Lifetime measurements of the radiative $3p\pi\ D^1\Pi_u^-$ levels of H_2

M. Glass-Maujean,* J. Breton,† B. Thieblemont,† and K. Ito‡
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Centre National de la Recherche Scientifique et Université de Paris—Sud, Bâtiment 209C, F-91405 Orsay (Cédex), France
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Lifetimes of $3p\pi\ D^1\Pi_u^-$ vibrational levels of molecular hydrogen, $v'=3$—15, excited by vuv synchrotron radiation, were measured by time-resolved spectroscopy. The observed lifetimes range from 2.3 to 3.0 ns and are almost constant (about 2.6 ns) and independent of vibrational quantum number within experimental error. This value agrees with calculated radiative lifetimes. The emission corresponding to the *D-E* transition is observed in the 6000—7500-Å spectral range, and a cascade in the 3000—6000-Å range is identified to *I* and *G* to *B* transitions. The *D-F* transition could not be detected.

I. INTRODUCTION

The symmetry of the orbital wave function with respect to the nuclear plane of rotation (when the spin-orbit fine structure is small compared to the Λ doubling) defines molecular states of very specific dynamical behavior. This property is well illustrated in the hydrogen molecule where the $D\ 3p\pi\ ^1\Pi_u^+$, $v'\geq 3$ levels are strongly predissociated;[1] in contrast, the whole $D^1\Pi_u^-$ vibrational series, up to the dissociation limit, has been observed in emission on the *D-E,F* transition,[2] and is only weakly predissociated.[3]

The aim of the present work was to study their lifetimes in order to test the behavior of the $^1\Pi_u^-$ state on a large range of internuclear distances which are explored for higher-v' levels. In the course of this investigation a cascade was observed which gives us new information on the gerade singlet levels.

II. EXPERIMENTAL SETUP

Pulsed [1.0-ns full width at half maximum (FWHM)] synchrotron radiation from l'Anneau de Collisions de l'Accélérateur Linéaire d'Orsay (ACO) storage ring, dispersed by a 1-m normal incidence. McPherson monochromator equipped by a 2400-line/mm holographic Jobin-Yvon grating, crosses a differentially pumped fluorescence cell filled with hydrogen gas at a pressure below 3×10^{-2} torr measured by a Baratron gauge. The weak fluorescence signal typically 10—200 count per sec is observed at a right angle with either of two photomultipliers *A*, a 56 TVP RTC covering the 3000—7500-Å range, and *B*, and XP 2020 RTC covering the 3000—6000-Å range.

The monochromator bandwidth was adjusted to allow excitation of individual rotational lines (i.e., 0.1 Å). Fluorescence decay curves were observed using the single photon counting technique, with the fluorescence photon pulse acting as the start and the delayed reference signal from pickup electrodes in the storage ring acting as the stop to a LeCroy TDC multichannel time-to-digital converter whose content was read after a preset time into a Tektronix 4051 microcomputer.

III. RESULTS

The data observed with the red-sensitive photomultiplier *A* show biexponential decay with a short lifetime, about 3 ns, as expected for the $3p\pi\ ^1\Pi_u^-$ and a longer one necessarily due to a cascade process. The same behavior was observed independently of the vibrational quantum number ($v'=3$—15). A typical decay curve is shown in Fig. 1.

The $3p\pi$ lifetime being of the same order as the apparatus response time (i.e., ~1.3 ns), in order to improve the measurement accuracy, we calculated the decay curve resulting from a cascade and fitted it to the observed data (the details are reported in the Appendix). From this fitting both decay times $\tau_{3p\pi}$ and τ_{casc} could be determined together with the cascade efficiency *X*. The $\tau_{3p\pi}$ lifetimes are listed in Table I.

