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Alignment of the H_2^+ Molecular Ion by Selective Photodissociation. I*

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On the basis of experimental results obtained by Linlor *et al.*, Fischer, and in this laboratory, demonstrating photodissociation time constants as short as 0.1 sec and trapping times as long as several seconds as practical for the H_2^+ molecular ion, the feasibility is discussed theoretically of a novel technique to align trapped molecular ions and also monitor the alignment by selective photodissociation. First the limiting case of no electronic and nuclear spins and very large rotational quantum numbers is treated, based on the concept that the photodissociation rate R is proportional to the average squared component of the electric light vector perpendicular to the axis of molecular rotation. This angular dependence of R when a bunch of ions created by a short electron bombardment pulse is subsequently irradiated causes the ions in certain magnetic sublevels to decay much more slowly than others. Consequently when conditions for the preservation of alignment are favorable, the sample becomes increasingly aligned. Furthermore, since a partially aligned sample photodissociates more slowly than an unaligned one, more molecular ions $\bar{N}$ will remain when alignment is allowed to develop than when it is continuously destroyed, resulting in only N ions. Next the nuclear and electronic spins are taken into account and numerical values for the dissociation rates of the 30 magnetic sublevels for the first three rotational states of the H_2^+ ion are evaluated for linear light polarization. One sees that on the basis of a sample of 10^9 H_2^+ ions decaying due to photodissociation to 2×10^7 ions, one might expect an optimum signal $(\bar{N}-N)/N\approx0.25$ compared to a statistical uncertainty of about 0.0003 for two consecutive pulses. The possibilities inherent in the scheme to observe the rf spectrum of H_2^+ are pointed out.

INTRODUCTION

THE recently developed collision techniques to polarize or align free atoms using electrons,[1,2] photons (optical pumping),[3] or other atoms[4] as collision partners, have so far not been applied to molecules. This note will serve to discuss the feasibility of a new variant which should be capable of aligning certain molecular ions by virtue of the orientation dependence of their photodissociation cross sections. As a specific example, the H_2^+ molecular ion will be treated in some detail here. Since it is the simplest known molecule, there is considerable academic interest in its radiofrequency spectrum. The possible extension to the other hydrogen isotopes widens this interest by providing a potential source for additional information on the structure of these nuclei.

PHOTODISSOCIATION OF TRAPPED H_2^+ IONS

The photodissociation of H_2^+ is due to an electrical dipole transition[5] from the electronic $1s\sigma$ ground (N) state to the first excited repulsive $2p\sigma$ (E) state. It can be effected by visible or ultraviolet light depending on the vibrational excitation of the ground state. Linlor *et al.*[6] have measured the dissociation cross section as about 10^{-17} cm^2 using the unfiltered output of a 1000-watt high-pressure mercury arc. With this source and reflective cylindrical optics they were able to realize a dissociation time constant T as short as 0.1 sec. Similar times T have been found for trapped H_2^+ ions in this laboratory using a 500-watt HBO 500 mercury arc from the effect of the light for varying irradiation times on resonance signals[7] due to an ion sample created by a short electron burst. Theoretical T values[8] are in agreement with the above experimental values. Even though it might be possible to decrease T to 0.01 sec experimentally, in order to dissociate an appreciable fraction of the irradiated ions special steps will have to

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be taken to trap them for 0.1—1 sec without any collisions occurring during this time. Fischer,[7] using rf quadrupole traps of the type developed in W. Paul's laboratory, reports trapping times as long as 15 msec for $N_2{}^+$ ions and a N_2 background pressure of 6×10^{-6} mm Hg corresponding to a $N_2{}^+-N_2$ collision time of 0.4 msec. In this laboratory, employing similar techniques but using a sealed-off bakeable tube evacuated by a getter-ion pump and pulsing the electron gun, trapping times of several seconds have been observed for $H_2{}^+$ and He^+ ions at background pressures around 10^{-8} mm. These data indicate that it should be possible to make the photodissociation time T short compared to the lifetime against all other reactions, which therefore will be neglected in the following. Next in the order of interest is the number of ions which can be trapped simultaneously. Fischer's[7] data indicate that it should be possible to trap about 10^9 ions without going to extremely large traps. Allowing for decay due to photodissociation to about 10^7 particles the statistical uncertainty in the number of ions counted would amount to 3 parts in 10 000 so that rather small changes in the average ion lifetime due to alignment should be detectable.

