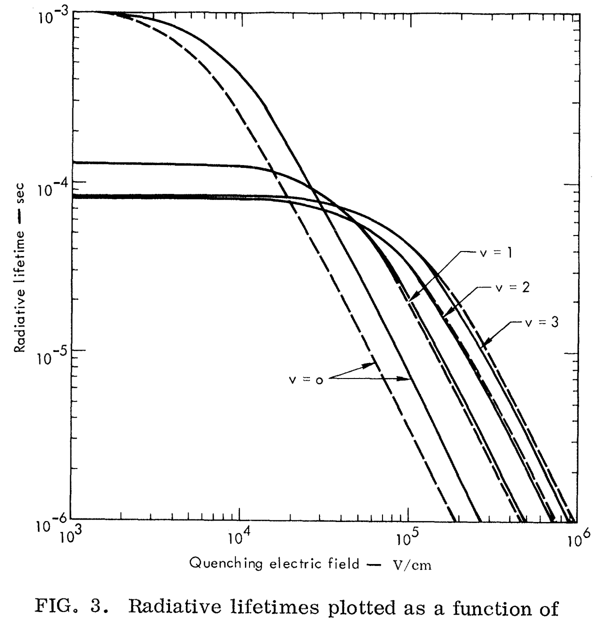

FIG. 3. Radiative lifetimes plotted as a function of electric field for the $v=0, 1, 2$, and 3 vibrational levels for molecules in the $N=1$ rotational level. Solid curves: orthohydrogen; dashed curves: parahydrogen.

values resulting from the approximate nature of the $^3\Pi_u$ potential and causing the computed lifetimes to be in error by about a factor of 2.

With reference to the problem of energetic molecular beam formation, the radiative lifetimes are sufficiently long that keV molecules can drift several meters without appreciable decay; the radiative lifetimes are relatively insensitive to external fields: Moderate fringe fields up to the order of 10^4 V/cm will not affect the decay. Whether or not those rotational levels which are susceptible to allowed predissociation can contribute effectively to molecular beam formation can only be judged when a more accurate estimate of the lifetime for this dissociation mode becomes available.

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[1] W. Lichten, Phys. Rev. 120, 848 (1960); 126, 1020 (1962).

[2] G. H. Dieke, Phys. Rev. 47, 870 (1935); 60, 523 (1941).

[3] G. Herzberg, *Molecular Spectra and Molecular Structure*, 2nd ed. (Van Nostrand, Princeton, N.J., 1950), p. 416.

[4] Reference 3, p. 410.

[5] W. Lichten, Bull. Am. Phys. Soc. 7, 43 (1962).

[6] L. Y. C. Chiu, Phys. Rev. 40, 2276 (1964).

[7] C. Bottcher and J. C. Browne (private communication).

[8] J. R. Hiskes, Bull. Am. Phys. Soc. 13, 308 (1968).

[9] J. R. Hiskes, Phys. Rev. 180, 146 (1969).

[10] J. R. Hiskes, Nucl. Fusion 2, 38 (1962).

[11] J. C. Browne, J. Chem. Phys. 40, 43 (1964).

[12] C. B. Wakefield and E. R. Davidson, J. Chem. Phys. 43, 834 (1965).

[13] W. Kolos and L. Wolniewicz, J. Chem. Phys. 48, 3672 (1968).

[14] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Springer, Berlin, 1957), p. 250.

[15] See Ref. 3, p. 119. Our N is designated as J on p. 118 and as K in Chap. V of Ref. 3.

[16] B. L. Moisewitsch, Monthly Notices Roy. Astron. Soc. 117, 189 (1957).

[17] S. Huzinaga, Progr. Theoret. Phys. (Kyoto) 17, 162 (1957).

[18] A. S. Coolidge and H. E. James, J. Chem. Phys. 6, 730 (1938).

[19] A. Amemiya, Proc. Phys. Math. Soc. Japan 21, 394 (1939).

[20] G. H. Dieke, J. Mol. Spectry. 2, 494 (1958).

[21] H. Beutler and H. O. Jünger, Z. Physik 101, 285 (1936).

[22] W. M. Wright and E. R. Davidson, J. Chem. Phys. 43, 840 (1965).

[23] H. M. James and A. S. Coolidge, Phys. Rev. 55, 184 (1939).

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K-Shell Fluorescence Yields for Light Elements*

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The K-shell fluorescence yield ω_K has been measured for the low-atomic-number elements beryllium, boron, carbon, fluorine, and magnesium. The primary vacancies in the K shell were produced by an intense beam of K x rays generated by electron bombardment of aluminum and carbon targets. The measured values of ω_K agree quite well with values calculated from a theoretical prediction of Wenzel. They exhibit only fair agreement with semiempirical formulas which include screening and relativistic effects, and with a recent calculation by McGuire based on the K-shell Auger transition rate.

I. INTRODUCTION

The occurrence of a vacancy in an atomic shell leads to an internal reorganization which ultimately results in the emission of a characteristic x ray or in the ejection of an Auger electron. Atomic excitation occurs in a wide range of processes, including nuclear decay by internal conversion and