The data obtained with the red-blind photomultiplier *B* show only the long component which can be analyzed in terms of a single exponential decay, as shown in Figure 2 by the semilog plot of a typical decay curve. The lifetimes thus obtained are listed in Table II and agree within

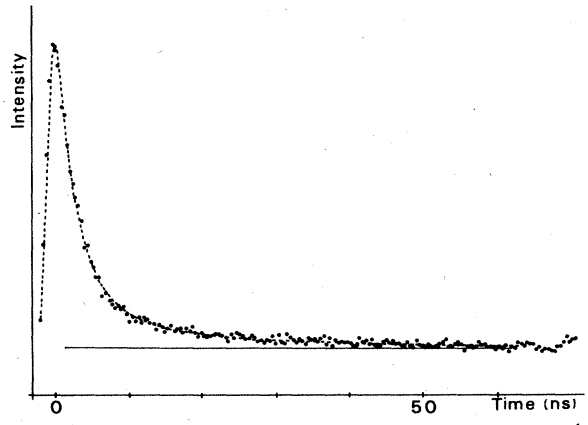

FIG. 1. Decay curve after excitation of the $3p\pi\ D^1\Pi_u^-$, $J'=1$, $v'=4$ level, observed on the fluorescence $3500<\lambda_f<7500$ Å. Dashed line, the fitting calculated cascade decay curve; solid line, background.

TABLE I. Measured values for lifetimes of the $3p\pi\ D^1\Pi_u^-$ levels (second row) and theoretical values for radiative lifetimes from Ref. 4 (third row).

$3p\pi\ ^1\Pi_u^-$ v'	J'	τ (ns)	τ_{theor} (ns)
3	1	3.0±0.4	3.14
4	1	2.9±0.2	3.19
6	1	2.7±0.5	3.27
7	1	2.3±0.5	3.29
8	1	2.3±0.5	3.28
9	1	2.3±0.5	3.27
10	1	2.3±0.5	3.49
12	1	2.3±0.5	3.66
13	1	2.3±0.5	3.54
14	1	2.5±0.5	
15	1	2.7±0.5	

experimental error with the previously determined τ_{casc}.

No pressure variation was observed for the $3p\pi$ decay times, in contrast with the levels involved in the cascade for which we systematically extrapolated the decay time to vanishing pressure.

IV. DISCUSSION

A. The $3p\pi\ ^1\Pi_u^-$ lifetimes

The observed values reported in Table I are very close to the calculated radiative lifetimes,[4] especially if one considers that the calculations include only the *D-X* emission, all the other channels being neglected, in particular the *D-E,F* transition. The corresponding atomic H radiation (H_α $3p$-$2s$) represents 15% of the $3p$ emission, and the $3p$-$3d$ transition, which cannot occur in H, may be not negligible in H_2.

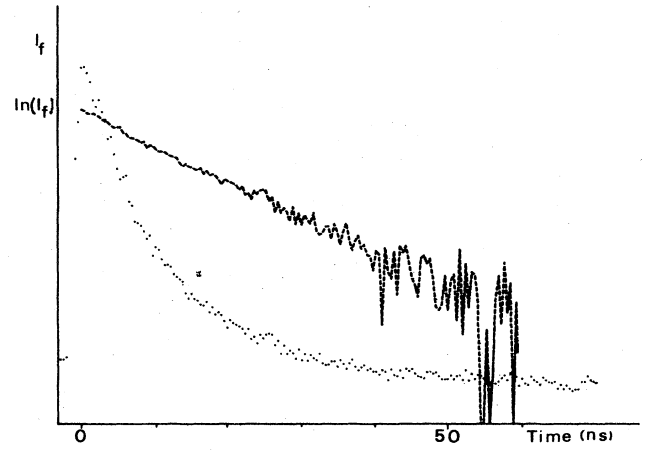

FIG. 2. Decay curve after excitation on the $3p\pi\ D^1\Pi_u^-$, $J'=1$, $v'=4$ level, observed on the fluorescence $3500<\lambda_f<6000$ Å, with the semilog plot.

TABLE II. Detection efficiences $X=B/A$ (as defined in Appendix) and decay times of the cascade observed after excitation of the $3p\pi\ ^1\Pi_u^-$, v', $J=1$ levels. τ_{casc}^t refers to the decay time obtained from fitting of two-exponential curves τ_{casc}^s to values deduced from single-exponential curves measured at roughly the same pressure ($\sim 2\times10^{-2}$ torr). τ_{corr} is the decay time corrected for pressure effect.