ORIENTATION DEPENDENCE WITHOUT ELECTRONIC OR NUCLEAR SPINS

Mulliken[5] has shown that the pulsating electric dipole moment which appears during the electronic transition always lies in the direction of the internuclear axis. In the limit of large rotational quantum numbers K, only the average squared component of the electric light vector $\mathbf{E}$ perpendicular to the axis of rotation $\mathbf{K}$ can be effective in causing the transition at all. That this component has to be further averaged over the molecular rotation is of no concern here. Therefore, one should expect the normalized photodissociation rate R, $\langle R\rangle_{\mathrm{av}}=1$, to be proportional to $\langle\sin^2(\mathbf{K},\mathbf{E})\rangle_{\mathrm{av}}$. Considering an initially unpolarized sample, this angular dependence of the cross section has two consequences. First, as more and more molecules are dissociated, the remaining ones exhibit an increasing alignment. Secondly, since the residual molecules crowd into the long living states, their number $\bar{N}$ decreases more slowly when alignment is allowed to develop than when it is continuously destroyed by some suitable agent. Quantitatively we have for the "no alignment" case $N=N_0e^{-t/T}$. For the undisturbed case with n initially equally populated substates, $m=1, 2, \cdots, n$, with varying decay rates R_m

$$\bar{N}=\frac{N_0}{n}\sum_1^n \exp[-(t/T)R_m]; \quad \langle R_m\rangle_{\mathrm{av}}=1.$$

As the "signal," S, resulting when the disaligning agent is switched on and off in otherwise identical cycles, we define $S=(\bar{N}-N)/N$. Since in practical cases the R_m values lie close to 1, we set $R_m=1+\delta_m$ and treat the δ_m as small quantities to obtain the following approximate expression, $\bar{N}\approx N+N(1/2)u^2\langle\delta_m{}^2\rangle_{\mathrm{av}}$. Here we have set $t/T=u$ and $\langle\delta_m\rangle_{\mathrm{av}}=0$ has been used. Third and higher powers in δ_m have been neglected, $\langle\delta_m{}^3\rangle_{\mathrm{av}}$ because it tends to cancel out, the higher ones because they are small. Herewith follows the desired approximate expression, $S\approx(1/2)\langle\delta_m{}^2\rangle_{\mathrm{av}}u^2$. Of practical interest is further when the optimum ratio of signal to relative statistical fluctuation $N^{-1/2}$ is attained. With $S\propto u^2$ and $N^{1/2}\propto e^{-(u/2)}$ we maximize $S/N^{-1/2}\propto u^2e^{-(u/2)}$ for the single cycle case and obtain $u=4$. This leads to the optimum signal $\mathcal{S}\approx8\langle\delta_m{}^2\rangle_{\mathrm{av}}$. For the sake of numerical illustration we now evaluate $\langle\delta^2\rangle_{\mathrm{av}}$ for very large K in three experimentally interesting cases. The normalized dissociation rates R are proportional to $\langle\sin^2(\mathbf{K},\mathbf{E})\rangle_{\mathrm{motion}}$, where the average has to be taken over the motion of $\mathbf{K}$ with respect to $\mathbf{E}$ or vice versa. With $\delta=R-1$ we form $\langle\delta^2\rangle_{\mathrm{sphere}}$, where the average is over all possible orientations of $\mathbf{K}$, that is the whole sphere, to provide a measure of the angular dependence profile of the dissociation rates. The direction of the inevitable residual magnetic field $\mathbf{H}$ is chosen as the $\mathbf{Z}$ direction and the angle $(\mathbf{K},\mathbf{Z})=\Theta$ is a constant of the motion.