Excitation v'	B/A	τ_{casc}^t	τ_{casc}	τ_{corr}
3	0.2	12.0±4.0		11.2±1.3
4	0.5		11.7±1.2	11.7±1.3
5				26.5±3.5
6	1.5	22.0±5.0	23.0±3.0	33.0±3.0
7	2.0	22.0±5.0	23.0±3.0	29.0±4.0
8	2.2	22.0±5.0	22.0±3.0	34.0±4.0
9	2.9	25.0±6.0	25.0±3.0	
10	1.9	22.0±3.0		
12	1.4	21.0±5.0		
13	1.8	21.0±5.0		
14	1.3	21.0±5.0		
15	1.2	18.0±5.0		

Under these conditions, the measured lifetimes of the $3p\pi\ ^1\Pi_u^-$ levels may be well explained only by radiative mechanisms. Preionization is known to be negligible (less than 1% from Dehmer and Chupka's data[5]). A very weak predissociation was noted for $v'=9$ and 10,[3] but the measured lifetimes do not show any variation for these values. The fluorescence detected as Ly-α, through the O_2 filter, may well be a molecular cascading emission *B-X* (8-5, 3-7, or 1-8) which will be discussed later.

The predissociation probabilities may be even less than previously reported values which were 6000 times smaller than the predissociation probabilities observed for the $3p\pi\ ^1\Pi_u^+$ component (Guyon *et al.*, Ref. 1) that beautifully illustrates the importance of the Π^+-Π^- symmetry on the dynamical behavior of the $3p\pi\ ^1\Pi_u$ states.

The constancy of the radiative lifetime over the progression up to the highest vibrational levels confirms the fairly small variation of the dipole moment function with the internuclear distance predicted by previous calculations.[6] It shows quite clearly that the $3p\pi\ ^1\Pi_u^-$ state is a good diabatic state (i.e., keeps a $3p$ character) at all internuclear distances.

One can finally remark that the observed radiative lifetime is about one-half that of the corresponding atomic $3p$ state, namely, 5.3 ns. This behavior was predicted by Dicke for a coherent emission of two atoms at a distance much smaller than the emitted wavelength.[7]

B. The cascade

The slow cascade decay was observed in the 3000—6000-Å visible spectral range whereas the fast decay was observed in the red or near ir only (i.e., 13 000—17 000 cm^{-1}). The relative positions of the levels involved are shown schematically in the diagram of Fig. 3. The only ungerade singlet receptor levels at such dis-

TABLE III. v_{FC} are the expected values of the most probable G, K, or I level assuming a Franck-Condon law for the D-G, D-K, and D-I transitions. The G and K wells are distinguished. G and K level labels are Crosswhite's ones (Ref. 13). τ_{th} are theoretical lifetimes values from Ref. 9. λ is the wavelength of the most intense line emitted on each transition.

			G branch			K branch				I branch		
D,v'	v_{FC}	τ_{theor}	$\lambda_{D\to G}$ [$Q(1)$] (μm)	$\lambda_{G\to B}$ [$R(0)$] (Å)	v_{FC}	τ_{theor}	$\lambda_{D\to K}$ [$Q(1)$] (μm)	$\lambda_{K\to B}$ [$R(0)$] (Å)	$v_{F\text{-}C}$	τ_{theor}	$\lambda_{D\to I}$ [$Q(1),P(2)$] (μm)	$\lambda_{I\to B}$ [$R(0),Q(2)$] (Å)
3	3 3D1	30.8	1.92	5005	0 Z0	77.2	1.32	4662	3	21.6	7.8	3978
										16.2	7.9	3882
4	1 3D0	20.8	1.08	4629	0 Z0	77.2	1.06	4662	3	21.6	3.2	3978
										16.2	3.2	3882
6	3 3D1	30.8	9641	5005	0 Z0	77.2	7843	4662				
					2 X0	87.5	8990	4884				
7	3 3D1	30.8	8434	5005	4 W1	69.9	9303	5031				
8	5 3D2	36.4	8965	5748	4 W1	69.9	8250	5031				
9	5 3D2	36.4	8062	5748	6 W2	74.2	8773	5124				
10	7 3D3	38.0	8485	5880	6 W2	74.2	7985	5124				
11	7 3D3	38.0	7823	5880								
12	8		(7630)	(5100)								
13	8		(7230)	(5100)								
14	8		(6950)	(5100)								
15	8		(6750)	(5100)								

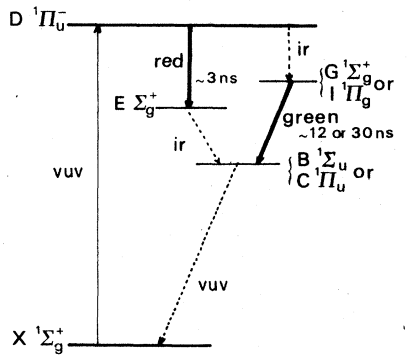

FIG. 3. Cascading process involved in the present measurement, dotted lines are for unobserved transitions.

tances from the D belong to the E,F state (see Fig. 4) (the D-E,F transition was first observed for the lower bands by Richardson[8].

Transitions to the E,F levels are necessarily followed by E,F-B or -C emissions which lie in the ir (Ref. 9) which is not observed in the present experiment. The last step which is B or C-X emission lies in the vuv (some of these lines may lie quite close to Ly-α radiation) and are not observed here.

Thus the observed cascade comes from another path which implies singlet gerade levels different from E,F. These can be G,K and $H,\bar{H}$ $^1\Sigma_g^+$, $I^1\Pi_g$, or $J^1\Delta_g$. Transition to any of these levels is in the far ir. As discussed later all these levels radiate in the observed spectral range

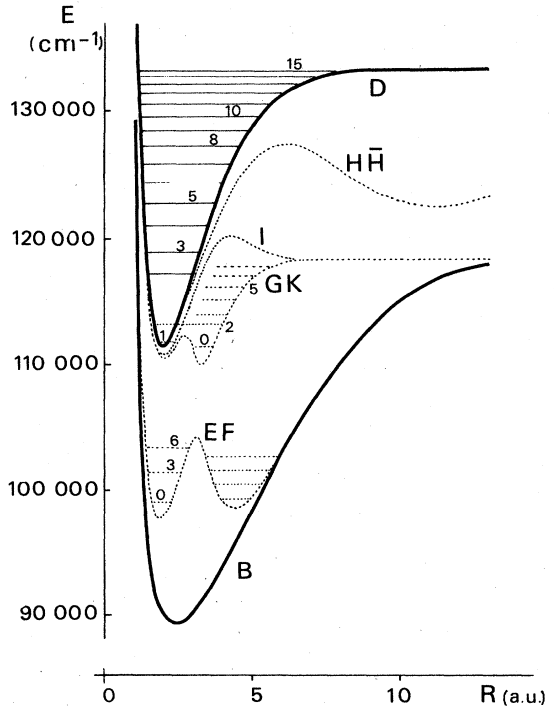

FIG. 4. Potential curves of the various states involved; data are from Ref. 14; ungerade states shown by solid line, gerade states by dotted line.

to either B or C levels. Böse and Linder[10] had also suggested this mechanism to explain their electron impact data.

By comparison of the cascade lifetimes with theoretical[9] or previously measured[11] lifetimes of singlet ungerade states, the intermediate level may be assigned to $I\ 3d\pi\ ^1\Pi_g$ when populated by the D, $v'=3$ and 4 levels and to $G\ 3d\sigma\ ^1\Sigma_g^+$ when populated by the D, $v'\geq 5$ levels.

The calculation of the Franck-Condon factors and the ν^3 terms[12] confirms that the only transitions which have a fair probability of occurring from the D state are those to the E,F, G,K, and I states. The D-G,K and D-I dipole moments are expected to be quite large due to a $3p$-$3d$ character at short internuclear distances. It confirms also that the $D\,v'-G,K\,v''$ transition probabilities are much smaller for $v'=3$ and 4 to any v'' than for $v'\geq 5$ while the $D\,v'-I\,v''$ one is important only for the first v' values to $v''=3$. All the spectral ranges involved are in agreement with the expected ones. In addition these calculations give us the vibrational quantum of the level most likely involved in the cascade.

The D', $v'=3$ and 4 levels seem to populate mainly the $I\ 3d\pi\ ^1\Pi_g$, $v''=3$ level though our measured lifetime value is less than the calculated one.[9] An imperfect extrapolation to null pressure may be the origin of the discrepancy.