(a) The light vector $\mathbf{E}$ is parallel to $\mathbf{H}$ and $(\mathbf{K},\mathbf{E})=\Theta$. With $\langle\sin^2\Theta\rangle_{\mathrm{sphere}}=2/3$, we have $R_\Theta=(3/2)\sin^2\Theta$, $\delta_\Theta=1-(3/2)\sin^2\Theta$, and finally $\langle\delta_\Theta{}^2\rangle_{\mathrm{sphere}}=(1/5)$, and for the signal $S_{||}=(1/10)u^2$. For $u=1$ or $t=T$ this corresponds already to the large effect $S_{||}=0.1$.

(b) The light is linearly polarized perpendicular to $\mathbf{H}$; $\mathbf{E}=E_x$. With $\cos^2(\mathbf{K},\mathbf{E})=\sin^2\Theta\cos^2\phi$, we have

$$\langle\sin^2(\mathbf{K},\mathbf{E})\rangle_{\mathrm{av}}=1-\sin^2\Theta\langle\cos^2\Phi\rangle_{\mathrm{circle}}=1-(1/2)\sin^2\Theta,$$

where the motion average is over the precession circle. This gives

$$R_\Theta=3/2-(3/4)\sin^2\Theta \quad\text{and}\quad -\delta_\Theta=(3/4)\sin^2\Theta-1/2.$$

Comparing this with δ_Θ for case (a) we get $\langle\delta_\Theta{}^2\rangle_{\mathrm{sphere}}=(1/20)$ and $S_\perp=(1/40)u^2$.

(c) The light is circularly polarized; $\mathbf{E}$ is perpendicular to $\mathbf{H}$. Here one has to average also over the fast rotation of the $\mathbf{E}$ vector. The result is the same as in case (b).

Case (c) shows that there appears to be no advantage in the use of circular polarization, which is more difficult to realize experimentally. In the following, therefore, we shall limit ourselves to linearly polarized light. Observing the results for cases (a) and (b) shows that turning H from parallel to perpendicular to E provides a convenient experimental way[9] if not to destroy at least to reduce appreciably the molecular alignment. One expects the experimental signal here $S^*=S_{||}-S_\perp$ and with $S_\perp=(1/4)S_{||}$, $S^*=(3/4)S_{||}$.

The above results can also be obtained using the asymptotic M dependence derivable from standard

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atomic theory formulas[10] and observing the selection rules[11] $\Delta K=\pm 1$ and $\Delta M=0$. Using in addition sum rules taking into account the statistical weights of the K levels involved, the rates R_{KM} for finite K can be derived. For **E** parallel **H**, one finds in this manner

$$R_{KM}=(3/2)[K(K+1)-M^2]/K(K+1).$$

To justify the use of standard atomic spectra theory ls-coupling intensity formulas here and in the following, we refer in further detail to the fact that the whole KM dependence of the molecular electronic transition $KM-K'M$ matrix element for the case of light polarized parallel to the Z axis is contained in the factor[11]

$$\int P_{K'M}(\cos\theta)\,\cos\theta P_{KM}(\cos\theta)\,\sin\theta d\theta,$$

the angle θ referring to the internuclear axis. This KM dependence is identical to that for a one electron $lm\rightarrow l'm$ atomic electric dipole transition and the selection rule $\Delta K=\pm 1$ applies obviously. That the H_2^+ molecule in the (E) state is falling apart does not create any difficulties since one may invoke a version of the Franck-Condon principle. If one imagines the incident flat white spectrum to be generated by pulses short compared to the dissociation time of the (E) state, about 10^{-13} sec, it must be irrelevant if the state is stable or repulsive. Since for weak light intensities the result can only depend on the power spectrum intensity[12] the specific assumption of short pulses is quite legitimate here. The form of the expression obtained for R_{KM} above suggests writing it as the expectation value of an operator $K^2-K_Z^2$,

$$R_{KM}\propto |(KM|K^2-K_Z^2|KM)|,$$

involving only the KM sublevel of the electronic ground state. This expectation value can be interpreted in analogy to the classical proportionality $R_\Theta\propto \sin^2\Theta$ as a measure of the average squared component of the electric light vector perpendicular to **K**.

DISSOCIATION RATES FOR THE H_2^+ ION

It is now necessary to take electronic and nuclear spins into account. Theoretical studies of the hyperfine structure of the H_2^+ ion have been undertaken by several authors.[13–15] Dalgarno *et al.* which we will follow here, give approximately the following effective spin Hamiltonian: $H_{\text{eff}}[\text{Mc/sec}]=880\mathbf{I}\cdot\mathbf{S}+129I_ZS_Z-150\mathbf{S}\cdot\mathbf{K}$, stating that the electron spin-molecular rotation interaction constant is chosen arbitrarily. Their corresponding energy eigenvalues are given in Table I. The naive assumption, that for odd K the nuclear moment resultant $I=1/2+1/2$ couples to the electron spin S via the contact interaction of similar magnitude as in the H-atom plus a smaller dipole-dipole term which in the atom vanishes because of spherical symmetry, is in agreement with this Hamiltonian. Further, one would expect this spin resultant $\mathbf{F}_2=\mathbf{I}+\mathbf{S}$ to couple to the rotation vector **K** via an appreciably weaker magnetic interaction to form the final resultant $\mathbf{F}=\mathbf{K}+\mathbf{F}_2$. The corresponding vector model is depicted in Fig. 1. Having established the vector frame of the (N) state, we are now in a position to evaluate the normalized dissociation rates R_{FM} for its sublevels FM. One way is to calculate the individual transition probabilities $|(FM|\cos\theta|F'M)|^2$ and to sum over the appropriate sublevels $F'M$ of the (E) state. Here θ refers to the inter-

TABLE I. Photodissociation rates R of hfs sublevels of the three lowest rotational states of the H_2^+ molecular ion for electric light vector parallel to static magnetic field. Hfs energies W_F, g factors g_F, and residual population numbers a_4 after irradiation for four dissociation time constants are listed also $a_0=1$.

K	F_2	F	$W_F[Mc/\text{sec}]$	g_F	$\|M\|$	R	$100a_4$
2	1/2	3/2		−2/5	3/2	0.650	7.43
					1/2	1.350	0.45
		5/2		+2/5	5/2	0.500	13.50
					3/2	1.100	1.23
					1/2	1.400	0.37
1	3/2	3/2	+546	+22/45	3/2	1.200	0.82
					1/2	0.800	4.08
		1/2	+544	+10/9	1/2	1.000	1.83
		5/2	+378	+2/5	5/2	0.750	4.98
					3/2	1.050	1.50
					1/2	1.200	0.82
			0				
	1/2	3/2	−898	−2/9	3/2	0.750	4.98
					1/2	1.250	0.67
		1/2	−973	+2/9	1/2	1.000	1.83
0	1/2	1/2		+2	1/2	1.000	1.83

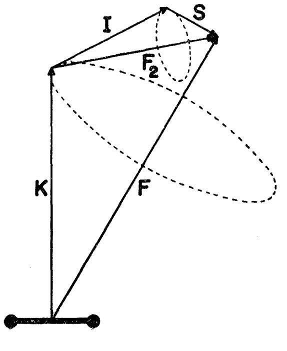

FIG. 1. Vector model for the H_2^+ molecular ion.

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[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 387.