The D', $v'\geq 6$ levels populate mainly the G,K levels and more precisely the first levels lying in the G well labeled $3D1$, $3D2$, and $3D3$ by Crosswhite.[13] The "K" levels are expected to be less populated than the "G" ones, due to a smaller dipole moment, but we cannot conclude about their excitation: the observed data can be fitted by a single-cascade model or double one as well. The decay time of the second expected cascade due to K being around 70 ns (Ref. 9) is very near the repetition time of our experiment (i.e., 73 ns) and the signal-to-noise ratio is quite poor. All these results are summarized in Table III.

C. The D-E,F transition

The D-E,F transition is observed to occur at short internuclear distance in the E well only. The Franck-Condon factor predicts a noticeable transition from D, $v'=9$ and 10 to E,F, $v''=2$, which lies in the F well. This transition would occur at about 3500 Å (see Table IV) and would be detected by photomultiplier (PM) B with the $\tau_{3p\pi}$ decay time which is not. From the data obtained with both PM's and the calculated Franck-Condon factor,[9] we deduced

$$M^2_{D\text{-}F}(R\sim 4.5a_0)\leq 130 M^2_{D\text{-}E}(R\sim 1.2a_0)$$

for the values of the dipole moment squared in the E and F wells, respectively. This ratio is large but not completely surprising as the main electronic configuration of the F state is $(2p)^2$ while the D configuration remains $(1s,3p)$ at large internuclear distance, the dipole moment between these configurations is zero.

V. CONCLUSION

The lifetimes of the $3p\pi\ ^1\Pi_u^-$, $J'=1$ levels were measured for the whole vibrational series, showing that radiation is the most probable decay channel even for levels lying far above the dissociation limit and even far above the ionization limit, demonstrating clearly how the orbital wave-function symmetry may affect the dynamical properties of the levels.

The observed values of the radiative lifetime are fairly constant over the whole vibrational progression, showing that the $3p\pi\ ^1\Pi_u^-$ state is good diabatic one, keeping a $3p$ character of all internuclear distances.

Cascades were detected showing that strong ir transitions occur from the $D\ 3p\pi\ ^1\Pi_u^-$ levels to the $I\ 3d\pi\ ^1\Pi_g$ and $G\ 3d\sigma\ ^1\Sigma_g^+$ levels. The D-E,F, -G, and -I transitions may well represent up to 20% of the total emission probability of the D levels and would explain the discrepancy

TABLE IV. v_{FC} are the expected values of the most probable vibrational E,F level assuming a Franck-Condon law for the D-E,F transitions. The E and F wells are distinguished. λ is the wavelength of the corresponding $Q(1)$ line from Ref. 13 when available or estimated from computation (noted in parentheses), E and F level labels are Crosswhite's ones (Ref. 13). τ_{th} are theoretical lifetimes values from Ref. 9. Energies of the D, v' levels are from Takezawa (Ref. 15).

		E branch				F branch			
D, v'	Energy (cm^{-1})	Label	v_{FC}	$\lambda(D\rightarrow E)$	$\tau_{theor}(E)$ (ns)	Label	v_{FC}	$\lambda(D\rightarrow F)$	$\tau_{theor}(F)$ (ns)
3	119216	$2A3$	9	7240	99				
4	121061	$2A4$	12	7340	223				
5	122786	$2K6$	13	6814	265				
6	124392		14	(6420)	309				
7	125877		16	(6375)	335				
8	127248	$V0$	18	6300	535		4 5	(3915) (4087)	448 315
9	128496	$Y1$	21	6566	106		2	(3580)	655
10	129621	$U1$	23	6620	206		2	(3441)	655
11	130618	$X1$	25	6644	168		4	(3458)	448
12	131484	$Z2$	26	6466	34.5		5	(3484)	315
13	132212	$Y2$	28	6540	195	$2K2$	7	3522	245
14	132788	T	29	6487	265	$2K3$	8	3564	178
15	133217	T	29	6291	265	$2K3$	8	3508	178

observed between the measured and calculated values of the $3p\pi\ ^1\Pi_u^-$ lifetimes.

No evidence of the *D-F* transition could be observed leading to the conclusion that the *D-F* dipole moment is at least 1 order of magnitude smaller than the *D-E* one.