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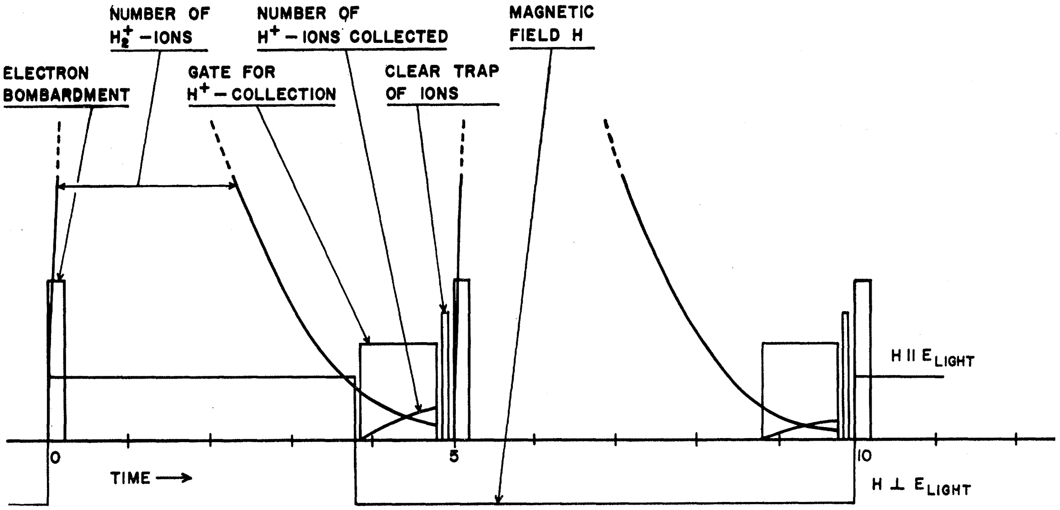

FIG. 2. Periodic sequence of events in pulse scheme to create and detect alignment of the H_2^+ ion by selective photodissociation.

nuclear axis. Noting that in both (N) and (E) state **S** couples most strongly to **I** while the electric light vector interacts with neither, we assume the selection rule $\Delta F_2=0$. It is also necessary that $\Delta K=\pm 1$ and $\Delta F=0$, ± 1. Because of the analogy with the atomic case pointed out earlier standard atomic spectra tables and formulas[16] may be employed in conjunction with suitable sum rules in the same way as one would calculate atomic hfs intensities. We have made the tacit assumption that both (N) and (E) states exhibit the same type of coupling scheme. Actually, because of the summation over the (E) state sublevels, the R_{FM} are independent of this assumption. The numerical values obtained in this way are given in Table I. Another approach, namely evaluating the electronic ground-state expectation values of the operator $K^2-K_Z{}^2$ constructed earlier, $R_{FM}\propto |(FM|K^2-K_Z{}^2|FM)|$, gives the same results much quicker. These calculations are most conveniently carried out using a numerical table of the Clebsch-Gordan coefficients,[17] and then normalizing according to

$$\sum_{M=-F}^{M=+F} R_{FM}=2F+1.$$

We note that, while the addition of the spin angular momenta on the whole exerts a leveling influence on the angular dependence of the dissociation rates, nevertheless appreciable structure remains. To illustrate the degree of alignment building up in an initially statistical sample, population numbers $a_0=1$ at $u=0$ initially, the residual population numbers a_4 after irradiation for four average dissociation time constants, $u=4$, are listed in Table I also. To evaluate the corresponding optimum signal $\mathcal{S}$ as defined before we have to make assumptions concerning the relative populations A_K of the K levels. Assuming that the ionization process does not change K, these populations[18] are the same as for the H_2 molecules from which the ions are formed. The corresponding values, for room temperature, are listed in Table II, together with $\langle\delta_K{}^2\rangle_{\text{av}}$ values averaged separately over all the M_F sublevels of each K state. The proper average $\langle\delta^2\rangle_{\text{av}}=\sum A_K\langle\delta_K{}^2\rangle_{\text{av}}$, $\sum A_K=1$, yields $\mathcal{S}=8\langle\delta^2\rangle_{\text{av}}=0.34$.

EXPERIMENTAL WORK IN PROGRESS

The first experimental goal will be to demonstrate any alignment. The partial destruction of alignment when the magnetic field direction is switched through 90° will be employed in the following scheme, compare Fig. 2. H_2^+ ions which are created by short electron bombardment pulses and trapped are continuously irradiated with linear polarized light from a suitable high intensity arc. Consecutive ion bunches are subjected to a small magnetic field alternately parallel and perpendicular to the electric light vector for a time $t\approx 4T$, then counted whereupon the trap is cleared of ions. The relative difference in ion numbers counted S^* should then be $S^*=S_{\parallel}-S_{\perp}$. Assuming the relation $S_{\perp}=\frac{1}{4}S_{\parallel}$ to hold quite generally we have with our

TABLE II. Rotational level populations A_K and average quadratic dissociation rate deviations $\langle\delta_K{}^2\rangle_{\text{av}}$.

K	A_K	$\langle\delta_K{}^2\rangle_{\text{av}}$	$A_K\langle\delta_K{}^2\rangle_{\text{av}}$	$\langle\delta^2\rangle_{\text{av}}$
0	0.145	0	0	0.0423
1	0.728	0.0349	0.0254	
2	0.127	0.133	0.0169	

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[16] Reference 10, p. 241–243, and 387.

[17] E. G. and E. R. Cohen, North American Aviation Report NAA-SR-2123 (unpublished).

[18] Compare T. R. Carson, Proc. Roy. Soc. (London) **68**, 900 (1954); note that H_2 molecule and H_2^+ ion have the same symmetry.

TABLE III. Vibrational level populations and approximate photodissociation threshold wavelength for H_2^+.

Vibrational level v	0	1	2	3	4	5	$6-\infty$
Population[a]	0.071	0.172	0.190	0.171	0.130	0.086	0.180
Threshold (mμ)	···	···	···	247	286	326	380

[a] After G. Gibson, reference 8.

numerical optimum value $S_{\parallel}=0.34$, $\mathcal{S}=0.25$. Combined with the minimum background uncertainty estimated earlier, this would correspond to a signal to noise ratio of about 500 on the basis of comparison of only two ion bunches. There is, however, another obstacle to be overcome, not mentioned before. When using practical high-power light sources,[19] it is not possible to obtain much output below 2500 A. This coincides roughly with the threshold wavelength for photoionization out of the third vibrational level, $v=3$, of the H_2^+ ion; see Table III. In order to achieve roughly the same dissociation rate for all the higher vibrational levels, $v\geqq 4$, it would be desirable to have a flat spectrum above about 2600 A with zero intensity below this wavelength; then still about 40% of the H_2^+ ions created from room temperature H_2 molecules would be dissociable by the incident light and our alignment analysis would apply to them. Since the alignment in our numerical example is bought at the loss of about 98% of the dissociable ions and the detection method is based on counting remaining ions, clearly it would be very desirable to eliminate the large undissociable background. Experimentally, this is possible as follows. After the alignment period, duration $4T$, not the remaining H_2^+ ions are counted, but one collects instead the H^+ photodissociation products for the duration T and counts them. This effects essentially without loss counting only the residual dissociable fraction of the remaining H_2^+ ions. These considerations lead to the periodic sequence of events sketched in Fig. 2. It should be obvious that rf transitions between any two hfs levels with different dissociation rates R_{FM} could partially take the place of the alternating H field. The low-field $\Delta F=0$ transitions for which approximate g factors are listed in Table I should be comparatively easy to detect. In order to detect the weaker $\Delta F=\pm 1$ transitions, it might be desirable to integrate over 100 or more cycles and thereby decrease the theoretical minimum detectable signal to 5×10^{-5} or less. Experimental linewidth as low as 10 to 100 cps might be realizable.

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[19] Since a single monochromatic lightpulse from a commercial ruby laser may contain as many as 10^{19} photons, while the H_2^+ photodissociation cross section is about 10^{-17} cm^2, nearly complete dissociation of the molecules in certain vibrational levels could be achieved in this way too. Under some conditions this type laser may have advantages over the conventional continuous broadband light sources considered here.