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APPENDIX

Let us call a and b the upper and lower levels, respectively, n_a and n_b their populations, and τ_a and τ_b their decay times. The equations of the cascade process are

$$dn_a = -n_a\, dt/\tau_a + \mathcal{S}(t)\ ,$$

$$dn_b = -n_b\, dt/\tau_a - dn_a\ .$$

$\mathcal{S}(t)$ is the source function determined experimentally from the observation of a very fast decay; its FWHM is 1.3 ns. The equations being solved numerically, the observed signal is of the form

$$S(t_i) = An_a(t_i)/\tau_a + Bn_b(t_i)/\tau_b\ ,$$

t_i being the characteristic time of channel i, A and B the efficiencies in the detection of each stage of the cascade.

A decay curve such as the one observed on Fig. 1 occurs only if the shortest lifetime belongs to the upper level.

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*Also at Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure, Université Pierre et Marie Curie, Tour 12, 4 place Jussieu, F-75230 Paris (Cédex 05), France.

†Also at Laboratoire d'Electrodynamique des Gaz Ionisés, Université Pierre et Marie Curie, 4 place Jussieu, F-75230 Paris (Cédex 05), France.

‡Present address: Photon Factory, National Laboratory for High Energy Physics (KEK), Zukuba 305, Japan.

[1]J. J. Hopfield, Nature (London) **125**, 927 (1930); H. Beutler, A. Deubner and H. O. Jünger, Z. Phys. **98**, 181 (1935); A. Monfils, Acad. R. Belg. Sci. **47**, 316 (1961); F. J. Comes and Schumpe, Z. Naturforsch. **26**, 538 (1971); P. J. Julienne, Chem. Phys. Lett. **8**, 27 (1971); F. Fiquet-Fayard and O. Gallais, Phys. Lett. **16**, 18 (1972); P. M. Guyon, J. Breton, and M. Glass-Maujean, Chem. Phys. Lett. **63**, 591 (1979).

[2]P. Borrell, P. M. Guyon, and M. Glass-Maujean, J. Chem. Phys. **66**, 818 (1977); J. Breton, P. M. Guyon, and M. Glass-Maujean, Phys. Rev. A **21**, 1909 (1980).

[3]M. Glass-Maujean, J. Breton, and P. M. Guyon, Chem. Phys. Lett. **68**, 314 (1979).

[4]M. Glass-Maujean, At. Data Nucl. Data Tables **30**, 301 (1984).

[5]P. M. Dehmer and W. A. Chupka, J. Chem. Phys. **65**, 2243 (1976).

[6]S. Rothenberg and E. R. Davidson, J. Mol. Spectrosc. **22**, 1 (1967).

[7]R. H. Dicke, Phys. Rev. **93**, 99 (1954).

[8]O. W. Richardson, Proc. R. Soc. London, Ser. A **160**, 487 (1937).

[9]M. Glass-Maujean, P. Quadrelli, K. Dressler, and L. Wolniewicz, Phys. Rev. A **28**, 2868 (1983); M. Glass-Maujean, P. Quadrelli, and K. Dressler, J. Chem. Phys. **80**, 4355 (1984); At. Data Nucl. Data Tables **30**, 273 (1984).

[10]N. Böse and F. Linder, J. Phys. B **14**, 2499 (1981).

[11]D. J. Kligler and C. K. Rhodes, Phys. Rev. Lett. **40**, 309 (1978); R. L. Day, R. J. Anderson, and F. A. Sharpton, J. Chem. Phys. **71**, 3683 (1979); C. W. T. Chien, F. W. Dalby, and J. van der Linde, Can. J. Phys. **56**, 827 (1978).

[12]M. Glass-Maujean (unpublished).

[13]*The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke*, edited by H. M. Crosswhite (Wiley-Interscience, New York, 1972).

[14]W. Kolos and L. Wolniewicz, Can. J. Phys. **53**, 2189 (1975); W. Kolos and J. Rychlewski, J. Mol. Specrosc. **62**, 109 (1976); **66**, 428 (1977); L. Wolniewicz and K. Dressler, *ibid.* **67**, 416 (1977); **77**, 286 (1979).

[15]S. Takezawa, J. Chem. Phys. **52**, 2575 (1970).